

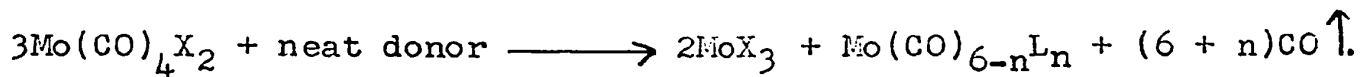
To Anthony and Andrew

ABSTRACT

This thesis describes certain aspects of the coordination chemistry of molybdenum and tungsten in low oxidation states. The more purely "inorganic" aspects of the chemistry were of principal interest, therefore organometallic systems are not included in the study.

The highly reactive halocarbonyl compounds $M(\text{CO})_4\text{X}_2$ ($M = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$) were found to be convenient starting materials for much of the work. The molybdenum compounds reacted with electron donors to give products of various types. Donors capable of stabilizing low oxidation states gave partially substituted products of the type $\text{Mo}(\text{CO})_x\text{L}_y\text{X}_2$ where $x + y = 6$ or 7 . Use of pure liquid donors did not normally affect the stoichiometry of the products but in one case, the reaction with neat phenylisocyanide, a compound of $\text{Mo}(\text{III})$ was formed in which all carbonyl groups had been replaced.

Electron donors with no special ability to stabilize low oxidation states, e.g. nitriles, gave partially substituted halocarbonyls only when used in stoichiometric amounts in an inert solvent but when used in large excess provided complexes of trivalent and zerovalent molybdenum according to the equation:-



The compounds, MoX_3L_3 ($\text{X} = \text{Cl}, \text{Br}$), served as effective starting materials for further synthetic operations.

The nitrile and tetrahydrofuran complexes of the type MoX_3L_3 and molybdenum(III) iodide which was made by an improved method were used to prepare complexes of 1,10-phenanthroline and 2,2'-bipyridyl. Measurements of solution conductivity showed that some of these latter complexes behave as 1:1 electrolytes.

The behaviour of the tungsten halocarbonyls $\text{W(CO)}_4\text{Cl}_2$ and $\text{W(CO)}_4\text{Br}_2$ contrasts with that of the molybdenum analogues. Of the donors used, only pyridine induced the disproportionation to occur and even in this case there were differences. The disproportionation was complete only at about 80°C or higher and reaction gave W(IV) rather than W(III). Compounds of W(III) were produced only at still higher temperatures ($\sim 140^\circ\text{C}$). From the reaction of $\text{W(CO)}_3\text{py}_2\text{I}_2$ with hot pyridine, WI_4py_4 was recovered. The reaction of $\text{W(CO)}_3\text{py}_3$ with iodine led to the same product. The compounds $\text{W(CO)}_3\text{py}_2\text{X}_2$ were made by treating $\text{W(CO)}_4\text{py}_2$ with the appropriate halogen or alternatively by reaction of $\text{W(CO)}_4\text{X}_2$ with the stoichiometric amounts of pyridine.

The less powerful donor, benzonitrile, gave $[\text{WX}_2(\text{NCPh})_2]_x$ at elevated temperatures. These are presumably cluster compounds.

The far infrared spectra ($600\text{--}250\text{ cm.}^{-1}$) of some complexes of molybdenum(III) and those of tungsten ($600\text{--}200\text{ cm.}^{-1}$) have been studied. Various assignments for metal-ligand vibrations have been made.

The trans configuration has been assigned to the complex WBr_3py_3 on the basis of the far infrared spectrum. The same configuration was also assigned to the complex $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$ on the basis of the NMR spectrum.

Electronic and magnetic properties of molybdenum(III) and tungsten(III) compounds isolated were typical of d^3 ions. The spin-forbidden bands in electronic spectra of complexes of the type MoX_3L_3 and WX_3py_3 showed splitting of bands expected from theory.

The analytical methods used to determine various elements in complexes of molybdenum and tungsten are described.

A C K N O W L E D G E M E N T S

Many people, both in and outside the University of Ottawa, have helped toward the preparation of this work. I should like to offer my special thanks to the following:-

Professor A. D. Westland, for invaluable guidance throughout the course of this work and particularly during the preparation of this thesis; my former Professor, Dr. Maurice Woodhead (Yorkshire, England), for encouragement to undertake postgraduate work; the members of the staff of this Department and particularly Dr. J. B. Milne, for help in obtaining some of the spectra and discussion of various problems related to this work; Dr. B. A. Morrow, for help in interpretation of some of the spectral data; Mr. Egon Kristof, for help in glass blowing; Dr. Michael Parris (Carleton University), for recording the far infrared spectra of tungsten(III) compounds; friends and colleagues within the Department especially D. Lal, S. Sharp, D. Moffett and P. Bunting; Mr. & Mrs. Bill McLeish, Jr. (Gloucester) and Mr. & Mrs. David Kimotho (Lucerne, PQ), for help in typing part of this thesis; many friends of St. Andrew's and Erskine Presbyterian Churches, Ottawa, and particularly Rev. & Mrs. A. J. Morrison, Miss C. Jean Phillips, Mrs. George Saunders (all of Erskine) and Rev. Dr. & Mrs. A. W. Currie, whose warm friendship has made my family's stay in Ottawa very pleasant; the Canadian International Development Agency, for a Commonwealth Scholarship; Professor A. D. Westland, for Research Assistantship; and to my wife, Damaris, for her deep understanding and encouragement throughout the course of this work.

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LIST OF ABBREVIATIONS

bipy	2,2'-bipyridine ($\equiv$ dipyridyl or bipyridyl), $C_{10}H_8N_2$.
$\pi-C_5H_5$	π -cyclopentadienyl anion
dam	bis(diphenylarsino)methane, $Ph_2AsCH_2AsPh_2$.
diarsine	O-phenylenebis(dimethylarsine), $O-C_6H_4(AsMe_2)_2$.
diphos	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$.
dithia	2,5-dithiahexane.
8-dmaq	8-dimethylarsinoquinoline, $8-C_9H_6N(AsMe_2)$.
dte	NN-diethyldithiocarbamate, $Et_2NCS_2^-$.
DMF	N,N-dimethylformamide.
DMSO	dimethylsulphoxide.
en	ethylenediamine.
Et	C_2H_5 .
Lut	2,6-lutidine.
MeCN	acetonitrile.
Ph	C_6H_5 .
phen	1,10-phenanthroline.
pip	piperidine.
PhNC	phenylisocyanide.
py	pyridine
RCN	alkyl or aryl nitrile.
THF	tetrahydrofuran.
THT	tetrahydrothiophene.
tmen	NNN'N'-tetramethylethylenediamine.
TPCB	tetraphenylcyclobutane, Ph_4C_4 .
γ -triars	1,1,1-tris(dimethylarsino)ethane, $CH_3C(AsMe_2)_3$.

CHAPTER 1

INTRODUCTION

A. GENERAL:

The Group VIB elements, chromium, molybdenum and tungsten form compounds in all oxidation states from -2 to +6 (1). Very little is, however, known about some of the low oxidations, e.g. -2, -1, +1 although it is in this area that some of the unusual properties of transition metal ions are found. We may cite, as an example, their role as catalysts. One aspect of catalysis that has greatly stimulated interest in the chemistry of low oxidation states of transition metal ions is activation of molecular nitrogen (2). In this respect, the chemistry of molybdenum is of special interest because it has now been established that reduction of molecular nitrogen to ammonia by the natural catalyst, nitrogenase, requires presence of a molybdenum-containing protein (3). Furthermore, recent work indicates that molybdenum forms the active site (4).

The work reported in this thesis was undertaken in an attempt to gain a better understanding of the chemistry of the low oxidation states of molybdenum and tungsten. It deals mainly with compounds of bivalent molybdenum and tungsten with special reference to the reactions of the halocarbonyl compounds, $M(CO)_4X_2$, where $M = Mo, W$; $X = Cl, Br$.

In this chapter, a brief review of the chemistry of bivalent and trivalent molybdenum and tungsten will be made. No attempt is made here to discuss all known compounds of

bivalent and trivalent molybdenum and tungsten. The few selected examples are intended to illustrate the various types of compounds that are known and hence, to identify ligands that stabilize the oxidation state +2 and those that stabilize the oxidation state +3. Besides showing the areas that have been developed, the review should also indicate those areas in which research is particularly lacking.

B. THE CHEMISTRY OF BIVALENT MOLYBDENUM AND TUNGSTEN

The various types of compounds of molybdenum and tungsten in which the element is formally in oxidation state +2 include:-

(a) Cyclopentadienyl complexes.

(b) The halocarbonyls $M(CO)_4X_2$ ($M = Mo, W$; $X = Cl, Br, I$).

(c) Derivatives of type $M(CO)_xLyX_2$ which may be regarded as derivatives of the compounds $M(CO)_4X_2$.

(d) Binary halides MX_2 ($M = Mo, W$; $X = Cl, Br, I$) and their derivatives.

(e) Bivalent molybdenum and tungsten carboxylate compounds.

(a) COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)
STABILIZED BY THE CYCLOPENTADIENYL GROUP

Until the past ten years, the chemistry of bivalent molybdenum and tungsten was mostly that of the binary halides,

MX_2 , ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) or π -bonded complexes of the cyclopentadienyl group.

The most general method of making cyclopentadienyl complexes of molybdenum(II) and tungsten(II) is the following:-

The hexacarbonyl is refluxed with sodium cyclopentadienide, $\text{C}_5\text{H}_5\text{Na}$ (5), in a suitable organic solvent such as tetrahydrofuran. The sodium salt, $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{Na}$, ($\text{M} = \text{Mo}, \text{W}$) may then be acidified with acetic acid to give the hydrides $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$, which are extremely useful starting materials for making other derivatives. E.g. $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ reacts with carbon tetrachloride, N-bromosuccinimide and methyl iodide to give, respectively, $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Br}$ and $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$ (5). Derivatives of this kind react with electron donors such as phosphines to give substituted products of type $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_x\text{L}_y\text{X}$ (6). A few examples of complexes of molybdenum(II) and tungsten(II) with π -cyclopentadienyl anion as a ligand are given in Table 1. A notable feature about the cyclopentadienyl group is its ability to stabilize low oxidation states of transition elements. For this reason, many of the compounds of molybdenum(II) and tungsten(II) that have been reported are those containing this group as one of the ligands. In fact, until the early sixties, the only mononuclear complexes of bivalent molybdenum and tungsten reported were those stabilized by this ligand.

TABLE 1

Some cyclopentadienyl complexes of bivalent
molybdenum and tungsten.

REACTANTS	PRODUCTS ISOLATED	REF.
I $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H} + \text{C}_2\text{N}_2$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{CH}_3$	5
II $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H} + \text{CCl}_4$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Cl} + \text{CHCl}_3$	5
III $\pi\text{-C}_5\text{H}_5\text{W(CO)}_3\text{Cl} + \text{PPh}_3 + \text{NH}_4\text{PF}_6$	$\left[\pi\text{-C}_5\text{H}_5\text{W(CO)}_3(\text{PPh}_3) \right] \left[\text{PF}_6^- \right]$	7
IV $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{I} + \text{diphos}^*$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3(\text{diphos})\text{I}^*$	6
V $\left[(\pi\text{-C}_5\text{H}_5)_2\text{Mo(NO)I} \right]_2 + \text{TiC}_5\text{H}_5$	$(\pi\text{-C}_5\text{H}_5)_2\text{Mo(NO)I}$	8
VI $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Cl} + 2\text{PPh}_3$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3(\text{PPh}_3)_2\text{Cl}$	6
VII $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Cl} + 2\text{NaS}_2\text{CNEt}_2$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2(\text{S}_2\text{CNEt}_2)$	9
VIII $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3(\text{TPCB})\text{Cl} + \text{Me}_3\text{C-MgCl}$	$\pi\text{-C}_5\text{H}_5\text{Mo(TPCB)}(\text{CO})\text{H}^*$	10
IX $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2 + \text{N}_2(250 \text{ atmos.})\text{Hg-Na}$	$(\pi\text{-C}_5\text{H}_5)_2\text{Mo(N}_2)_2$	11

See page xx for explanation of abbreviations

(b) SUBSTITUTED HALOCARBONYLS OF MOLYBDENUM AND TUNGSTEN OF THE TYPE $M(CO)_xL_yX_2$ ($M = Mo, W$; $X = Cl, Br, I$; $L =$ NEUTRAL LIGAND)

1. Methods of preparation: Three methods for making complexes of this type have been reported.

Method (i):

In this method, introduced first by Nyholm and co-workers a decade ago (12), the metal hexacarbonyl is treated with the appropriate ligand to obtain a partially substituted carbonyl compound such as $Mo(CO)_4(diars)^*$ (12) or $W(CO)_2(diars)_2$ (13). The substituted carbonyl compound is then oxidized with a calculated amount of the appropriate halogen to obtain the substituted halocarbonyl such as $Mo(CO)_3(diars)Br_2$ (12), $W(CO)_3(diars)Br_2$ (13), $Mo(CO)_3(bipy)Br_2$ (14), $Mo(CO)_3(diphos)I_2$ (15), $Mo(CO)_3(\nu-triars)Br_2$ (16) or $Mo(CO)_3(dithia)I_2$ (17).

It should be noted for comparison purposes that substituted halocarbonyls of chromium, the first member of the Group VIB elements, can be made similarly (18). Thus, bromine or iodine oxidation of $Cr(CO)_2(diars)_2$ gives $[Cr(CO)_2(diars)_2]X$ ($X = Cl, Br$) (18).

Most complexes of molybdenum(II) and tungsten(II) that have been made by this method are usually those containing chelating ligands such as diarsine. While this work was in

* All abbreviations used in this thesis are explained on page xx.

progress, Moss and Shaw reported substituted halocarbonyls such as $W(CO)_3(PMe_2Ph)_2Br_2$ and $Mo(CO)_3(PMePh_2)_2Br_2$ made by halogen oxidation of the substituted halocarbonyls $M(CO)_4L_2$ (19). Some earlier work by Lewis and Whyman (20) had shown that oxidation of substituted carbonyl compounds of type $M(CO)_4(PPh_3)_2$ and $M(CO)_3(PPh_3)_3$ ($M = Mo, W$) with three equivalents of bromine or iodine gives phosphonium salts of type $(PPh_3H)M(CO)_3(PPh_3)X_3$ ($X = Br, I$).

This method of obtaining bivalent molybdenum and tungsten complexes by halogen oxidation has been used by King (21), and Gonarkar and Stiddard (22) to make the anions $M(CO)_4X_3^-$ in which $M = Mo, W$; $X = I$ (21) or $M = Mo$ or W , and $X = Br$ or I (22) by halogen oxidation of the anions $M(CO)_5X^-$ (23). A few examples of complexes of molybdenum and tungsten obtained by this method are given in Table 2.

Method (ii):

In an alternative method of making substituted halocarbonyls of bivalent molybdenum and tungsten, the halocarbonyls $M(CO)_4X_2$ ($M = Mo, W$; $X = Cl, Br, I$) are treated with the appropriate electron donor. This method was introduced by Colton and Tomkins in 1966 (24, 25). These authors showed for the first time that molybdenum hexacarbonyl reacts with liquid chlorine at $-78^\circ C$ to give dichlorotetracarbonylmolybdenum(II) (24). Dibromotetracarbonylmolybdenum(II) (25), dibromotetracarbonyltungsten(II) and its chloro analogue (26) were subsequently made. In these latter cases, a few drops of the

TABLE 2

Some compounds obtained from halogen oxidation
of substituted carbonyls of molybdenum and
tungsten.

<u>REACTANTS</u>	<u>CONDITIONS</u>	<u>PRODUCTS</u>	<u>REF.</u>
I $\text{Mo}(\text{CO})_4 + \text{bipy} + \text{Br}_2 \text{ or } \text{I}_2$	1:1 mole ratio	$\text{Mo}(\text{CO})_3(\text{bipy})\text{X}_2$	14
II $\text{W}(\text{CO})_4(\text{bipy}) + \text{Br}_2 \text{ or } \text{I}_2$	1:1 mole ratio	$\text{W}(\text{CO})_3(\text{bipy})\text{X}_2$	14
III $\text{W}(\text{CO})_2(\text{diphos})_2 + \text{I}_2$	1:1 mole ratio in benzene at room temperature	$[\text{W}(\text{CO})_2(\text{diphos})_2]\text{I}_3^*$	13
IV $\text{W}(\text{CO})_2(\text{diars})_2 + \text{Br}_2 \text{ or } \text{I}_2$	Excess halogen at room temp. or in boiling CHCl_3	$[\text{W}(\text{CO})_2(\text{diars})_2\text{X}]\text{X}_3$	13
V $\text{W}(\text{CO})_4(\text{diars}) + \text{I}_2$	Excess iodine in chloroform at room temperature	$[\text{W}(\text{CO})_4(\text{diars})\text{I}]\text{I}_3$	13
VI $\text{W}(\text{CO})_4(\text{diars}) + \text{Br}_2$	Excess bromine in chloroform at room temperature	$[\text{W}(\text{CO})_3(\text{diars})\text{Br}_2]\text{Br}^{**}$	13
VII $\text{Mo}(\text{CO})_4(\text{PET}_3)_2 + \text{Br}_2 \text{ or } \text{I}_2$	1:1 mole ratio	$\text{Mo}(\text{CO})_3(\text{PET}_3)_2\text{X}_2$	19
VIII $\text{W}(\text{CO})_4(\text{AsMe}_2\text{Ph})_2 + \text{Br}_2 \text{ or } \text{I}_2$	1:1 mole ratio	$\text{W}(\text{CO})_3(\text{AsMe}_2\text{Ph})_2$	19
IX $\text{Mo}(\text{CO})_4(\text{PET}_2\text{Ph})_2 + \text{Cl}_2 \text{ or } \text{Br}_2$	Excess halogen	$\text{MoX}_4(\text{PET}_2\text{Ph})_2$	19

* The metal atom in compound is monovalent.

** " " " " " trivalent.

TABLE 3

SOME COMPLEXES OBTAINED FROM DIHALOTETRACARBONYLS
OF MOLYBDENUM(II) AND TUNGSTEN(II).

<u>REACTANTS</u>	<u>SOME OF THE PRODUCTS</u> <u>ISOLATED</u>	<u>REF.</u>
I $\text{Mo}(\text{CO})_4\text{Cl}_2 + 2\text{AsPPh}_3$	$\text{Mo}(\text{CO})_3(\text{AsPPh}_3)_2\text{Cl}_2$	24
II $\text{Mo}(\text{CO})_4\text{Br}_2 + 2\text{SbPh}_3$	$\text{Mo}(\text{CO})_3(\text{SbPh}_3)_2\text{Br}_2$	25
III $\text{W}(\text{CO})_4\text{Cl}_2 + 2\text{PPh}_3$	$\text{W}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$	26
IV $\text{Mo}(\text{CO})_4\text{Br}_2 + \text{phen}$	$\text{Mo}(\text{CO})_3(\text{phen})\text{Br}_2$	28
V $\text{Mo}(\text{CO})_4\text{Br}_2 + 2\text{Na} [\text{Et}_2\text{NCSS}]^-$	$\text{Mo}(\text{CO})_3(\text{dtc})_2;$ $\text{Mo}(\text{CO})_2(\text{dtc})_2$	29
VI $\text{Mo}(\text{CO})_4\text{Cl}_2 + 2\text{dam}$	$\text{Mo}(\text{CO})_3(\text{dam})_2\text{Cl}_2;$ $\text{Mo}(\text{CO})_2(\text{dam})_2\text{Cl}_2$	30
VII $\text{W}(\text{CO})_4\text{I}_2 + 2\text{dpm}$	$[\text{W}(\text{CO})_3(\text{dpm})_2\text{I}] \text{I};^*$ $\text{W}(\text{CO})_3(\text{dpm})_2\text{I}_2$	31
VIII $\text{W}(\text{CO})_4\text{Cl}_2 + 2\text{NH}_4\text{NCS} + 2\text{PPh}_3$	$\text{W}(\text{CO})_3(\text{PPh}_3)_2(\text{NCS})_2$	32
IX $\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{Excess isocyanide}$	$\text{Mo}(\text{CNR})_5\text{Cl}_2$	33
X $\text{W}(\text{CO})_4\text{Cl}_2 + 2(8\text{-dmaq})$	$\text{W}(\text{CO})_2(8\text{-dmaq})_2\text{Cl}_2$	34
XI $\text{W}(\text{CO})_4\text{Br}_2 + \text{Et}_4\text{NBr}$	$\text{Et}_4\text{N} [\text{W}(\text{CO})_4\text{Br}_3]^-$	35

* dpm = bis(diphenylphosphino)methane, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$

see p. xx for other abbreviations.

appropriate halogen are added to a cold suspension of the hexacarbonyl in methylene dichloride. This procedure may also give higher halides of these metals (26).

Diiodotetracarbonylmolybdenum(II) and the analogous tungsten compound have also been made by Colton and co-workers. These halocarbonyls are obtained by ultraviolet irradiation of a mixture of the appropriate hexacarbonyl and iodine in hexane at room temperature (27). Examples of derivatives of these halocarbonyls are given in Table 3.

Method (iii):

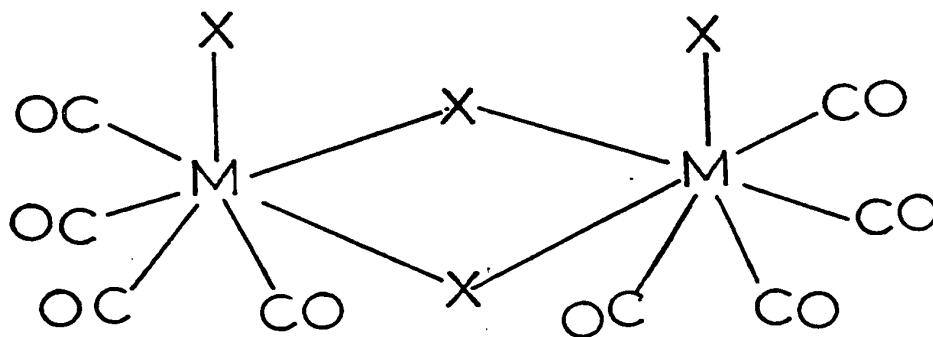
According to a very recent report, reduction of $\text{MoCl}_4(\text{PPh}_3)_2$ or WCl_4 with EtAlCl_2 in heptane in presence of carbon monoxide gives acetone-soluble products (36). Addition of PPh_3 to such solutions precipitates the well-known complexes $\text{Mo}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ (24) and $\text{W}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ (26).

2. PROPERTIES OF THE HALOCARBONYLS $\text{M}(\text{CO})_4\text{X}_2$ AND THEIR DERIVATIVES

The halocarbonyls, $\text{M}(\text{CO})_4\text{X}_2$, ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) are thermally unstable (25, 26, 27). When the chloro and bromo complexes $\text{M}(\text{CO})_4\text{X}_2$ of both molybdenum and tungsten are left standing for several hours at room temperature, they give grey products (37) believed to be the dihalides MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$). This has been shown to be the case at least for $\text{Mo}(\text{CO})_4\text{Cl}_2$ by Holste and Schäfer who have shown that thermal decomposition of the halocarbonyl gives molybdenum

dichloride (38). Although these halocarbonyls are unstable, their great chemical reactivity makes them useful starting materials for preparing more stable derivatives such as $\text{Mo(CO)}_3(\text{PPh}_3)_2\text{Cl}_2$ (21) or similar compounds listed in Table 3.

The structures of the halocarbonyls $\text{M(CO)}_4\text{X}_2$ are not known. The compounds are, however, diamagnetic (27, 35) and on this basis, they are believed to be dimeric (24) with halogen bridging as shown below:-

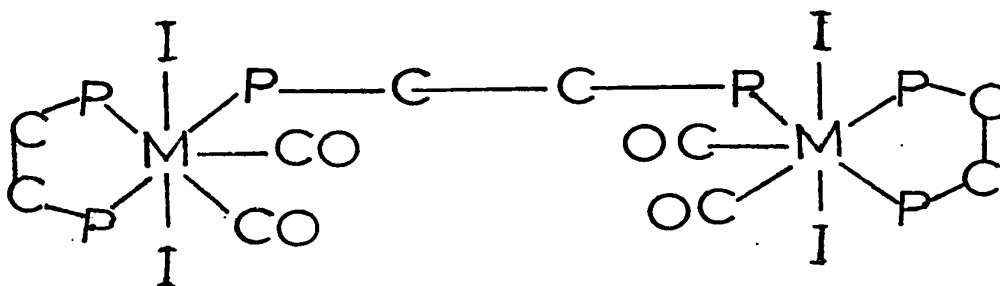


The triphenylphosphine complexes, $\text{M(CO)}_3(\text{PPh}_3)_2\text{X}_2$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}, \text{I}$), but not the corresponding triphenylarsine or triphenylstibine compounds, lose carbon monoxide when refluxed in methylene chloride to give blue complexes of the type $\text{M(CO)}_2(\text{PPh}_3)_2\text{X}_2$ (24-27, 29). The complexes absorb carbon monoxide rapidly to give back the yellow complexes, $\text{M(CO)}_3(\text{PPh}_3)_2\text{X}_2$ (29). All the blue complexes, $\text{M(CO)}_2(\text{PPh}_3)_2\text{X}_2$, are diamagnetic and in this respect differ from the pyridine analogues, $\text{Mo(CO)}_2\text{py}_2\text{Cl}_2$ and $\text{Mo(CO)}_2\text{py}_2\text{Br}_2$, which are paramagnetic (39). The bromo complex, $\text{Mo(CO)}_2(\text{PPh}_3)_2\text{Br}_2$, has been shown by x-ray structural studies to be a distorted

octahedron (40). Probably the other blue complexes have similar structures.

Mononuclear complexes of type $M(CO)_xLyX_2$ or $M(CO)_xDyX_2$ ($M = Mo, W$; $X = Cl, Br, I$; $L =$ a monodentate ligand; $D =$ bidentate ligand) are expected to be seven-coordinate and this has been shown to be the case where structural studies have been made, for example, in $Mo(CO)_2(PMe_2Ph)_3Cl_2$ (41) and $Mo(CO)_2(dam)_2Br_2$ (42) ($dam =$ bis(biphenylarsino)methane). In the last example, one of the bidentate ligands uses only one point of coordination (42). The anion $W(CO)_4Br_3^-$ has also been shown to be seven-coordinate (43).

When more than one bidentate ligand are present in a complex of the type $M(CO)_xDyX_2$, the structure is influenced by the steric effects of the coordinated ligands (44). This is illustrated by the reaction of diiodotetracarbonyltungsten(II), $W(CO)_4I_2$, with bis(1,2-biphenylphosphino)ethane ($\equiv$ diphos). Initial reaction gives $W(CO)_3(diphos)I_2$ which reacts with more of the electron donor to give a complex of empirical formula $W(CO)_2(diphos)_{1.5}I_2$. This complex is believed to be a dimer of type



in which one of the bidentate ligands (shown with hydrogens and phenyl groups omitted for clarity) acts as a bridge.

Addition of more ligand gives $W(CO)_2(diphos)_2I_2$, believed to have a structure similar to that of complexes of type $M(CO)_2(dpm)_2X_2$ ($M = Mo, W$; $X = Cl, Br, I$; $dpm = bis(diphenylphosphino)methane$) (45) in which NMR studies have shown that one of the bidentate ligands uses only one point of coordination (44). It will be recalled that this type of structure has been established in $Mo(CO)_2(dam)_2Br_2$ (42), page 11. When the iodo complexes $M(CO)_2(diphos)_2I_2$ are refluxed in methylene chloride, the salts $[M(CO)_2(diphos)_2I]I$ are formed (44). In such salts, each of the bidentate ligands is using both points of coordination. The analogous chloro- and bromo-complexes do not ionize in this way.

An interesting property of the substituted Group VIB carbonyls is their resistance to oxidation. The hexacarbonyls $Mo(CO)_6$ and $W(CO)_6$ react with chlorine or bromine at room temperature with complete loss of carbon monoxide giving halides such as $MoBr_4$ or WCl_6 (46). Iodine does not react with these hexacarbonyls at room temperature, but at elevated temperatures it does react with complete loss of carbon monoxide to give molybdenum and tungsten triiodides (47).

On the other hand, a substituted hexacarbonyl such as $W(CO)_4(diars)$ reacts smoothly with bromine or iodine to give the halocarbonyl $W(CO)_3(diars)X_2$ (13). Moreover, excess bromine either at room temperature or in boiling chloroform gives only the trivalent tungsten complex $[W(CO)_3(diars)Br_2]Br$ (13) (see Table 2). The resistance to oxidation seems to increase with increasing number of chelating ligands. Thus,

$W(CO)_2(diars)_2$ is not oxidized beyond the divalent state. Excess bromine or iodine merely gives $[W(CO)_2(diars)X]X_3$. The excess halogen can be reduced with sulphur dioxide to give $[W(CO)_2(diars)_2X]X$ (13). As can be seen from Table 2, it appears that resistance to oxidation is also dependent upon the chelates present. Thus, whereas $W(CO)_2(diars)_2$ reacts with excess iodine to give a tungsten(II) complex, $W(CO)_2(diphos)_2$ gives only a monovalent tungsten complex, $[W(CO)_2(diphos)_2]I_3$ (15). Further properties of the halocarbonyls of bivalent molybdenum and tungsten will be given when the details of experimental work have been given.

(c) BINARY HALIDES OF MOLYBDENUM(II) AND TUNGSTEN(II)

All of the dihalides MX_2 ($M = Mo, W$; $X = Cl, Br, I$) are known (48, 49). Although the halocarbonyls of type $M(CO)_4X_2$ and their derivatives may be regarded as derivatives of these dihalides, from a structural point of view, the relationship is only superficial. Thus, whereas the substituted halocarbonyls are mononuclear, the dihalides MX_2 and compounds directly made from them contain the polycations $M_6X_8^{4+}$ (48-50). For the few cases where the structures are known, it has been shown that the polycation contains an octahedron of metal atoms which has, on each face, a halogen atom covalently bonded to the three metal atoms forming the octahedron face. The structure of the polycation $Mo_6Cl_8^{4+}$ (51) found in $Mo_6Cl_8(OH)_4(H_2O)_2 \cdot 12H_2O$ (52) and $(Mo_6Cl_8)Cl_4(H_2O)_2 \cdot 6H_2O$ (53) is shown in Figure 1. This cation is also found in Mo_6Cl_{12} (54).

Similar cations are found in $(\text{Mo}_6\text{Br}_8)\text{Br}_4 \cdot 2\text{H}_2\text{O}$ (55), and $(\text{W}_6\text{Br}_8)\text{Br}_4 \cdot 2\text{H}_2\text{O}$ (56).

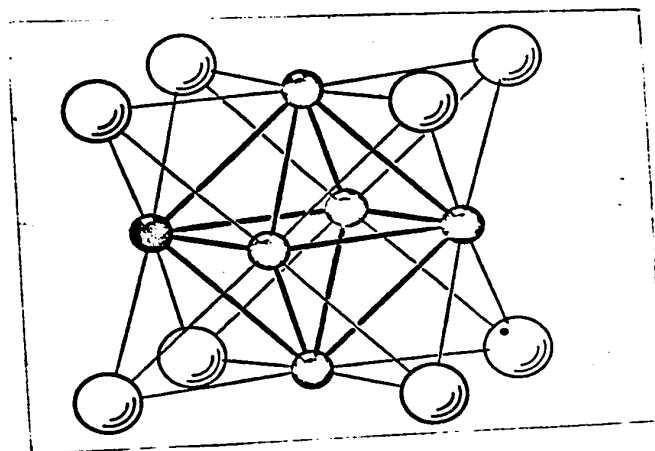
When molybdenum dichloride is dissolved in water, octa- μ_3 -chlorohexamolybdenum(II) $\text{Mo}_6\text{Cl}_8^{4+}$, remains intact so that only one-third of the chloride can be precipitated from such a solution when a solution of silver(I) is added (1, 45, 57, 58).

Cluster compounds are commonly found in transition metal ions in their low oxidation states (59-62). The tendency to form metal-metal bonds among transition metal ions is higher the higher the heat of atomization of the metal (59). It is of interest to note that tungsten has the highest heat of atomization (201.8 kcal/mole) (59), a factor of considerable importance in the low oxidation states chemistry of that element.

It is easy to understand from the foregoing discussion why dihalides of molybdenum and tungsten are not simple ionic salts of the type $\text{M}^{2+}(\text{X}^-)_2$. The values of heats of formation calculated assuming ionic salts, $\text{M}^{2+}(\text{Cl}^-)_2$, and those obtained experimentally for the formation of $\text{Mo}_6\text{Cl}_{12}$ and W_6Cl_{12} (59) are given in Table 4. Such values usually vary slightly according to the source of the data (63), but they are otherwise of the same order of magnitude. The discrepancy between the calculated and experimental values of ΔH arises because of the presence

FIGURE 1

THE STRUCTURE OF THE OCTA- μ_3 -CHLOROHEXAMOLYBDENUM(II)
CATION, $\text{Mo}_6\text{Cl}_8^{4+}$.



● = Mo

⊖ = Cl

of metal-metal bonds in $\text{Mo}_6\text{Cl}_{12}$ and W_6Cl_{12} (59). It is more favourable to form $\text{Mo}_6\text{Cl}_{12}$ and W_6Cl_{12} rather than $\text{Mo}^{2+}(\text{Cl}^-)_2$ and $\text{W}^{2+}(\text{Cl}^-)_2$ because to obtain the latter compounds, the metal-metal bonds in $\text{Mo}_6\text{Cl}_{12}$ and W_6Cl_{12} would have to be broken, a process that requires considerable energy (59).

Among the complexes of bivalent molybdenum and tungsten containing the cations, $\text{M}_6\text{X}_8^{4+}$, those containing $\text{Mo}_6\text{Cl}_8^{4+}$ are by far the most thoroughly studied. These include anionic species such as $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (64) and $[(\text{Mo}_6\text{Cl}_8)(\text{OH})_6]^{2-}$ (64, 65), the bromo analogue of which is known (66), or neutral complexes such as $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ (64) $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_2(\text{phen})_2]\text{Cl}_2$ (67) or $[(\text{Mo}_6\text{Cl}_8)\text{I}_3\text{terpy}]\text{I}$ (67). A recent paper by Schäfer et al. (49) contains interesting complexes, $(\text{M}_6\text{X}'_8)\text{X}''_4 \cdot 2\text{H}_2\text{O}$, in which for $\text{M} = \text{Mo}$ or W , the halogens X' and X'' may be the same or different. Some examples of such complexes with mixed halogens are $(\text{Mo}_6\text{Cl}_8)\text{Br}_4 \cdot 2\text{H}_2\text{O}$, $(\text{Mo}_6\text{I}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, $(\text{W}_6\text{Br}_8)\text{I}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{W}_6\text{I}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$.

The best known non-carbonyl mononuclear complexes of molybdenum(II) and tungsten(II) are the diarsine complexes $\text{M}(\text{diars})_2\text{I}_2$ (47) $\text{M} = \text{Mo}, \text{W}$; or $\text{Mo}(\text{diars})_2\text{X}_2$ (68) ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). It should be noted in this case, however, that the complexes are made from trivalent molybdenum or tungsten rather than from a direct reaction of diarsine with the appropriate dihalide.

(d) MOLYBDENUM(II) AND TUNGSTEN(II) CARBOXYLATES

It has been known for a long time that molybdenum hexacarbonyl, when refluxed with monocarboxylic acids, reacts

TABLE 4

CALCULATED HEATS OF FORMATION, ΔH , OF THE HYPOTHETICAL IONIC DICHLORIDES $\text{Mo}^{2+}(\text{Cl}^-)_2$ AND $\text{W}^{2+}(\text{Cl}^-)_2$ AND THE EXPERIMENTALLY OBTAINED HEATS OF FORMATION, ΔH , OF $\text{Mo}_6\text{Cl}_{12}$ AND W_6Cl_{12} .

<u>COMPOUND</u>	<u>ΔH</u>	
$\text{Mo}^{2+}(\text{Cl}^-)_2$	- 7	kcal/mole
$\text{W}^{2+}(\text{Cl}^-)_2$	+96	"
$\text{Mo}_6\text{Cl}_{12}$	-44	"
W_6Cl_{12}	-36	"

with the latter to give diamagnetic dimeric compounds of general formula $\text{Mo}_2(\text{OOCR})_4$ (69-71). The diacetate has an unusually short Mo-Mo bond of $2.11\text{\AA}$ (72). By treating the diacetate with a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride in the ratio 10:1, Cotton and Norman have prepared the trifluoroacetate dimer, $\text{Mo}_2(\text{OOCF}_3)_4$ (73), in which the Mo-Mo bond has been shown to be $2.09\text{\AA}$ (72).

Tungsten hexacarbonyl is unreactive under the same conditions that molybdenum hexacarbonyl reacts with carboxylic acids to give diacetates (74, 75). Recently, Cotton and Jeremic have shown that tungsten hexacarbonyl will react with carboxylic acids if the reactions are carried out in sealed tubes at elevated temperatures (74). The polymeric carboxylates of general formula $[\text{W}(\text{OOC.R})_2]_x$ where $\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, C_3H_7 and C_3F_7 were obtained by this method.

(e) MISCELLANEOUS COMPOUNDS

With a few exceptions, most compounds of bivalent molybdenum and tungsten are of the types discussed in (a)-(d) above. Among the few exceptions, we may note the following:-

A compound formerly formulated as $\pi\text{-C}_9\text{H}_7\text{Mo}(\text{CO})_2\text{I}$ (76) has now been shown to be iodo- π -indenyltricarbonylmolybdenum(II), $\pi\text{-C}_9\text{H}_7\text{Mo}(\text{CO})_3\text{I}$, (77). This compound has a very similar structure to that of related cyclopentadienyl complexes of type $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{X}$ (page 3) in which the 5-membered ring is π -bonded to the metal ion.

Recently, Green et al (78) have shown that the reaction

of the dibenzene complex $(\pi\text{-C}_6\text{H}_6)_2\text{Mo}$ with phosphines gives complexes of the type $\pi\text{-C}_6\text{H}_6\text{MoL}_3$ in which $\text{L} = \text{PMe}_2\text{Ph}$, or PMePh_2 . These complexes are diprotonated with trifluoroacetic acid to give hydride complexes of the type $\pi\text{-C}_6\text{H}_6\text{MoH}_2\text{L}_3$.

As pointed out earlier, (Table 3), excess isocyanide reacts with the halocarbonyls of molybdenum(II) to give complexes of the type $\text{Mo}(\text{CNR})_5\text{X}_2$ ($\text{RNC} = \text{an isocyanide}$; $\text{X} = \text{Cl, Br}$) (33). The more recent work of Lewis and Lippard has shown that higher substitution can be achieved by indirect methods (79) giving $[\text{Mo}(\text{CNR})_6\text{I}]\text{I}$. A complex of this type was obtained from a reaction of $\text{Ag}_4\text{Mo}(\text{CN})_8$ with tertiary butylisocyanide.

C. THE CHEMISTRY OF MOLYBDENUM(III) AND TUNGSTEN(III)

All the trihalides MX_3 ($\text{M} = \text{Mo, W}$; $\text{X} = \text{Cl, Br, I}$) and MoF_3 are known (63, 80). Tungsten trichloride, W_2Cl_6 or W_3Cl_9 , has been characterized only recently although the complex anion $\text{W}_2\text{Cl}_9^{3-}$, which may be regarded as derived from W_2Cl_6 has long been known.

In the cases where the magnetic measurements have been made, the trihalides have been shown to be antiferromagnetic (47, 84, 85). Prior to the present work, tungsten(III) iodide appears to have been the only well-characterized tungsten(III) compound showing the presence of three unpaired electrons per metal atom (47). The susceptibility was, however, reported to be field dependent and, therefore, no useful information could be deduced (47).

(a) SOME COMPLEXES OF MOLYBDENUM(III)

Trivalent molybdenum is relatively stable and a wide range of complexes derived from molybdenum(III) are known. A few examples of such complexes are given in Table 5. Among the important molybdenum(III) complexes are the trihaloanions MoX_6^{3-} ($\text{X} = \text{Cl}, \text{Br}$). These are commonly obtained by electrolytic reduction of molybdic acid. For instance, MoCl_6^{3-} is obtained by electrolytic reduction of molybdic acid in presence of 8-12M hydrochloric acid (86). The salts R_3MoCl_6 or $\text{R}_3\text{MoCl}_5(\text{H}_2\text{O})$ are obtained by adding to such a solution, the chloride RCl ($\text{R} = \text{NH}_4^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$)(87-89).

An alternative method for making such salts has been described recently by Brencic and Cotton (90). In this method, molybdenum diacetate is oxidized by a limited amount of oxygen to molybdenum(III) in presence of concentrated hydrochloric acid. The $\text{R}_2\text{MoCl}_5(\text{H}_2\text{O})$ salts are precipitated from 6M HCl solutions whereas the R_3MoCl_6 are precipitated from more concentrated solutions.

It is of interest to note here that reduction of tungstic acid in presence of concentrated hydrochloric acid does not give WCl_6^{3-} but rather the ditungsten anion, $\text{W}_2\text{Cl}_9^{3-}$, (83, 91, 92), which has been shown to contain a remarkably short W-W bond of $2.41\text{\AA}$ (93, 94). This tendency of tungsten to form W-W bonds even in the trivalent state is a direct consequence of the high heat of atomization of tungsten (page 14).

The hexabromoanion, MoBr_6^{3-} , can be made by a procedure identical to that of making MoCl_6^{3-} except that hydrobromic acid is used instead of hydrochloric acid (95). It has been

TABLE 5

Some complexes of molybdenum(III).

I	MoBr ₃ + alkyl nitriles in sealed tubes at 150°C for several days	MoBr ₃ ·3NCR	97
II	MoCl ₃ + Nitriles at room temperature	MoCl ₃ ·3NCR	98
III	(NH ₄) ₂ MoBr ₅ (H ₂ O) + Urea solution (50°C.)	[Mo(urea) ₆]Br ₃	99
IV	MoBr ₃ + Me ₂ NH	MoBr ₂ (NMe ₂)NHMe ₂	100
V	K ₃ MoCl ₆ + py ₃ (115°C.)	MoCl ₃ ·py ₃	101
VI	K ₃ MoCl ₆ + 0.1MEDTA	[Mo(EDTA)] -	96
VII	K ₃ MoCl ₆ and KCN oxygen-free water	K ₄ Mo(CN) ₇ ·2H ₂ O	102
	K ₃ MoCl ₆ + K(NCS)	K ₃ Mo(NCS) ₆	102
VIII	MoI ₃ + dipy (excess)	[Mo(dipy) ₃ ³⁺](I ⁻) ₃	103
IX	MoCl ₃ + en	MoCl ₃ ·(NH(CH ₂) ₂ NH ₂) ₂ ·en	104
X	Mo(CO) ₄ (diars) + Excess I ₂	[Mo(CO) ₂ (diars)I ₃]	13

claimed that the hexaiodomolybdenum(III) anion, MoI_6^{3-} , can be made in solution but no solid salts of this anion have been isolated.

Previously, nitrile complexes of molybdenum(III) have been made following one of two closely related methods. Fowles and co-workers found that molybdenum(III) bromide reacted with alkyl nitriles in a sealed tube to give nitrile complexes of the type $\text{MoBr}_3 \cdot 3\text{NCR}$ (97). It is recommended that the reaction be carried out at 150°C since at 100°C , the reaction was very slow and at much higher temperature, the nitriles decomposed.

Smith and Wedd have made nitrile complexes of the type $\text{MoCl}_3 \cdot 3\text{NCR}$ by treating molybdenum(III) chloride with the appropriate nitrile, presumably at room temperature (98). Molybdenum(III) chloride was obtained by reducing molybdic acid electrolytically in 10M HCl and evaporating the acid. The pyridine complexes MoCl_3py_3 can be made by refluxing K_3MoCl_6 with pyridine at $115\text{--}117^\circ\text{C}$ (101) or by heating molybdenum(III) chloride and pyridine in a sealed tube at 270°C (105). A new method by which complexes of the type MoX_3L_3 can be made is described in Chapter 4.

In 1957, Steele reported that $(\text{NH}_4)_3\text{MoCl}_6$ reacted with 1,10-phenanthroline or 2,2'-bipyridyl in dilute hydrochloric acid/ethanol mixture to give $\text{Mo}(\text{phen})_3\text{Cl}_3$ and $\text{Mo}(\text{bipy})_3\text{Cl}_3$ respectively (106). The bromo complexes were said to be made similarly using K_3MoBr_6 and the ligands whereas the iodo compounds were made from molybdenum(III) iodide. Although methods of making molybdenum(III) iodide were reported in the

literature for the first time in 1960 (85, 107), Steele's paper gives no details as to how the molybdenum(III) iodide was obtained. A more serious objection to this work, however, is that other workers have been unable to repeat it (96, 103, 108). Thus, Furlani and Piovesana report that Steele's method gave salts of the protonated ligands, namely

(phenH)[Mo(phen)Cl₄] and (bipyH)(Mo(bipy)Cl₄) for which, unfortunately, only chlorine analyses were given. On the other hand, Carmichael, Edwards and Walton report that reaction of K₃MoCl₆ with bipyridyl in water-ethanol-10M HCl (2:1:1) gives the complex Mo₂Cl₆(bipy)₃, which could also be made in a different procedure (103). This compound has been made during the present work by a slightly different method. On the basis of electrical conductivity, this complex and the bromo analogue have been formulated as [Mo(bipy)₂X₂][Mo(bipy)X₄] (X = Cl, Br) (103).

Marzilli and Buckingham repeated Steele's work using 1,10-phenanthroline and 2,2'-bipyridyl (108). In addition to the species reported by Furlani and Piovesana (96), and Carmichael et al. (103), these workers isolated other species namely, Mo₂O₃Cl₄(bipy)₂, NH₄[Mo(bipy)Cl₄], Mo₂O₄Cl₂(phen)₂H₂O and K(phenH)₂MoCl₆, some of which are molybdenum(V) complexes.

According to a recent report, when MoCl₃ is heated in aniline or piperidine at 70°C, complexes of the type MoCl₃L₃ are obtained (109). It is claimed that the products were characterized by means of infrared and x-ray diffraction methods. Formation of such complexes under these conditions

appears surprising in view of the fact that other workers, who appear to have characterized the reaction products more fully, report that both MoBr_3 (100) and MoCl_3 (104) react with primary or secondary amines with some solvolysis (see Table 5).

(b) SOME COMPOUNDS OF TUNGSTEN(III)

Perhaps the best known halo complex of tervalent tungsten is the anion $\text{W}_2\text{Cl}_9^{3-}$ which can be made by reduction of tungsten(VI) either chemically (83, 110, 111) or electrochemically (91, 112, 113). The potassium salt, $\text{K}_3\text{W}_2\text{Cl}_9$, (83, 91, 94) is precipitated from the tungsten(III) solution by addition of potassium chloride. Other salts have also been isolated with a wide range of cations such as $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Ag}(\text{NH}_3)_2^+$, NH_4^+ , Me_4N^+ , pyH^+ and a series of other cations derived from organic bases (113).

The bromo complex $\text{K}_3\text{W}_2\text{Br}_9$ may be made by reduction of tungsten(VI) with tin in presence of hydrobromic acid (114). Recently, Hayden and Wentworth (115) have shown that the anion $\text{W}_2\text{Br}_9^{3-}$ can be made by halogen exchange. Thus, when $\text{K}_3\text{W}_2\text{Cl}_9$ was dissolved in concentrated hydrobromic acid at 0°C and hydrogen bromide bubbled through the solution, exchange was complete in twenty-four hours. We should note here, for comparison purposes, that all the anions $\text{M}_2\text{X}_9^{3-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$) are known (116, 117). The main difference in these anions is that the metal-metal interaction is in the order $\text{W} > \text{Mo} > \text{Cr}$ (117).

According to Jonassen et. al. (91), treatment of $K_3W_2Cl_9$ with either refluxing pyridine or aniline gives neutral complexes of the type $W_2Cl_6L_3$. However, according to the more recent work of Saillant et. al. (92), reaction of $K_3W_2Cl_9$ with pyridine, 4-picoline and 4-isopropylpyridine gives complexes of the type $W_2Cl_6L_4$.

Two complexes of tungsten(III) that are most probably octahedral have been reported thus far. The fluoro complex, K_3WF_6 , is said to be obtained when a mixture of 50 gm. of KF, 50 gm. of KBF_4 and 0.1 mole of tungsten trioxide are heated in a graphite crucible at $900^\circ C$ (118). Probably, the graphite reduced tungsten(VI). No data, other than diffraction patterns, were given. The cyano complex, $K_3W(CN)_6$, and its molybdenum analogue are made by reducing the octacyano complexes $K_4M(CN)_8$ with hydrogen at $390^\circ C$ to get $K_4Mo(CN)_6$ and $K_4W(CN)_6$ which are then oxidized with air to give $K_3Mo(CN)_6$ and $K_3W(CN)_6$. In both cases, the complexes show presence of one unpaired electron per metal atom (119).

A black diamagnetic complex claimed to be $W(C_6H_5)_3, 3LiC_6H_5, Et_2O$ formed from the reaction of tungsten pentabromide with phenyllithium in diethyl ether (120) has been shown to be the tungsten(IV) complex $W(C_6H_5)_4, 2LiC_6H_5, 3Et_2O$ (121).

In 1968, Blight and Kepert reported that the complex WCl_4py_2 , when refluxed in pyridine, gives a tungsten(III) complex of formula WCl_3py_2 (122). The room temperature magnetic moment of this compound (2.11 B.M.) indicates that

the compound is not magnetically dilute. Green and co-workers have also found that tungsten(IV) can be reduced with bis-(1,2-biphenylphosphino)ethane to obtain the complexes $WCl_3(diphos)$ and $WCl_3(diphos)_2$ depending on reaction conditions (123). The room temperature magnetic moments of these compounds are 1.29 B.M. and 1.48 B.M. respectively, which again, as in the case of WCl_3py_2 , indicates that the compounds are not magnetically dilute.

In a recent paper, Blight et al. (124) reported the 2,2'-bipyridyl and trimethylamine complexes $WCl_3(bipy)$ and $WCl_3(NMe_3)_2$ which are similar to the pyridine complex, WCl_3py_2 . Like the pyridine compound, these complexes were obtained by reduction of tungsten(IV). The bipyridyl complex has a room temperature magnetic moment of 1.48 B.M. whereas the trimethylamine complex has an effective magnetic moment of 0.90 B.M. The values are too low for three unpaired electrons and it is suggested that the complexes have polymeric structures in which the W-W interactions are strong. The diarsine complex, $[W(CO)_3(diars)_2Br_2]Br$, the preparation of which has already been given (Table 2), is magnetically dilute ($\mu_{eff} = 1.54$ B.M. at room temperature) (12).

(c) SPECTRAL AND MAGNETIC PROPERTIES OF MOLYBDENUM(III) AND TUNGSTEN(III) COMPOUNDS.

Since molybdenum(III) and tungsten(III) are $4d^3$ and $5d^3$ ions, respectively, the ions in octahedral environments are ex-

pected to retain three unpaired electrons for all field strengths (125). The molybdenum compounds are expected to have magnetic moments of the order of 3.7 B.M. (126) whereas for tungsten compounds, magnetic moments of the order of 3.4 B.M. are expected (127). A discussion of the various d-d transitions that are expected in such ions will be deferred until the next chapter. We may note, however, that from electronic spectra of such ions (if the ions are in octahedral environments), it is possible to estimate parameters such as $10Dq$ and the spin-orbit coupling constant, S , (128).

In the case of molybdenum, numerous compounds, both octahedral, e.g. the hexahalo-salts or the related compounds, $R_3Mo(NCS)_6$, (129, 130) and pseudooctahedral complexes such as MoX_3L_3 are known. In these compounds, the magnetic moments (97, 130), the $10Dq$ values (96) and the spin-orbit coupling (128) for molybdenum(III) have been shown to be close to the theoretically predicted values. On the other hand, published work on compounds of tungsten(III) is mainly on diamagnetic compounds or paramagnetic compounds with very low moments such as $WCl_3 \cdot diphos$ (123). For this reason, no crystal field parameters for tungsten(III) have been found experimentally.

(D) RESUME: This review has shown that:-

(1) Mononuclear complexes of bivalent molybdenum or tungsten are restricted to those containing ligands that stabilize low oxidation states of transition metal ions. These are frequently ligands that are able to form π -bonds with

metal d-orbitals. Compounds without such ligands tend to form metal-metal bonds, the tendency being higher, the higher the heat of atomization of the metal.

(2) Ligands such as diarsine increase the resistance of the central atom toward oxidation.

(3) The halocarbonyl compounds, $M(CO)_4X_2$ ($M = Mo, W$; $X = Cl, Br, I$), though themselves thermally unstable, give, with π -bonding ligand more thermally stable derivatives of the type $M(CO)_xL_yX_2$. No similar compounds with non- π -bonding ligands were cited in the review as the reactions of these halocarbonyls with such donors had not been studied prior to the present work.

(4) The review showed that whereas the chemistry of molybdenum(III) is well known, very little is known about trivalent tungsten. Some of tungsten(III) compounds cited have been known for only a short time. $WCl_3(bipy)_2$ and $WCl_3(NMe_3)_2$, for example, were reported in early 1972. One consequence of this lack of simple octahedral complexes is that no ligand field parameters for tungsten(III) have been obtained experimentally.

(E) THE SCOPE AND PURPOSE OF THE PRESENT WORK

(a) Scope of research: The work reported in this thesis in-

cludes the following:-

(1) A study of the reactions of $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with some carbon, nitrogen, phosphorus, arsenic, oxygen and sulphur electron donors. For some of these reactions:

(a) the halocarbonyl $\text{Mo}(\text{CO})_4\text{X}_2$ was treated with a stoichiometric amount of the electron donor, L, in a suitable organic solvent.

(b) the halocarbonyl $\text{Mo}(\text{CO})_4\text{X}_2$ was treated with a large excess of the electron donor, L, in a suitable organic solvent.

(c) the halocarbonyl $\text{Mo}(\text{CO})_4\text{X}_2$ was dissolved in pure liquid electron donor, L.

(2) A study of the reactions of $\text{W}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{W}(\text{CO})_3\text{py}_2\text{I}_2$ with pyridine as the solvent. For $\text{W}(\text{CO})_4\text{Cl}_2$ and $\text{W}(\text{CO})_4\text{Br}_2$, the reactions with neat benzonitrile have also been studied.

(3) A study of reactions of MoCl_3L_3 , MoBr_3L_3 and MoI_3 (L = a neutral ligand such as a nitrile) with 2,2'-bipyridyl and 1,10-phenanthroline.

(4) An improved method of preparing molybdenum triiodide.

(5) A study of some physical properties, e.g. magnetic, or spectral of some of the compounds prepared.

(b) Purpose of present work: (1) In view of the fact that substituted halocarbonyl compounds of type $\text{Mo}(\text{CO})_x\text{LyX}_2$ that had

reported at the time this work was begun were only those in which electron donor, L, had some ability to stabilize low oxidation states, it was of interest to see whether similar complexes could be made with ligands such as nitriles that have no tendency to form π -bonds with metal d-orbitals.

(2) It was of interest to discover how much substitution could be achieved by treating the halocarbonyl compounds, $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with a large excess of a monodentate electron donor, L, that has some ability to stabilize low oxidation states. Prior to the present work, substituted halocarbonyls containing such ligands that had been reported were of the type $\text{Mo}(\text{CO})_3\text{L}_2\text{X}_2$. It seemed reasonable, however, that other compounds of the type $\text{Mo}(\text{CO})_2\text{L}_3\text{X}_2$ and $\text{Mo}(\text{CO})\text{L}_4\text{X}_2$ might also be stable. The reason for this expectation was that ligands such as isocyanides that form π -bonds with metal d-orbitals stabilize low oxidation states. For example, isocyanide complexes of the type $\text{Mo}(\text{CNR})_6$ or $\text{W}(\text{CNR})_6$ (131), and the phosphorus trifluoride complexes $\text{Mo}(\text{PF}_3)_6$ (132-134) and $\text{W}(\text{PF}_3)_6$ (135) are known. There are not as yet other complexes of the type MoL_6 or WL_6 , similar to $\text{Mo}(\text{PF}_3)_6$, that are known. It should, however, be noted that phosphine, phosphite and arsine complexes such as $\text{Pt}(\text{PPh}_3)_4$ (136), $\text{Pd}(\text{PPh}_3)_4$ (137), $\text{Pd}[\text{P}(\text{OPh})_3]_4$, $\text{Ni}(\text{AsPh}_3)_4$ (138) and $\text{Ni}[\text{P}(\text{OPh}_3)]_4$ (139) are known.

Ligands such as phosphines may also be expected to form such complexes on the grounds that while like carbon monoxide,

phosphines and arsines stabilize low oxidation states, unlike the former, they also stabilize unusually high oxidation states. This is probably due to their higher Lewis basicity than that of carbon monoxide or more likely, because of the soft nature of the donor atoms (140). For example, the tri-valent and tetravalent nickel complexes, $\text{Ni}(\text{PEt}_3)_2\text{Br}_3$ (141) and $[\text{Ni}(\text{diars})_2\text{Cl}_2](\text{ClO}_4)_2$ (142), respectively, do not have any carbonyl analogues.

(3) It was of interest to find out how $\text{Mo}(\text{CO})_4\text{Cl}_2$ and $\text{Mo}(\text{CO})_4\text{Br}_2$ would react with a large excess of an electron donor such as a nitrile or an ether.

Whereas the significance of π -bonding in phosphine complexes has been questioned (140), it is generally accepted that the stability of carbonyl complexes such as $\text{Mo}(\text{CO})_6$ depends on the fact that the ligand has low energy anti-bonding orbitals of the right symmetry into which excess charge on the metal atom (or ion) can flow (143). On the other hand, the energy of anti-bonding orbitals in a ligand such as tetrahydrofuran is high and this type of back-donation cannot be expected. In view of this fact and what has been said in Section B (c), it seemed reasonable that since complexes of the type MoL_4X_2 (L = a neutral ligand such as nitrile) cannot be expected to be stable, products of the type $\text{Mo}_6\text{X}_{12}\text{L}_2$ might be formed. To anticipate the results somewhat, it was found that contrary to this expectation, dissolution of $\text{Mo}(\text{CO})_4\text{Cl}_2$

or $\text{Mo}(\text{CO})_4\text{Br}_2$ in nitriles gave trivalent molybdenum complexes of type MoX_3L_3 . This observation was significant for two reasons:-

(a) This reaction has provided a new method for making trivalent molybdenum complexes of type MoX_3L_3 ($\text{X} = \text{Cl}, \text{Br}$; L = a neutral ligand such as a nitrile, tetrahydrofuran or pyridine) in a very pure form under very mild conditions.

(b) Extension of this work to the related tungsten compounds $\text{W}(\text{CO})_4\text{Cl}_2$ and $\text{W}(\text{CO})_4\text{Br}_2$ made it possible to make the then unknown tungsten complexes WBr_3py_3 and WCl_3py_3 .

(4) It was of interest to find out whether molybdenum(III) complexes of type MoX_3L_3 could give, with 2,2'-bipyridyl and 1,10-phenanthroline, complexes of type $\text{MoX}_3(\text{bipy})_2$ and $\text{MoX}_3(\text{phen})_2$. Such complexes, if they could be made, would be of interest for two reasons. Firstly, no such complexes had been reported for molybdenum(III) when this work was begun though similar complexes were known for other metal ions. Secondly, in view of the fact that 2,2'-bipyridyl and 1,10-phenanthroline form stable complexes such as $\text{Mo}(\text{bipy})_3$ (144, 145) with transition metal ions in their low oxidation states, complexes of type $\text{Mo}(\text{bipy})_2\text{X}_3$ or $\text{Mo}(\text{phen})_2\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), if they could be made, might be useful starting materials for making complexes of molybdenum in lower oxidation states. Partial reduction of $[\text{Mo}(\text{phen})_2\text{Br}_2]\text{Br}$, for example, might give complexes such as $\text{Mo}(\text{phen})_2\text{Br}_2$. Anticipating the results somewhat, the iodo analogue of this compound has now been made but in a slightly different method.

CHAPTER 2

THEORETICAL CONSIDERATIONS

In this chapter, a brief review of some of the theories used in discussion of experimental work will be given. Familiarity with basic ideas of the Ligand Field Theory will be assumed.

A. LIGAND FIELD TERMS OF A METAL ION WITH THREE d-ELECTRONS

1. Terms of a free d^3 ion:

In a free metal ion with 2 to 9 d-electrons, interelectronic repulsions give various electronic arrangements of different energies. The various energy levels are referred to as terms (146).. The terms of a free d^3 ion are 4F , 2G , 4P , 2P , 2D and 2H (146).

2. Splitting of free ion terms by ligand fields:

If a metal ion is put in a chemical environment it is then said to be subjected to ligand fields. If the ligand fields are less strong than interelectronic repulsions but stronger than spin-orbit coupling, the ion is said to be in a weak field. On the other hand, if the field is greater than interelectronic repulsions, the ion is said to be in a strong field (147).

In the weak field case, the electric fields of the ligands

split the free ion terms in exactly the same way that they split d-orbitals (148). For example, whereas the d-orbitals are split by an octahedral field into t_{2g} and e_g sets, D terms are split into T_{2g} and E_g terms. Similarly, free ion F terms are split into A_{2g} , T_{1g} and T_{2g} terms. We imply, by terms such as T_{2g} and E_g arising from a D term, that the free ion term, D, is split by the octahedral field into the two components, T_{2g} and E_g , which belong to the irreducible representations T_{2g} and E_g respectively, in the group O_h . The splitting of a term by weak fields does not affect the multiplicities. Hence, each of the component terms has the same multiplicity as the parent free ion term.

In a strong field, the terms arising from a two-electron configuration are readily obtained by the aid of Group Theory. The terms of the electronic configuration t_{2g}^2 , for example, are obtained from the Direct Product

$$T_{2g} \times T_{2g} = {}^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}.$$

The direct product gives terms but not their multiplicities. The latter are obtained by the method suggested by Bethe (149) or from correlation diagrams (150).

For more complex systems, e.g. t_{2g}^3 , the direct product method may give fewer or more terms than permitted (151).

The direct product

$$T_{2g} \times T_{2g} \times T_{2g} = ({}^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}) + {}^2A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$$

for example, gives more terms than are allowed. Of these terms,

only those enclosed in the brackets are valid because they represent antisymmetric wave functions whereas those outside the brackets represent "orbital wave functions symmetrical in the three electrons, and so, are not allowed by the exclusion principle" (151). The methods for obtaining the terms in such complex systems have been discussed by Griffith (152).

The terms from all possible electronic configurations of a d^3 ion in a strong octahedral field, are listed below:

<u>Configuration</u>	<u>Terms</u>
t_{2g}^3	$4A_{2g} + 2E_g + 2T_{1g} + 2T_{2g}$.
$t_{2g}^2 e_g$	$4T_{1g} + 4T_{2g} + 2A_{1g} + 2A_{2g} + 2^2E_g + 2^2T_{1g} + 2^2T_{2g}$.
$t_{2g} e_g^2$	$4T_{1g} + 2^2T_{1g} + 2^2T_{2g}$.
e_g^3	$2E_g$

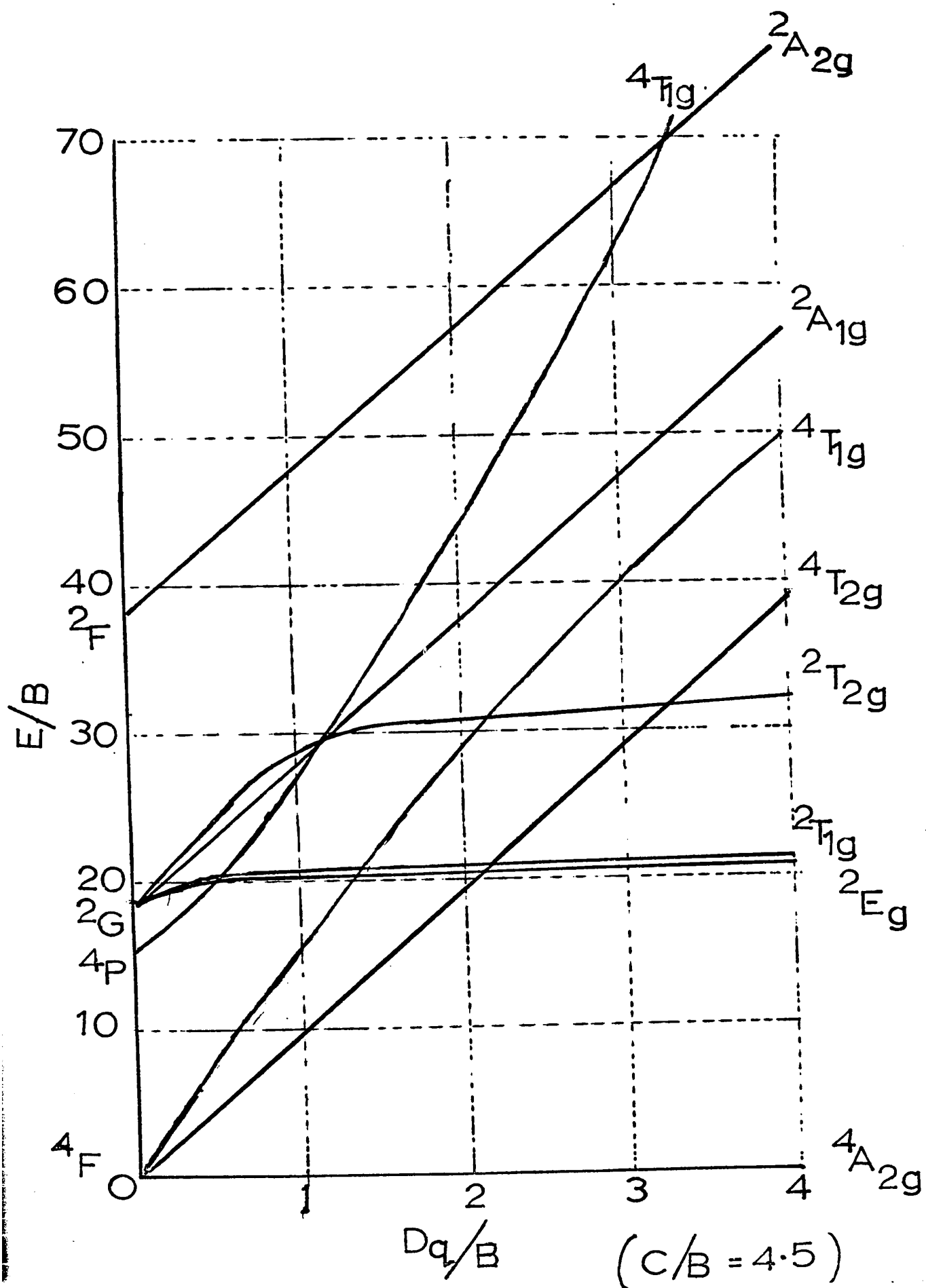
B. TANABE-SUGANO ENERGY LEVEL DIAGRAMS AND d-d TRANSITIONS

Electronic spectra of complex ions are appropriately discussed in terms of the so-called Tanabe-Sugano diagrams (153). In such diagrams, the energies of crystal field terms are plotted as a function of the ligand field, Dq . In both cases, the energies are expressed in units of the Racah parameter, B , which is a measure of interelectronic repulsions (154). The Tanabe-Sugano diagram for a d^3 ion in an octahedral field, e.g. $MoBr_6^{3-}$, is given in Figure 2.

An electronic rearrangement such as $(t_{2g})^3 \longrightarrow (t_{2g})^2 e_g^1$ is referred to as an electronic transition. In terms of the

FIGURE 2

A Tanabe-Sugano energy level diagram for a d^3 ion showing only some of the crystal field terms.



Tanabe-Sugano diagram in Figure 2, this rearrangement corresponds to the transition*



It should be noted that all such transitions take place between the ground state and the various excited states. Transitions occurring between terms of the same multiplicity such as the one just cited are said to be spin-allowed. On the other hand, transitions between terms of different multiplicities such as



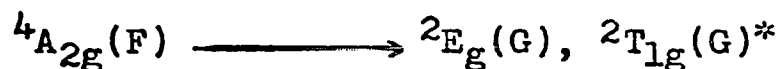
are said to be spin-forbidden.

For some metal ions such as those with A ground terms, the energy of the spin-allowed band occurring at the lowest wavenumber gives a direct measure of the 10Dq value (155). For instance, in the spectrum of MoCl_6^{3-} (Figure 3), the band at $19,000 \text{ cm.}^{-1}$ corresponds to the first spin-allowed transition

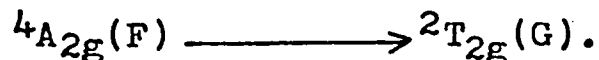


The bands at $9,000 \text{ cm.}^{-1}$ and $15,000 \text{ cm.}^{-1}$ (Figure 3) are both spin-forbidden. The low energy band corresponds to the transition

* The term outside the bracket originates from the one in parenthesis.



whereas the band at $15,000\text{ cm.}^{-1}$ corresponds to the transition



C. ELECTRONIC SPECTRA OF COMPLEXES OF THE TYPE MX_3L_3
(M = Mo, W; X = Cl, Br; L = A NEUTRAL LIGAND).

Complexes of the general formula MX_3L_3 such as those described in Chapter 4, e.g. $MoBr_3 \cdot 3NCCH_2CH_3$ or WBr_3py_3 are pseudooctahedral in that although they have six ligands at the apices of an octahedron, the local symmetry is lower than O_h . Electronic spectra of such complexes show multiple structure (Chapter 5, Sec. C) where single absorption bands are observed in octahedral complexes. The origin of such multiplets is readily understood by considering the effects of ligand fields of low symmetry on such terms.

(1) Splitting of ligand field terms by fields of low symmetry

The two possible geometrical isomers of a complex of the type MX_3L_3 are shown in Fig. 4. In the facial isomer, the complex belongs to the point group C_{3v} whereas in the meridional

* In an octahedral environment, the terms ${}^2E_g(G)$ and ${}^2T_{1g}$ are accidentally degenerate.

isomer, the complex belongs to the point group C_{2v} . As the symmetry is lowered from O_h to either C_{3v} or C_{2v} , the crystal field terms are also changed to appropriate terms in the lower symmetry groups as follows (149):-

<u>O_h</u>	<u>C_{3v}</u>	<u>C_{2v}</u>
A_{1g}	A_1	A_1
A_{2g}	A_2	A_2
E	E	$A_1 + A_2$
T_{1g}	$A_2 + E$	$A_2 + B_1 + B_2$
T_{2g}	$A_1 + E$	$A_1 + B_1 + B_2$

From the above correlation of terms, we notice that E-terms are split by fields of C_{2v} symmetry but not by those of C_{3v} symmetry. T_1 and T_2 -terms are split by fields of both C_{3v} and C_{2v} symmetries. Such splittings may also occur due to spin-orbit coupling.

(2) Splitting of terms by spin-orbit coupling:

In octahedral field, spin-orbit coupling transforms as the irreducible representation T_{1g} (156). Hence, a term of orbital symmetry, Γ , will be split by spin orbit coupling if the triple direct product

$$\Gamma \times T_{1g} \times \Gamma$$

contains the totally symmetric irreducible representation A_1 (or A_{1g}). Let us write $\Gamma_{s.o.}$ for the irreducible representation (or sum of irreducible representations) which has

FIGURE 3

Absorption spectrum of MoCl_6^{3-} in 12M HCl.

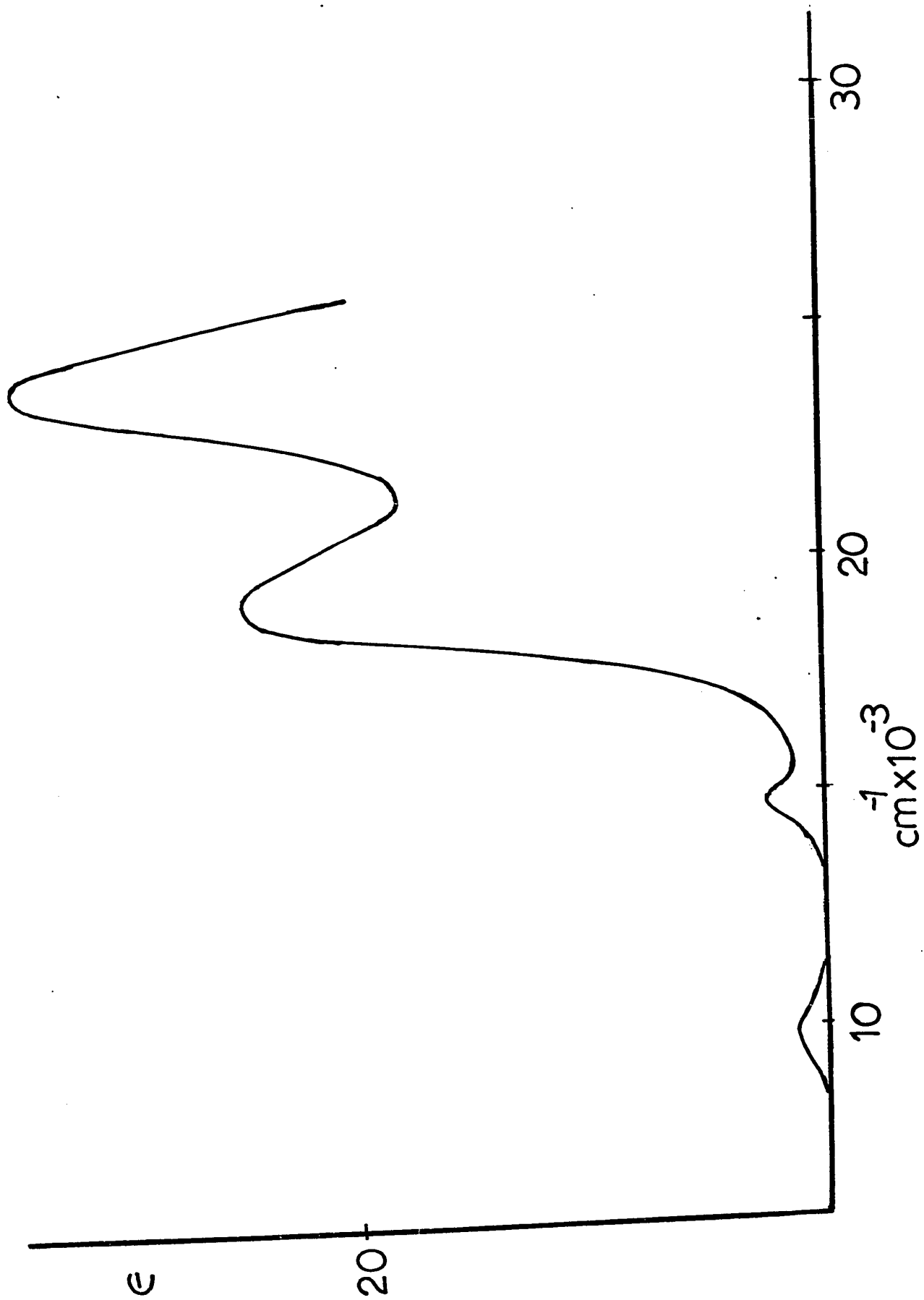
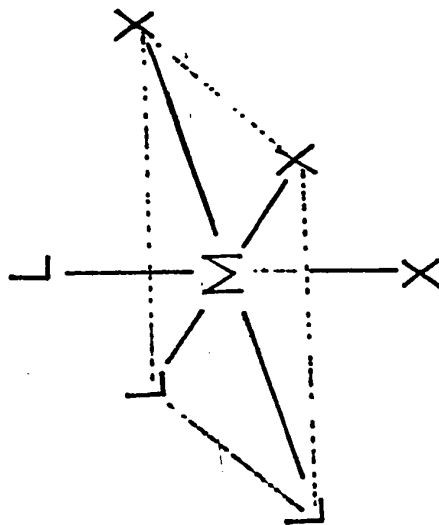


FIGURE 4

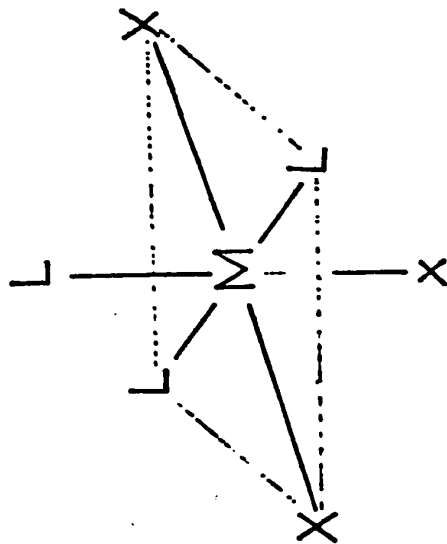
THE POSSIBLE GEOMETRICAL ISOMERS OF COMPLEXES OF THE TYPE MX_3L_3 .

- (a) Facial isomer (C_{3v} symmetry).
- (b) Meridional isomer (C_{2v} symmetry).



(a)

C_{3v} symmetry



(b)

C_{2v} symmetry

(or have) the same symmetry properties as the spin-orbit coupling. We can then write the following triple direct products (multiplicities not included)

Γ	Group	$\Gamma \times \Gamma_{s.o} \times \Gamma$
T_{1g}	O_h	$T_{1g} \times T_{1g} \times T_{1g} = A_{1g} + A_{2g} + 4T_{1g} + 3T_{2g}^*$
T_{2g}	O_h	$T_{2g} \times T_{1g} \times T_{2g} = A_{1g} + 2E_g + 5T_{1g} + 2T_{2g}$
E_g	O_h	$E_g \times T_{1g} \times E_g = 2T_{1g} + 2T_{2g}$
E	C_{3v}	$E(A_2 + E)E = 2A_1 + 2A_2 + 4E$

From these direct products, it follows that:- (a) T-terms are split by spin-orbit coupling in octahedral environments. (b) E-terms are not split by spin orbit coupling in octahedral environments. (c) E-terms are split by spin-orbit coupling in fields of C_{3v} symmetry.

D. INTENSITIES OF BANDS.

If assumption be made that Beer-Lambert's law is obeyed, the intensity of an absorption band can be estimated (157) from equation 2-1.

$$\log_{10} \frac{I_0}{I} = \epsilon lc \quad 2-1$$

where I_0 is the intensity of the incident monochromatic beam, and I is the intensity of the same beam after traversing a length, l , of a solution of concentration, c . ϵ is the molar absorption coefficient. Table 6 summarizes approximate ϵ values for transitions of various types.

* Not all the terms obtained from the direct product are valid. See pp. 34-35.

TABLE 6

APPROXIMATE MOLAR ABSORPTION COEFFICIENT,
 ϵ , FOR VARIOUS TYPES OF TRANSITIONS

<u>Type of transition</u>	<u>ϵ</u>
Spin-forbidden, Laporte forbidden	0.1
Spin-allowed, Laporte forbidden	10
Spin-allowed, Laporte forbidden, but with d-p mixing (T_d symmetry)	100
Spin-allowed, Laporte forbidden, but with 'intensity stealing'	1,000
Spin-allowed, Laporte allowed (charge transfer)	10,000

Transitions that are Laporte forbidden are usually observed because molecular vibrations cause mixing up of the electronic states with vibrational states of odd parity. This mixing up of electronic and vibrational wavefunctions is the so-called vibronic coupling. Laporte forbidden transitions which are also spin-forbidden will, however, be very weak and may not be observed in some cases.

Spin-forbidden transitions can gain intensity by means of intensity-stealing mechanism whereby spin-orbit coupling mixes terms of different multiplicities (159). Consider, for instance, the d^3 ion which gives quartet and doublet terms. Suppose there is a quartet term of energy, E_Q , above the ground state (also a quartet) which can be described by a wavefunction ψ_Q . If there is a doublet term for which the energy and wavefunction are E_D and ψ_D , respectively, this doublet term will have some quartet character, α , given by

$$|\alpha| = \frac{\int \psi_Q |H_{s.o.}| \psi_D d\tau}{(E_D - E_Q)} \quad 2-2$$

where $H_{s.o.}$ is the spin-orbit operator. It follows from equation 2-2 that spin-forbidden bands in ions with high spin-orbit coupling should have high intensities. This has been confirmed experimentally, particularly for the tungsten(III) complexes (see Chapter 5, Section C.).

E. ON THE THEORY OF MAGNETIC SUSCEPTIBILITY (159-162)

If a substance is put in a magnetic field, the field

strength, B, inside the substance is different from the free space value, H. The two are related via equation 2 - 3.

$$B = H + 4\pi I \quad 2-3$$

in which I is the intensity of magnetization and is equal to the induced magnetic moment per unit volume (162). If both sides of equation 2-3 are divided by H, we obtain

$$B/H = 1 + 4\pi I/H = 1 + 4\pi K \quad 2-4$$

The ratio B/H is the magnetic permeability. The ratio $I/H = K$ is the volume susceptibility of a substance and is a measure of how readily the substance is polarized by a magnetic field.

The Gouy Method for measuring magnetic susceptibilities depends on the fact that when a substance is weighed in presence and in absence of a magnetic field, there is an apparent change in weight ΔW_{gm} . ($\equiv \Delta w$ dynes) which is given by

$$\Delta w_g = \frac{1}{2} (K - K_0) (H^2 - H_0^2) A \quad 2-5$$

In this equation, K is the volume susceptibility of the substance and K_0 is the corresponding value for the surrounding medium. H is the field strength, in oersteds, at the lower end of the sample (Fig.14) while H_0 is the corresponding value at the upper end of the sample; A is the cross-section area of the sample in cm^2 . If the length of the sample is large, the field at the upper end of the sample is very much smaller than the field at the pole gap and, therefore, $H^2 \gg H_0^2$.

Hence, H_0^2 may be neglected without introducing much error.

K_0 can be made negligibly small in comparison with K if the surrounding medium has a low value of K_0 . During the present work, K_0 was made approximately zero by evacuating the Gouy tube (see Chapter 3, page 100). With these approximations, equation 2-5 reduces to

$$\Delta w g = \frac{1}{2} \kappa H^2 A \quad 2-6$$

In practice, the quantity determined experimentally is the gram susceptibility, χ , which is obtained by dividing κ by the density of the sample, d . If the weight of the sample is W , the density is given by

$$d = \frac{W}{A l} \quad 2-7$$

If we divide both sides of equation 6 by $\frac{W}{A l}$ and write χ for $\frac{\kappa A l}{W}$, we obtain equation 2-8.

$$\frac{\Delta w A l}{W} g = \frac{1}{2} \chi H^2 A \quad 2-8$$

which, on simplification and rearrangement, gives the fundamental equation

$$\chi = \frac{\Delta w \ 2 l g}{W H^2} \quad 2-9.$$

Equation 2-9 is the link between theory and experiment since it shows how the susceptibility of a substance is obtained

from experimentally measurable quantities. χ may be positive or negative depending on the type of the compound in question (Table 7). The molar susceptibility, χ_M , is obtained by multiplying χ with the molecular weight of the compound. To calculate the effective magnetic moment, μ_{eff} , a correction due to the diamagnetism of the constituent ions or molecules in a compound is added to χ_M to get χ'_M . Diamagnetic susceptibilities of molecules are usually obtained from experimentally determined values. Alternatively, they may be estimated from Pascal's constants (163).

The effective magnetic moment is then calculated from equation 2-10:

$$\mu_{\text{eff}} = 2.83(\chi'_M T)^{1/2} \text{ BM.} \quad 2-10$$

T is the absolute temperature, in degrees Kelvin, at which the measurement was made.

B.M. = Bohr Magnetons. A Bohr magneton is equal to $0.9174 \times 10^{-20} \text{ erg gauss}^{-1}$.

The total spin momentum, S, is given by $S = n/2$ where n = number of unpaired electrons. If the total angular momentum is L, the effective magnetic moment may also be obtained from equation 2-11 (162).

$$\mu_{\text{eff}} = [4S(S + 1) + L(L + 1)]^{1/2} \text{ B.M.} \quad 2-11$$

If the orbital contribution is zero, equation 2-11 reduces to the "spin-only" value of

TABLE 7

FIELD DEPENDENCE OF SPECIFIC SUSCEPTIBILITY, χ .

<u>Type of magnetic susceptibility, χ</u>	<u>Sign</u>	<u>Magnitude (cgs)</u>	<u>Dependence on field</u>
Diamagnetism	Negative	1×10^{-6}	Independent
Paramagnetism	Positive	$0 - 100 \times 10^{-6}$	Independent
Antiferromagnetism	Positive	$10^{-2} - 10^4$	Dependent
Ferromagnetism	Positive	$0 - 100 \times 10^{-6}$	May be dependent

$$\mu_{\text{eff}} = [4S(S + 1)]^{\frac{1}{2}} = [n(n + 2)]^{\frac{1}{2}} \text{ B.M.} \quad 2-12.$$

Magnetic and non-magnetic terms:

A term for which there is an orbital contribution to the effective magnetic moment (see equation 2-11) is said to be magnetic. On the other hand, terms for which L in equation 2-11 is zero are said to be non-magnetic (164). T-terms are magnetic whereas A- and E-terms are non-magnetic (165). It follows that an octahedral complex of an ion such as molybdenum(III) which has an A-ground term should have a magnetic moment close to the spin-only value. In practice, however, the A- and E-terms are never truly non-magnetic because spin-orbit coupling gives them some character of T-terms (see equation 2-2). In an octahedral field, the effective moment with A-ground term is given by equation 2-13 (126, 165).

$$\mu_{\text{eff}} = [\text{Spin-only value}] \left[1 - \frac{4\lambda}{10Dq} \right] \text{ B.M.} \quad 2-13.$$

λ is the spin orbit coupling and 10Dq has its usual meaning (166).

According to equation 2-13, if spin orbit coupling is positive, the observed moment is less than the spin-only value, and is lower the higher the value of λ . Values of λ are positive for metal ions with less than half full subshells. On the other hand, if λ is negative, which is the case for ions with more than half full subshells, the observed moment is expected to be larger than the spin-only value. Notice

that in either case, the $10Dq$ value has just the opposite effect. For example, if λ is positive, the effect of a large $10Dq$ value is to make the observed moment close to the spin-only value.

Effects of distortions from cubic symmetry on magnetic moments:

Asymmetric fields quench the orbital magnetic moment (167). Therefore, a metal complex with low symmetry is expected to have a magnetic moment close to the spin-only value.

Diluting effect of the ligands:

The ligands in a metal complex keep the metal ions far apart and thus reduce the interactions between them. A compound is said to be magnetically dilute (160, 162) if these interactions are low. When the interactions are high as is common in many transition metal oxides or halides e.g. Fe_2O_3 or MnF_3 , the complexes then may show ferromagnetic, or more commonly, antiferromagnetic behaviour (162).

CHAPTER 3

EXPERIMENTAL TECHNIQUES

In this chapter, experimental techniques other than methods of preparing specific compounds will be discussed. These include:-

(a) The purification and handling of materials.

(b) Details of making various physical measurements, e.g. magnetic susceptibility measurements.

(c) Analytical methods. Preparative work will be discussed in Chapter 4.

A. HANDLING OF COMPOUNDS

Unless otherwise specified, all the preparations were done in an atmosphere of dry oxygen-free nitrogen or argon.

Routine glassware cleaning:

Grease was washed off joints with petroleum ether (30-60°C). The glassware was then put in a bath of chromic acid for about two hours. The filtration apparatus (Fig. 11) could not be put in the bath. Instead, the acid was passed through the glass frit. The acid was washed off with tap water and the apparatus cleaned with dilute ammonium or

sodium hydroxide and finally with water and rinsed thoroughly with distilled water. The glassware was then dried at 180°C for two hours in an electric oven.

The conductivity cell (Fig.12) and NMR tube were normally cleaned several times with water and N,N-dimethylformamide, and finally rinsed several times with acetone or ethanol and allowed to dry in air. The quartz cells used for electronic spectra were cleaned with chromic acid as the rest of the glassware but instead of being dried in the furnace, they were rinsed with 99% ethanol and allowed to dry in air.

B.

MATERIALS

(i) MOLYBDENUM AND TUNGSTEN HEXACARBONYLS

Molybdenum and tungsten hexacarbonyls were obtained from Alfa Inorganics, K and K Laboratories Incorporated, Research Organic/Inorganic Chemical Corporation, or Matheson, Coleman and Bell, and were used without further purification. In all cases, however, the metal carbonyl was thoroughly powdered in a blender and dried over P_4O_{10} in a vacuum desiccator for at least twelve hours before use.

(ii) THE HALOGENS

Chlorine: Chlorine was dried by bubbling it through concentrated sulphuric acid in a Drechsel bottle and then passed over phosphorus pentoxide supported on pumice in glass tubes

each about 25 mm. diameter and one meter long.

Bromine: AnalaR grade bromine (B.D.H.) was purified by distillation from P_4O_{10} . The middle fraction (B.Pt. 58-59°C, 760 mm. Hg.) was collected in a flask which had been dried and cooled while being flushed with dry oxygen-free nitrogen.

Iodine: Iodine was purified by sublimation. AnalaR grade material (B.D.H.) was put in a pyrex tube with constrictions as shown in Figure 5. With the iodine in compartment 1, the tube was evacuated and sealed at A. The iodine was sublimed into compartments 2 and 3, and the tube sealed at C. To recover the iodine, a scratch was made at B with a sharp glass cutter and the tube broken open.

(iii) NITRILES

Spectrograde liquid nitriles were obtained from the Fisher, Aldrich and Eastman Companies. The method of purification depended on volatility of the nitrile. Water was removed initially from those of low boiling point ($<150^\circ\text{C}$, 760 mm. Hg.) by repeated distillation from P_4O_{10} (168, 169). The distillate was collected, in each case, in a flask that had been dried at 180°C and cooled by flushing with dry oxygen-free nitrogen.

Finally, the nitrile was dried by vacuum distillation from Linde Molecular Sieves Type 4A. This method was used for drying other solvents and will be described in detail . The apparatus used for vacuum distillation is shown in Fig. 6.

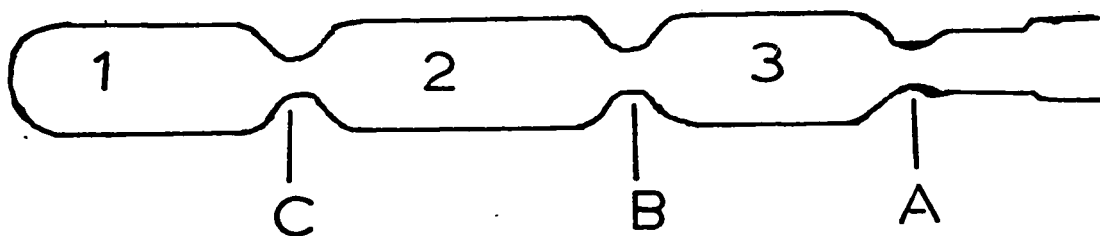


FIGURE 5

APPARATUS FOR SUBLIMATION OF IODINE

Essentially, the apparatus consisted of two Schlenk tubes, A and B. The well-cleaned tubes which had been dried at 180°C were cooled by flushing with dry nitrogen, the ground joints lightly greased, and the tubes clamped vertically as shown in Figure 6. (The clamps are omitted for clarity).

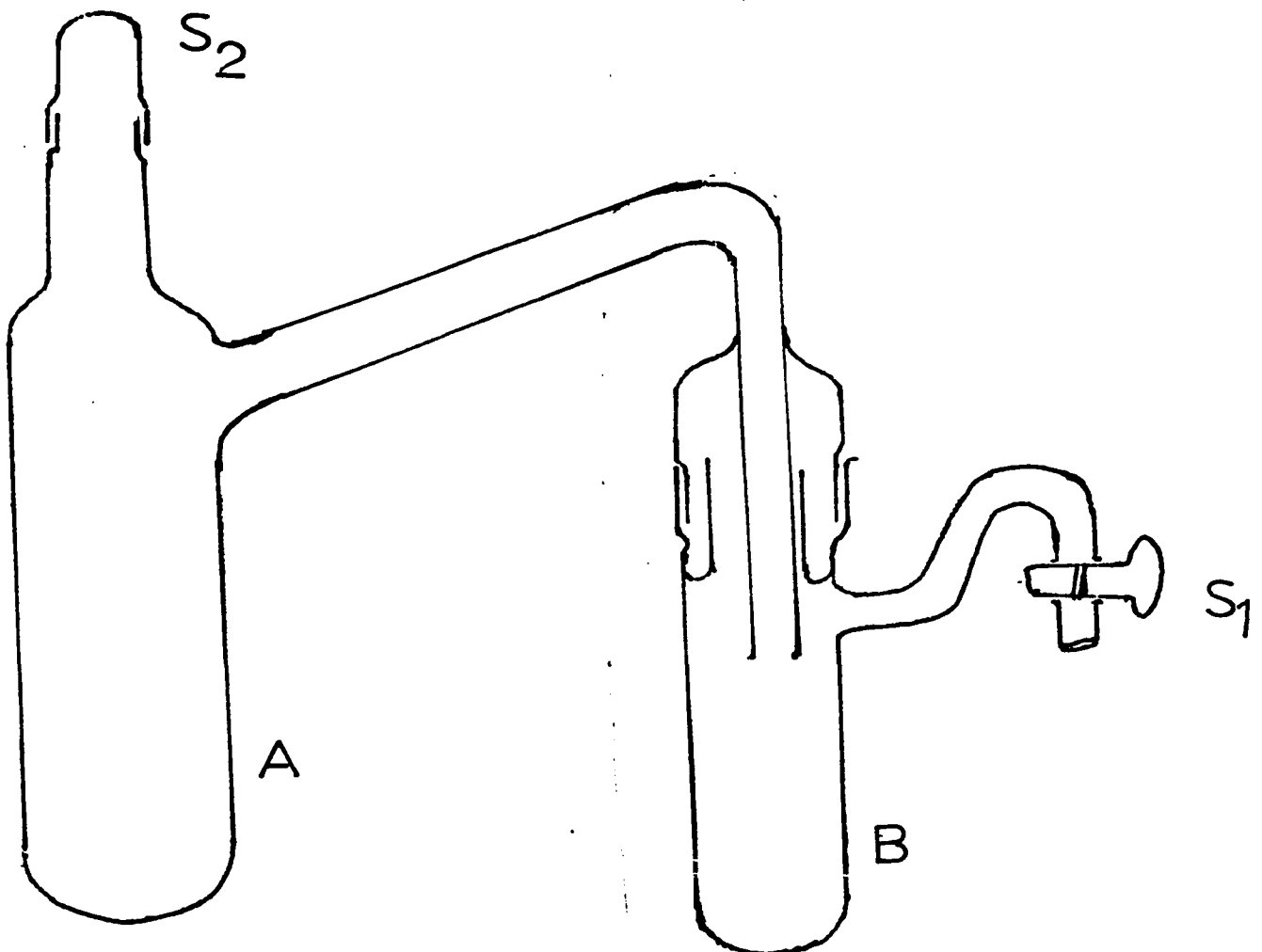
The system was connected to the vacuum line and by opening stop-cock S_1 , it was thoroughly evacuated and the tubes flamed out. Nitrogen was introduced through the same stop-cock, and when the tubes had been filled, stopper S_2 was opened. With the gas flowing through the system, Linde Molecular Sieves Type 4A, which had been heated to $350-400^{\circ}\text{C}$ and cooled in a desiccator were put in tube A to a depth of about 3-15 cm., depending on the amount of nitrile (or other solvent) to be dried. The solvent to be dried was added to about the same depth and the system degassed by evacuating for about one minute. The mixture was shaken manually for a few minutes to ensure proper contact of the solvent molecules with the sieves.

Tube A was put in liquid nitrogen and the solvent frozen. The system was evacuated further and stop-cock S_1 closed. Tube B was put in the liquid nitrogen bath and A was allowed to warm up to room temperature. The solvent was slowly distilled off from A into B. When sufficient solvent had distilled off, tube B was removed from the cold bath, the system filled with dry nitrogen and allowed to warm up to room temperature.

Phenylacetonitrile and benzonitrile were, like the low-

FIGURE 6

APPARATUS FOR VACUUM DISTILLATION



boiling nitriles, refluxed with P_4O_{10} and then distilled. The nitriles thus obtained were refluxed with barium oxide or calcium oxide and distilled. In each case the middle fraction, with boiling point within $0.5^\circ C$ of the published value, was collected.

(iv) AMINES

AnalaR grade Reagents obtained from vendors mentioned in the previous section were employed. Liquid amines were routinely purified by distillation from potassium hydroxide or calcium hydride. Whenever vacuum distillation was carried out the procedure was as described for nitriles. The solid amines 1,10-phenanthroline (anhydrous and monohydrate) and 2,2'-bipyridyl were used as obtained without further purification.

(v) ETHERS AND THIOETHERS

Anhydrous reagents were employed. When only ordinary reagent grade materials were available, they were distilled from calcium chloride and the distillates collected in dry flasks. When a distillate had been thus obtained or when an anhydrous reagent was available, the reagent was refluxed with lithium aluminium hydride and distilled.

(vi) MISCELLANEOUS REAGENTS

Triethylphosphine and triethylarsine were prepared by Professor A. D. Westland in previous work in this Laboratory.

They were used without further purification. Trimethylphosphite (Aldrich) was distilled once to separate it from any hydrolysis products. Triphenylphosphine oxide and triphenylarsine oxide were Baker analysed reagents and were used without further purification. Dimethylsulphoxide and N,N-dimethylformamide were dried over calcium chloride and distilled. Benzene and toluene were dried using the procedure described for drying ethers. Halogen-containing solvents such as methylene chloride were dried over P_4O_{10} and distilled as required.

Reagent grade tetrahydronaphthalene (B.D.H.) was washed with concentrated sulphuric acid and finally with water, separating the products, in each case, by means of a 500-ml. separatory funnel. The wet solvent was dried by refluxing with anhydrous calcium chloride, distilled and the middle fraction distillate finally dried by distillation from calcium hydride. AnalaR grade naphthalene (B.D.H.) was purified by the sublimation method described for purifying iodine.

(vii) DRY OXYGEN-FREE NITROGEN

The nitrogen supplied in cylinders contained sufficient oxygen to oxidize most complexes of molybdenum or tungsten described and thus ruin experiments. The oxygen was removed from the nitrogen by passing the nitrogen over a copper furnace at 250-300°C (Fig. 7). The nitrogen was then passed through columns of magnesium perchlorate, silica gel and bubbled over concentrated sulphuric acid. It was finally passed through three columns of phosphorus pentoxide.

FIGURE 7

THE COPPER FURNACE FOR REMOVING OXYGEN
FROM COMMERCIALY AVAILABLE NITROGEN.

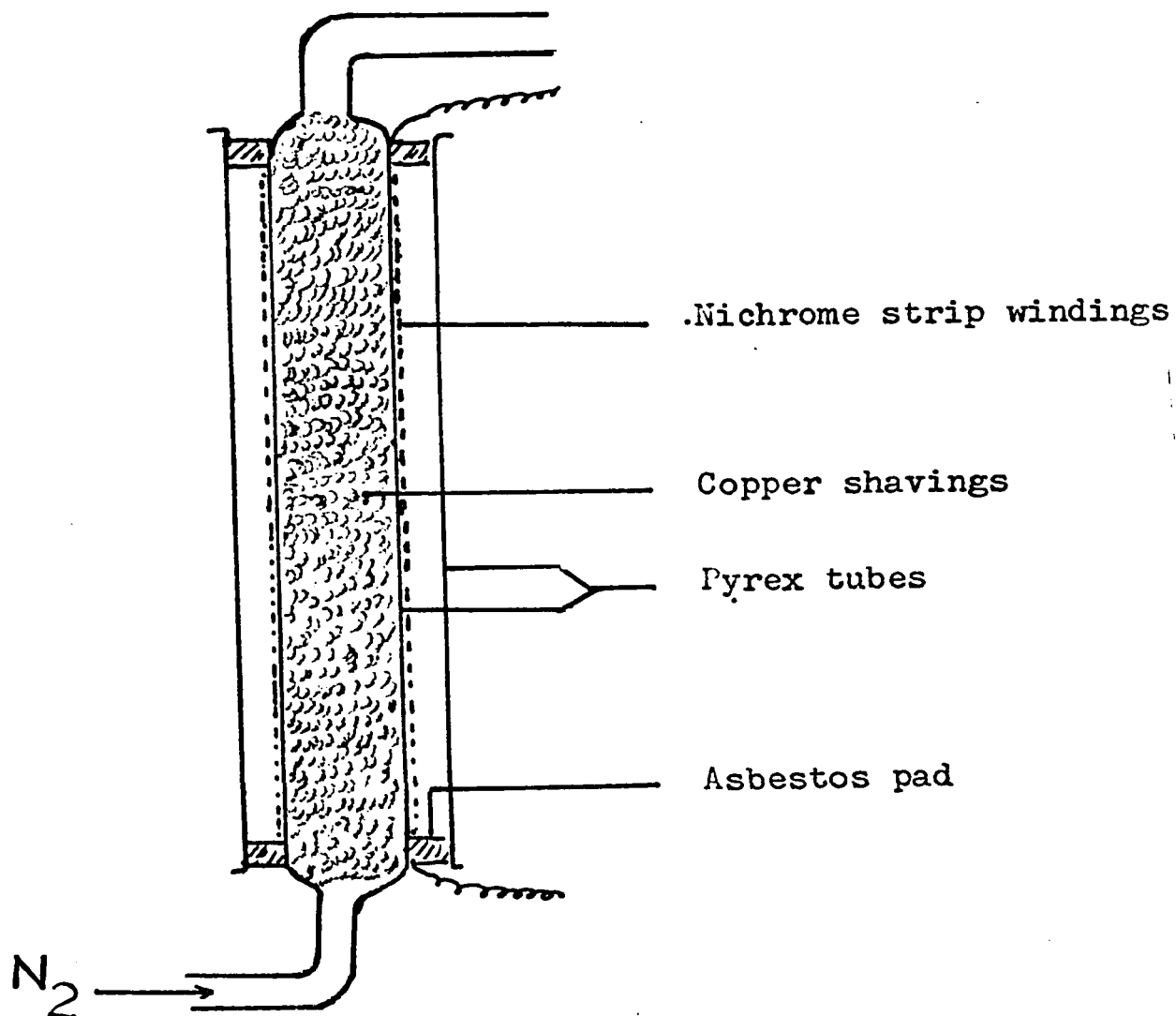


FIGURE 8

Apparatus for removal of oxygen and nitrogen
from argon.

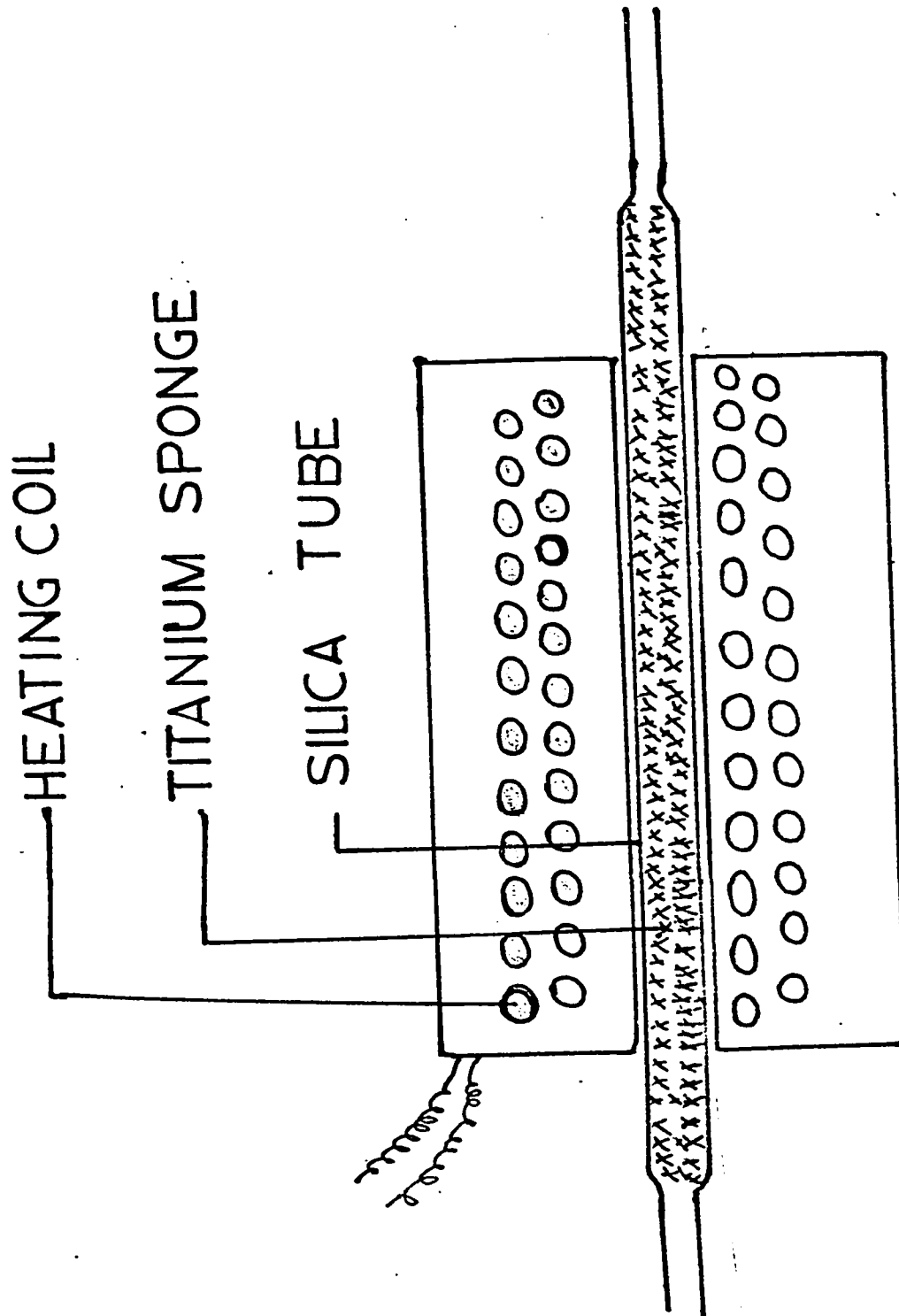


FIGURE 8.

(viii) NITROGEN- AND OXYGEN-FREE ARGON

Both oxygen and nitrogen were removed from argon by passing the gas over titanium sponge in a silica tube which had been heated to 600°C (Fig. 8).

C. ANALYTICAL TECHNIQUES

(a) General: Carbon, hydrogen, nitrogen, oxygen, phosphorus, arsenic and boron were estimated by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany. Occasionally, this microanalytical laboratory also checked sulphur and the halogens but these elements, together with molybdenum and tungsten, and sometimes phosphorus, were estimated by the present author following standard literature methods with the appropriate modifications. A few compounds were analysed for carbon, hydrogen, the halogens, oxygen and nitrogen by Dr. C. Daessle, Organic Microanalyses, Montreal, Quebec. In this section, the details of analytical work which was done by the present author will be given.

With the exception of iodine, the non-metals were determined after sodium peroxide fusion of the compound. Molybdenum was also occasionally determined after sodium peroxide fusion.

(b) Sodium peroxide fusion of molybdenum and tungsten complexes (171-175).

Procedure: Approximately 500 mg. of the sample were

accurately weighed and put in a 22-ml. Parr bomb. About 15 gm. of sodium peroxide (oxidant) and one gram of lactose were added. The contents were thoroughly mixed and the lid screwed on tightly. The bomb, inside a steel shield, was heated at the bottom with a sharp flame. As soon as a hissing sound was heard (indicating fusion of the mixture), the bomb was quickly removed from the shield and immersed in cold water. When the bomb was cool, it was washed with distilled water, opened and the melt extracted with distilled water. The solution was filtered and the filtrate plus washings made up to standard volume, usually 250 ml.

Sodium peroxide fusion decomposes a sample as follows:- Molybdenum and tungsten are oxidized to the hexavalent state. Chlorides are decomposed to sodium chloride whereas bromides form sodium bromide (174). Sodium bromate is also formed if a sample is heated in an open crucible to 600°C (174, 175).

Iodine-containing compounds are decomposed to iodides and iodates (173, 174) if the fusion is done in a bomb but to iodates if the fusion is done at 600°C (174). Sulphur in low oxidation states is oxidized to sulphate (170, 171). Phosphorus is converted to orthophosphate (176). Carbon is converted to carbon dioxide which reacts with sodium oxide to form sodium carbonate. Hydrogen first forms water which reacts with sodium oxide to form sodium hydroxide.

(c) Determination of molybdenum.

Molybdenum was determined gravimetrically by one of three

methods, namely by weighing as molybdenum trioxide, by weighing as lead molybdate or as molybdenyl oxinate. The method chosen depended on the particular compound being analysed and the amount of material available for analysis.

(i) Determination of molybdenum by weighing as the oxide
(178, 179)

This method was chosen if the complex did not contain interfering elements such as phosphorus and when the sample available could give at least 50 mg. of MoO_3 per weighing.

Procedure:

A known weight of the sample was put in a previously heated, cooled and tared porcelain crucible and carefully oxidized with concentrated nitric acid. The latter was added dropwise and when all gas evolution was complete, excess acid was evaporated by heating the crucible gently on a yellow flame. The carbonaceous matter was burnt off at the lowest temperature possible without inflaming. The crucible was then put in a muffle furnace and heated to constant weight at $525-550^\circ\text{C}$. Weighings were done on a Sartorius semi-micro balance and were reproducible to ± 0.03 mg.

(ii) Determination of molybdenum by weighing as lead molybdate
(177, 178, 179).

This method was used for complexes containing no sulphur, phosphorus or arsenic. Chlorine and bromine also interfere

as they precipitate as PbCl_2 or PbBr_2 , respectively, but their interference was avoided by addition of ammonium acetate (178). Acetate prevents precipitation of lead dihalide by forming a complex, $\text{Pb}(\text{OAc})_3^-$ (180). Addition of a large excess of lead acetate, the precipitant, was avoided.

Procedure:

The standard solution was prepared after sodium peroxide fusion as explained above. Aliquot portions, e.g. 50 ml., were transferred to 250-ml. beakers. Each portion* was neutralized by slowly adding the calculated amount of glacial acetic acid and then made acidic by adding about two ml. in excess. 25 ml. of 50% ammonium acetate solution** were added, the solution made up to about 150 ml. with distilled water and heated to near boiling. Molybdenum was precipitated by slowly adding a solution of 4% lead acetate. When precipitation was complete, the beaker was gently heated on a hot plate for at least one hour to effect coagulation. The precipitate was separated by filtering through a porcelain filtering crucible, Staatlich, Berlin No. OOA2, washed several times with hot water by decantation, and heated to constant weight at 600°C .

* All determinations, including those for other elements, were done in duplicate.

** This was omitted if the complex being analysed did not contain halogen.

(iii) Determination of molybdenum by weighing as molybdenyl oxinate, $\text{MoO}_2(\text{C}_9\text{H}_6\text{NO})_2$ (181, 182).

This method was used whenever the sample to be analysed contained interfering elements such as phosphorus.

Procedure:

The standard solution was prepared after sodium peroxide fusion. Aliquot portions were put into 250-ml. beakers and each portion neutralized to methyl red with acetic acid. About 25 ml. of 20% ammonium acetate solution were added to each portion and the solution heated to near boiling. Molybdenum was precipitated by slowly adding a 4% solution of 8-hydroxyquinoline in dilute acetic acid until the solution was perceptibly yellow. The precipitate was heated for about fifteen minutes to effect coagulation, filtered through a previously tared porcelain filtering crucible, washed several times with hot water and heated to constant weight at 140°C .

Appraisal of the three methods:

The oxide method has the advantage of being very rapid* but has the drawback that a large amount of sample must be used. Molybdenum trioxide should be heated in the furnace for only a limited time because volatilization occurs at elevated temperatures. According to Brinton and Stoppel,

* A determination could be completed in less than two hours.

the loss of molybdenum trioxide is not greater than 0.1 mg. per hour between 500°C and 600°C. It is, however, advisable to avoid heating the oxide close to 600°C (183). At about 620°C, the oxide sublimes visibly (37).

The lead molybdate method was used whenever possible because of its several advantages. Adjustment of pH is not as critical as in the oxine method. Therefore, a large amount of acetic acid (but not mineral acids in which lead molybdate is soluble) can be added without any harmful effect (178). The precipitate is usually dried at 600°C. However, the temperature can rise much higher (e.g. to 800°C) without affecting the results. Lead molybdate has a large molecular weight and, therefore, only a small amount of sample is necessary for a determination.

The oxine method has the advantage that it can be used when the complex under investigation contains interfering elements such as phosphorus or arsenic. Furthermore, the precipitate, $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$, has a large molecular weight. The main disadvantage of this method is the somewhat narrow pH range (pH 3.6-7.3) (182) over which complete precipitation occurs. There is a disagreement as to what is the exact pH range for complete precipitation and the correct temperature for drying the precipitate (181).

It has been observed during the present work that if 5 ml. of glacial acetic acid are added to a 150-ml. solution slightly acidified relative to methyl red (pH 4.2-6.3), the solution remains yellow without precipitation when oxine is

added. Addition of ammonia colours the solution red, and the process cannot be reversed by adding more acid. Moreover, precipitation is incomplete. The procedure recommended by Vogel (184) was adopted during the present work but instead of using only 10 ml. of 2% ammonium acetate, about 25 ml. of 20% ammonium acetate (182) were employed.

A large excess of the precipitant was avoided because it made washing of the precipitate difficult, and if all oxine was not washed off, it caused positive errors. When these two sources of error were avoided, the oxine method gave very good results.

(d) Determination of tungsten

Tungsten in complexes containing interfering elements such as phosphorus can be determined, after precipitating the oxide with the aid of cinchonine, by weighing as the oxide (185, 186).

In complexes with no interfering elements, the element was determined following the procedure described for determining molybdenum by the oxide method. The only difference in the determination of the two elements is that tungstic acid requires a higher temperature (750-780°C) to dehydrate it to the trioxide whereas molybdic acid is dehydrated at 500-525°C.

(e) Determination of chloride and bromide in complexes
of molybdenum and tungsten

(i) Introduction:

Chloride and bromide in molybdenum and tungsten complexes were determined either after sodium peroxide fusion or after distilling the hydrogen halide.

If chloride or bromide, in the presence of molybdate or tungstate solutions, is to be precipitated as the silver salt, care should be taken to avoid the precipitation of silver molybdate or tungstate. As is well known, precipitation of silver molybdate from weakly acidic solutions provides an accurate gravimetric method of determining molybdenum (187). Interference by silver molybdate or tungstate may be stopped by adding citric acid or sodium citrate before precipitating the halide with silver ion (188, 189). Roizenblat et al overcame interference by molybdates or tungstates by reducing the interfering ions with zinc amalgam prior to the halide determination (190). Interference by molybdates can be stopped by means of strong mineral acids such as nitric acid (191). This method is not applicable to tungstate solutions, however, because tungstic acid is insoluble in mineral acids (186). Interference by tungstates may be stopped by means of polycarboxylic acids such as citric acid (188, 189), oxalic acid (192, 193), tartaric acid (186, 193) or their sodium salts. For analytical work, previous workers have used citric acid in determining a small amount of chloride (188, 189). During

the present work, chloride and bromide were determined potentiometrically or gravimetrically. It was, therefore, essential to establish by means of some preliminary tests the best conditions under which these ions could be determined in molybdate or tungstate solutions.

(ii) Preliminary tests to ascertain the effects of a large excess of silver(I) ion and the effect of molybdates in the determination of chloride and bromide

The nature of the tests should be clear from Table 8 in which the effects of a large excess of silver(I) ion in the determination of chloride in molybdate solutions are shown. Two observations were of interest in these simple tests:-

(a) Once a precipitate formed, it could not be re-dissolved completely by addition of more acid. This most probably implies that the precipitate is not of a simple molybdic acid, H_2MoO_4 , but of acids of condensed species such as the paramolybdates, $[\text{Mo}_7\text{O}_{24}]^{6-}$ (1). It is, therefore, essential that sufficient mineral acid be added initially to ensure that no molybdates are precipitated at any stage.

(b) It was noted that if a slight precipitate formed, and then the beaker set aside, more white precipitate slowly formed. This suggested that the acids mainly caused a supersaturation of molybdate solution and once a slight precipitate formed, it acted as a nucleus for further crystallization of the con-

TABLE 8

EFFECTIVENESSES OF NITRIC, SULPHURIC AND ACETIC
ACIDS IN STOPPING PRECIPITATION OF SILVER MOLYBDATE.

<u>Acid (2N)</u>	<u>Initial volume (ml.)</u>	<u>Molybdenum(VI) (mg.) per 100 ml. of solution</u>	<u>Total volume (ml.) of 1/10 N AgNO₃ added before ppt appears</u>	<u>Total volume (ml.) of solution</u>	<u>Normality of solution (in acid) when ppt appears</u>
HNO ₃	50	1586	225	275	0.182
H ₂ SO ₄	50	1586	140	190	0.263
CH ₃ COOH	50	1586	2	52	0.962

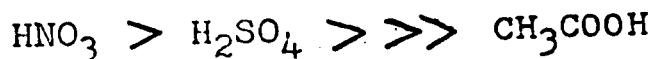
TABLE 9

PERCENTAGE OF CHLORIDE IN A SAMPLE OF SODIUM CHLORIDE AS
DETERMINED IN THE ABSENCE AND IN THE PRESENCE
OF A LARGE EXCESS OF MOLYBDENUM.

<u>Method</u>	<u>Volume of solution after titration or addition of silver nitrate</u>	<u>Wt. of Mo(VI) (mg.) per 100 ml. of solution</u>	<u>% of chloride in a sample*</u>
Potentiometric	75	0	60.65
Potentiometric	100	120	60.59
Gravimetric	150	330	60.46

* Theoretical value = 60.64%

densed species. The figures in Table 8 do not, therefore, give a true measure of the amount of molybdenum(VI) that can be kept in solution in the presence of the various acids. The figures merely show that the relative effectiveness of these acids in preventing precipitation of molybdenum(VI) is in the order



It was also confirmed quantitatively (Table 9) that chloride or bromide in the presence of a large amount of molybdate can be determined gravimetrically, provided sufficient nitric or sulphuric acid is added to the solution prior to the precipitation of the halide. For this reason, chloride and bromide in molybdate solutions were determined in solutions which were at least 0.25N in nitric or sulphuric acid.

(iii) Preliminary tests to establish relative effectiveness of citrate, oxalate and tartrate ions in preventing precipitation of tungstic acid.

During this work, interference by tungstic acid in halide determination was prevented by means of tartaric acid rather than with citric acid which previous workers have used. Tartaric acid was chosen because:-

(a) Tartrate ions are known to form stable complexes with tungsten(VI), (186, 194) a property used to separate tungsten from molybdenum, (186, 195).

TABLE 10

RELATIVE EFFECTIVENESSES OF CITRATE, OXALATE AND TARTRATE
IONS IN STOPPING PRECIPITATION OF TUNGSTIC ACID.

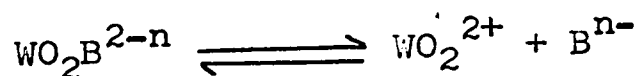
<u>Carboxylic acid salt added</u>	<u>Initial volume of solution (ml.)</u>	<u>Initial wt. of tungsten(VI) (mg.) per 100 ml. of solution</u>	<u>Volume of 2N H₂SO₄ (ml.) added before precipitate forms</u>
I Sodium citrate	150	570	35
II Sodium oxalate	150	570	80
III Sodium tartrate	150	570	64

(b) Preliminary tests on the relative effectiveness of citrate, oxalate and tartrate ions in preventing precipitation of tungstic acid showed that oxalate and tartrate ions are about twice as effective as citrate ions. The results are summarized in Table 10.

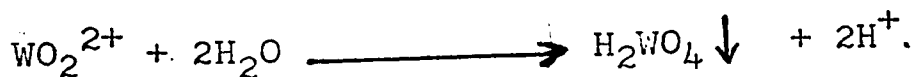
Basis for the tests:

The tests were based on the following assumptions:-

In view of the fact that aqueous chemistry of hexavalent molybdenum and tungsten involves species of the type MoO_2^{2+} which may be precipitated as the oxinates $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON}_2)_2$ (181) and $\text{WO}_2(\text{C}_9\text{H}_6\text{ON})_2$ (196), it seemed reasonable to assume that a polycarboxylic acid anion, B^{n-} , forms with tungsten(VI), 1:1 complexes of the type $\text{WO}_2\text{B}^{2-n}$. Addition of a mineral acid to a solution containing such species should increase the dissociation of such complexes because the carboxylate ion produced in an equilibrium such as



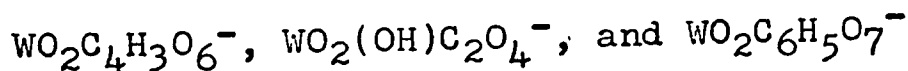
is protonated to give weakly ionized carboxylic acids. This pushes the equilibrium to the right. At the same time, the WO_2^{2+} species produced react with water to give the weakly ionized tungstic acid, H_2WO_4 , which precipitates:



If, therefore, a mineral acid is slowly added to different solutions of equal volume, each of which contains x mmoles of tungsten(IV) and x mmoles of carboxylate anions, B^{n-} , a precipitate should form first in the solution containing the least stable complex, WO_2B^{2-n} . On the other hand, the most stable complex, WO_2B^{2-n} , will dissociate appreciably only after the addition of a large volume of the mineral acid. Ideally, the comparison should be at the same pH.

The results in Table 9 show that the choice of citrate rather than oxalate or tartrate ions to stop precipitation of tungstic acid (188, 189) is unjustifiable since these ions are the least effective.

Some recent work by Termendzhyan et. al. (192, 193) has shown that at pH 2.1, the complexes formed by tungsten(VI) with tartrate, oxalate and citrate ions are, respectively,

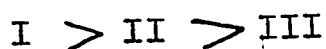


I

II

III

Note that the citrate and tartrate ions form complexes of the type WO_2B^{2-n} discussed above. According to these authors, the stability of these complexes is in the order



8

This order is slightly different from that indicated in Table 10 in that a tartrate-W(VI) complex is more stable than an oxalate-tungsten(VI) complex whereas the results of the present work show the reverse order. There is agreement,

however, between these results and those of the present work that a citrate-tungsten(VI) complex is less stable than either an oxalate-tungsten(VI) or a tartrate-tungsten(VI) complex.

Quantitatively, it was shown that chloride in a large quantity of tungsten(VI) can be determined gravimetrically provided sufficient tartaric acid (or its sodium salt) is added to the solution prior to precipitation of the chloride. For instance, the percentage of chloride in a sample of sodium chloride in tungstate solution containing 340 mg. of tungsten(VI) per 100 ml. of solution was 61.1 (theory: 60.64).

As in the case of molybdates, it was noticed that once a slight precipitate formed (Table 10), heavier precipitate which could not be re-dissolved completely by addition of more carboxylic acid salt or the acid itself was formed by letting the solution stand. On the basis of these tests, chloride and bromide in complexes of molybdenum and tungsten were determined as indicated below.

(iv) Procedure for chloride and bromide determination in complexes of molybdenum

Approximately 200-500 mg. of a sample were fused with sodium peroxide.. Aliquot portions were put in 250-ml. beakers and each portion neutralized by carefully adding the calculated

amount of 2N sulphuric* or nitric acid. The solution was then acidified by adding 25 ml. of the same acid and the solution made up to 150 ml. with distilled water. The solution was thoroughly stirred to expel all carbon dioxide and allowed to cool to room temperature. The sides of the beaker were wrapped with aluminum foil to cut down as much radiation as possible and the halide titrated potentiometrically with a standard silver nitrate solution.

Alternatively, the halide was determined gravimetrically as follows:-

After making the acidic solution to 150 ml. and stirring the solution to expel carbon dioxide, the halide was precipitated by slowly adding a solution of about 0.05N silver nitrate. The beaker was covered with a watch glass and wrapped on all sides, except the bottom, with an aluminum foil. After coagulating the precipitate, the latter was cooled to room temperature, separated by filtration using a porcelain filtering crucible, Staatlich, Berlin No. 00A2 and

* 2N sulphuric acid was used most of the time and it was always used when the sample contained a bromide, to avoid the possibility of oxidizing some bromide to bromine.

washed with dilute (1:100) nitric acid and distilled water. The precipitate was dried to constant weight at 130°C.

(v) Procedure for chloride and bromide determination in complexes of tungsten.

The preparation of the solution was exactly as described for molybdate solutions.

To each aliquot portion in a 250-ml. beaker, about one gram tartaric acid was added for every 10 mg. of W(VI). The solution was acidified (litmus) by means of 2N sulphuric acid and about 5 ml. added in excess. The rest of the procedure was as that for determining halide in molybdates gravimetrically. The only difference in the two was in the washing of the precipitates. Precipitates from tungstate solutions were washed with dilute (1:3) acetic acid and then with distilled water.

(vi) Determination of chloride and bromide in complexes of molybdenum and tungsten after distillation of the hydrogen halides.

Apparatus:

The apparatus used for distilling hydrogen chloride from complexes of molybdenum or tungsten is shown in Fig. 9.

Procedure:

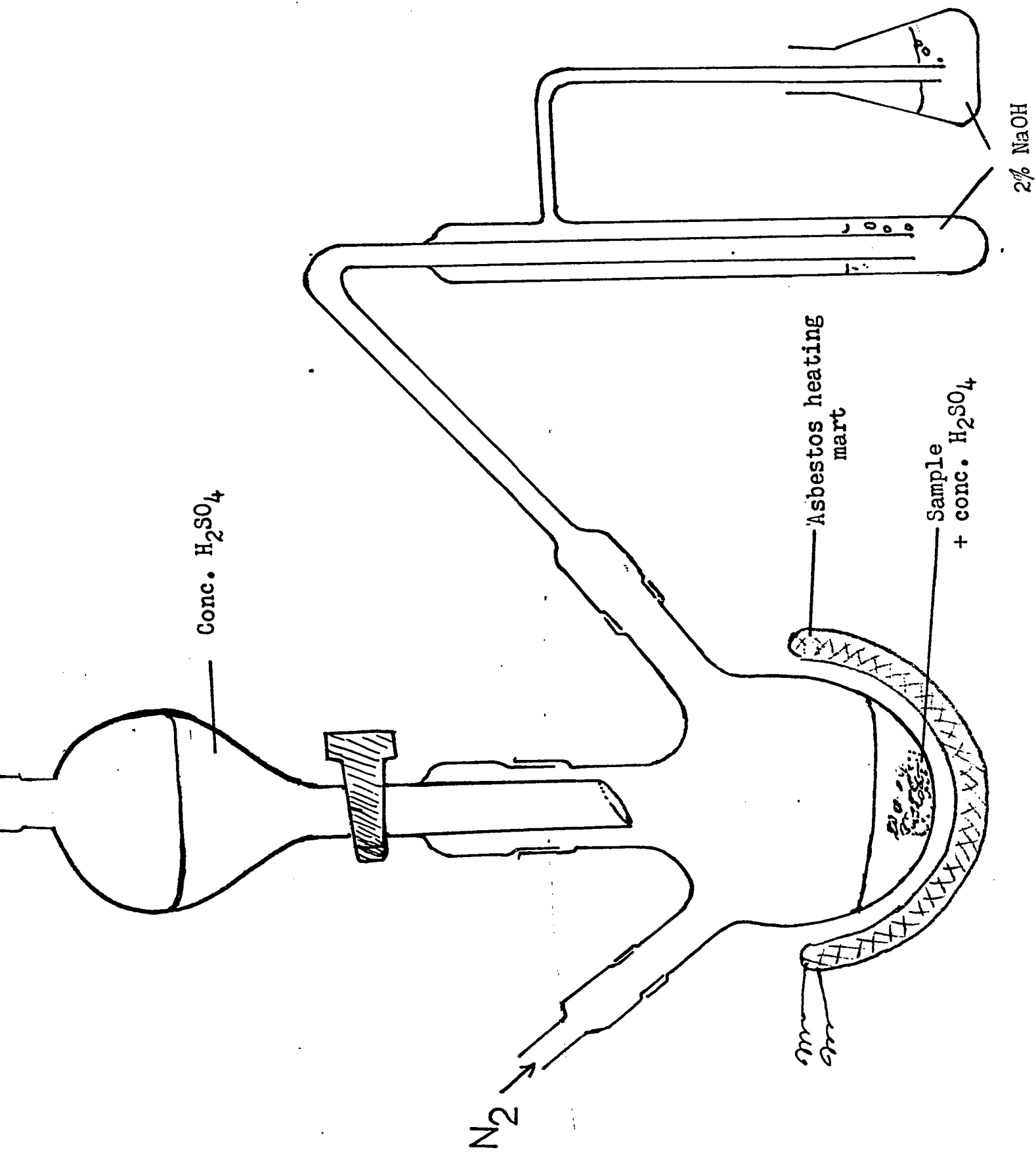
The apparatus was set up as shown in the figure, with all the joints air-tight and nitrogen slowly bubbling through the alkaline solution. With nitrogen flowing through the system, the sample was decomposed by digesting it with the concentrated sulphuric acid for two to three hours. The heating was stopped but nitrogen flow continued. When the three-neck flask was cool, the separatory funnel was removed from the flask, the distillate-collecting tube carefully removed and the alkaline solution (containing the chloride) transferred into a volumetric flask. The distillate-collecting tube and the Erlenmeyer flask were rinsed several times with distilled water and the washings added to the bulk of the solution. When the latter was cold, it was made up to the mark and the halide determined gravimetrically or potentiometrically.

The main draw-back of this method is that about three hours are necessary to ensure complete distillation of the hydrogen halide. It has the following advantages: A Parr bomb is not required for decomposition of the sample. When a Parr bomb is used, the alkaline solution has to be filtered to separate some nickel hydroxide always produced. This is not necessary when the halide is distilled from the complex. Furthermore, the halide is determined in a solution containing no interfering ions.

Note: If bromide is distilled this way, the alkaline solution should contain some sodium formate.

FIGURE 9

Apparatus for distillation of hydrogen chloride
from a halide complex of molybdenum or tungsten.



(f) Determination of iodine in complexes
of molybdenum and tungsten.

1. Introduction:

A commonly used method for determination of iodine (or bromine and chlorine) in complexes of molybdenum and tungsten is to mix the sample with solid silver nitrate and to digest it with concentrated nitric acid. The halides are then determined gravimetrically by weighing as the silver salt, AgX (9, 12). Unfortunately, no details are given. Probably silver iodide is separated from molybdic or tungstic acids by washing with ammonia.

If, on the other hand, a molybdenum or tungsten complex is fused with sodium peroxide, there are two possible sources of error in the subsequent determination of iodine. As we have already seen, some of the iodine is oxidized to iodate (172, 173, 174). To convert the iodate to iodide, a reducing agent such as hydrazine sulphate is used (170). However, reducing agents such as hydrazine sulphate, ferrous sulphate or sodium thiosulphate are inadmissible in molybdate solutions because they also reduce molybdenum(VI) into blue molybdenum(V) almost instantaneously (37). Sodium sulphite and sodium arsenite had no observable effect on the hexavalent molybdenum.

In acidic solution, iodide reduces molybdenum(VI) (197, 198). Contrary to claims in the literature that hydriodic acid does not reduce molybdic acid in the cold without the presence of phosphorus (198), the present author found that

a solution containing sodium molybdate and potassium iodide slowly became yellow and then light blue when acidified with 2N sulphuric acid. These colour changes were not observed when molybdenum was absent. Moreover, when the solutions were shaken with benzene, those containing molybdenum gave a purple colour in the organic layer.

Similar tests showed that reducing agents such as sodium thiosulphate which gave blue colour with molybdenum(VI) almost instantaneously also reduced tungsten(VI) but more slowly. In the method finally adopted, the iodide was oxidized with cerium(IV) and the liberated iodine distilled into a solution of potassium iodide, using the apparatus shown in Fig. 10.

2. Procedure:

An accurately weighed amount of the sample was placed in the two-necked flask. The calculated amount of ceric sulphate to oxidize all the iodide to iodine and the molybdenum or tungsten to the hexavalent state plus 1% in excess was weighed out and added to the complex in the flask. The apparatus was set up for distillation as shown.*

With nitrogen passing through the system, about 50 ml. of 2N sulphuric acid were put into the flask, and the latter stoppered quickly. The flask was heated and the iodine collected in about 150 ml. of 5% potassium iodide solution which

* The condenser was air-cooled.

FIGURE 10

Apparatus for distillation of elemental iodine
from its compounds.

was cooled in an ice bath. Heating was continued for 20-30 minutes, after which time the iodine solution was put into a volumetric flask, the Erlenmeyer flask washed with potassium iodide and the washings added to the bulk of the solution. When the solution was at room temperature, it was made up to the mark. Aliquot portions of standard arsenic(III) solution were put in 250-ml. Erlenmeyer flasks and titrated with the iodine solution using starch as an indicator.

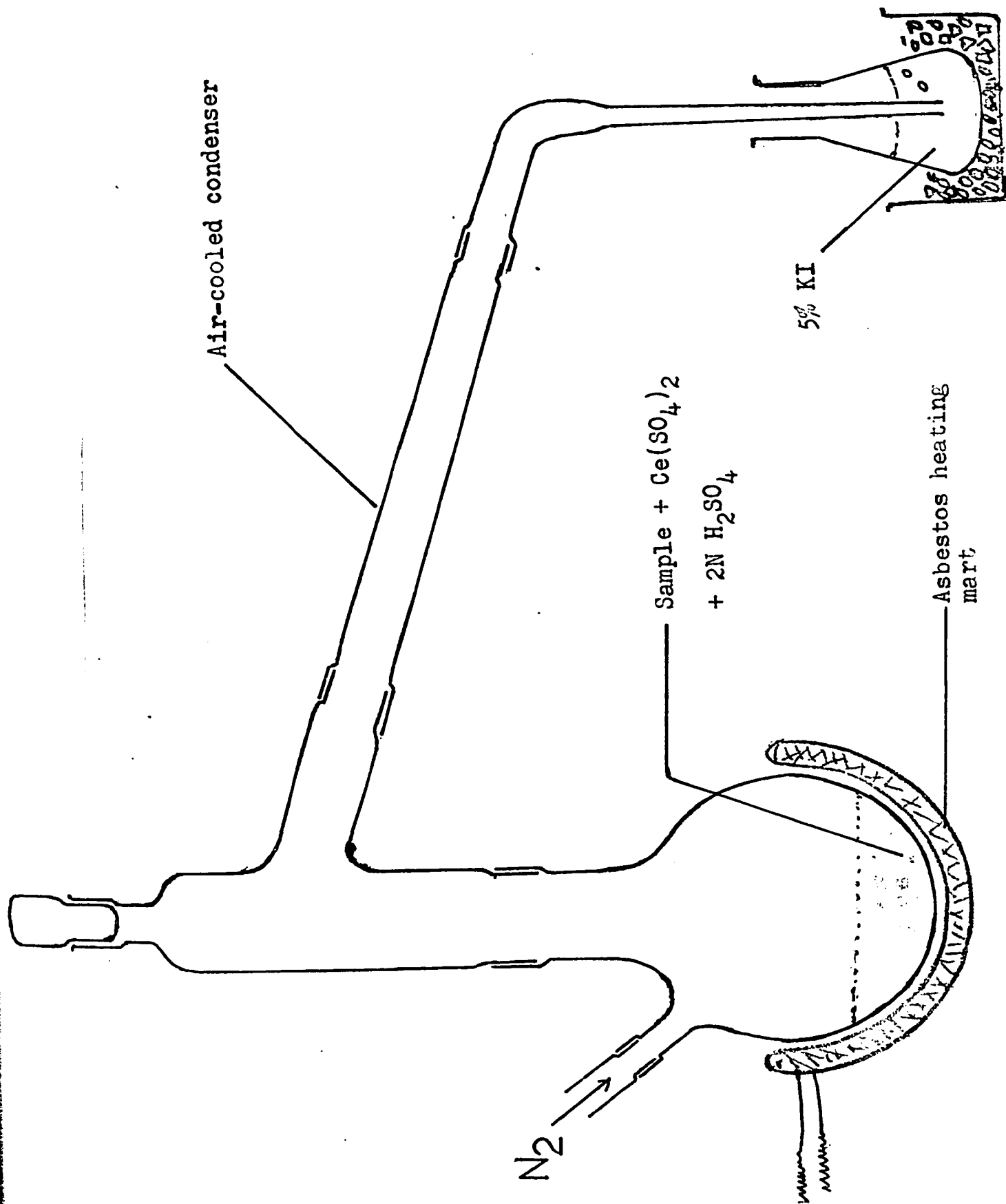
(g) Determination of sulphur in complexes of molybdenum

(i) Introduction:

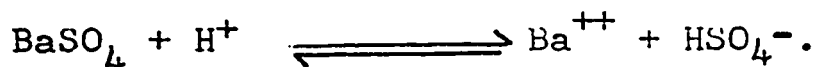
Although barium molybdate dissolves only to the extent of 0.0058 gm. per 100 gm. of water at room temperature (199), it is soluble in mineral acids. The sulphate may, therefore, be precipitated as barium sulphate from molybdate solutions without interference (200). Provided the solution is made sufficiently acidic, a large quantity of molybdate has little effect as verified by determining the percentage of sulphate in a sample of potassium sulphate containing 300 mg. of molybdenum(VI) per 100 ml. of solution.

	In absence of molybdate	In presence of molybdate	Theory
Percentage of sulphur in the K_2SO_4 sample	18.60	18.83	18.40

The differences are probably due to impurities in the sample rather than the presence of molybdates since analyses



of pure samples gave good results (see Chapter 4). Barium sulphate is fairly soluble in acids because of equilibria of the type



The solution must, however, be acidic not only to avoid precipitation of barium molybdate but also to improve the crystallinity of the precipitate (201). Losses due to equilibria of the above type were minimized by using excess barium chloride. A large excess of the precipitant was, however, avoided since it might give positive errors due to co-precipitation (201).

(ii) Procedure:

The sample was decomposed by means of sodium peroxide fusion.

Treatment of standard solution:

Aliquot portions were put into 250-ml. beakers and each acidified (methyl red) with 2N hydrochloric acid. 25 ml. more of the 2N HCl were added in excess and the solution made up to about 150 ml. The solution was heated to 90°C and the sulphate precipitated by slow addition of a 10% solution of barium chloride which had been heated to 80°C. The coagulated precipitate was collected in a porcelain filtering crucible, Staatlich, Berlin No. 00A2, in the usual way and heated to constant weight at 600°C.

(h) Determination of phosphorus in molybdenum complexes

Phosphorus was determined gravimetrically by weighing it as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$ (176).

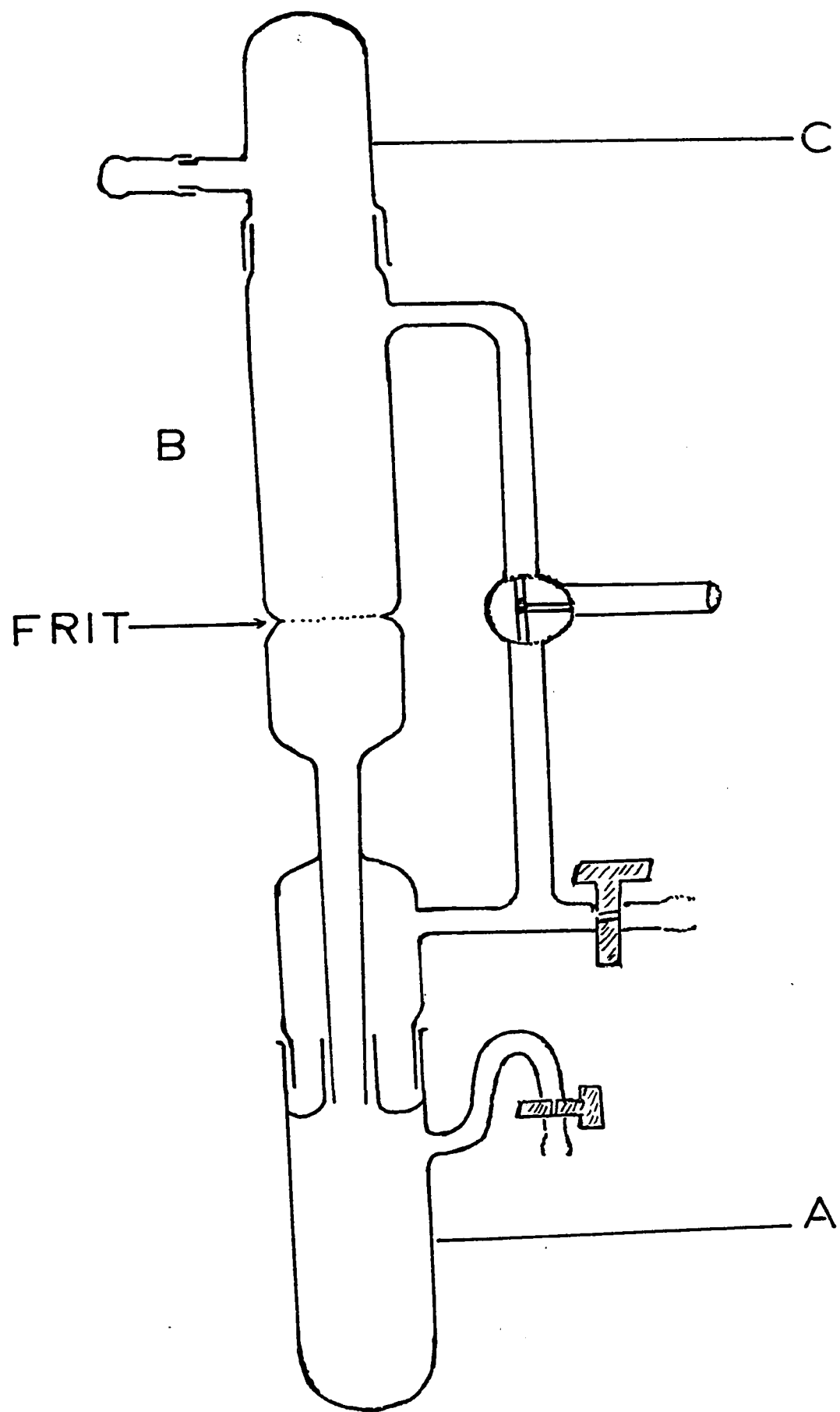
Procedure:

The sample was decomposed by sodium peroxide fusion. Aliquot portions were transferred to 400-ml. beakers and each portion acidified by adding the calculated amount of 4N hydrochloric acid. A few more drops of acid were added and the acidity checked with litmus paper. About 30 gm. of ammonium citrate were added, followed by 10 ml. of concentrated hydrochloric acid and 100 ml. of nearly neutral magnesia mixture. The solution was carefully neutralized (litmus) by slowly adding a solution of concentrated ammonia and then made basic by adding 3-5 ml. in excess. The solution was then diluted to about 250 ml., covered with a watch glass and left to stand overnight.

The precipitate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, was collected on a medium porosity sintered glass crucible, dissolved in dilute (1:4) hydrochloric acid and reprecipitated in the presence of 0.3-0.5 gm. of citric acid by adding 1-2 ml. of magnesia mixture. The precipitate was separated using a Whatman No. 41 filter paper, thoroughly washed with dilute ammonia (1:19) and ignited to constant weight at 1050°C .

FIGURE 11

Apparatus for filtration under inert atmosphere.



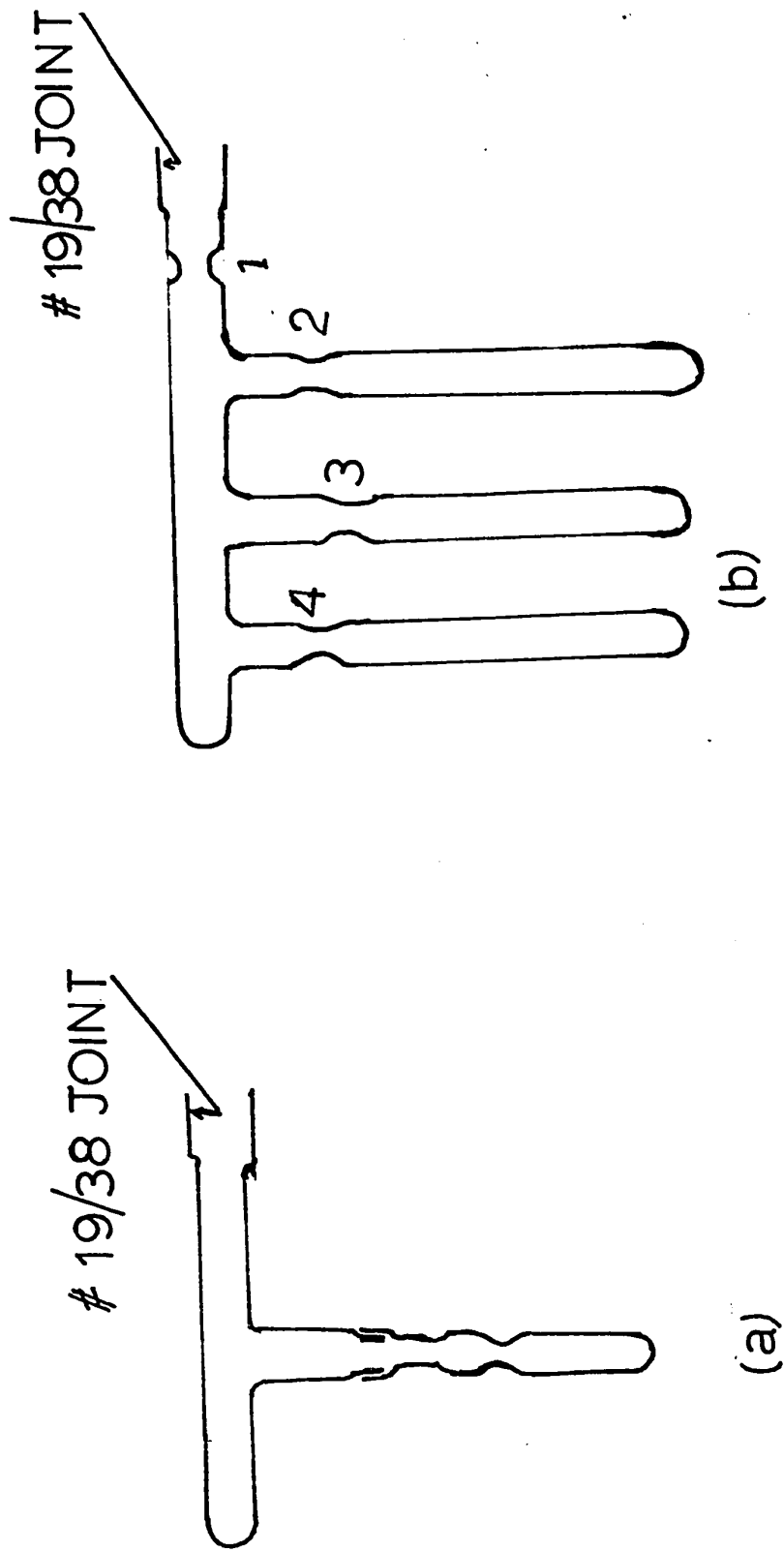


FIGURE 12

AMPOULES FOR (a) WEIGHING AND (b) STORING AIR-SENSITIVE SAMPLES.

(i) Methods of handling sensitive compounds

Most of the compounds handled during this work were sensitive to oxygen, water or both. In most cases, however, an analytical sample could be transferred to a vial, weighed and fused without taking any special precautions to exclude air. A few compounds such as $W(CO)_4Cl_2$ required special handling as described below:-

1. Apparatus:

Fig. 11 shows an apparatus described by Fritz et al. (202) for filtration in an atmosphere of nitrogen. Essentially, the apparatus has three separate parts, viz. two Schlenk tubes A and C, and a middle part, B, provided with a fritted glass disc for filtration. Throughout the rest of this thesis, reference to the filtration apparatus will mean this apparatus (Fig. 11) whereas "Schlenk tube" will be used to mean a Schlenk tube such as A. Fig. 12 shows ampoules used for (a) weighing substances such as $W(CO)_4Cl_2$ and (b) storing sensitive samples for long periods.

2. Procedure:

(i) Analytical samples: With the substance in B (Fig. 11) and nitrogen running through the system, the ampoule (Fig. 12a) was fitted on to the filtration apparatus, the system evacuated and a convenient amount of the substance transferred to the ampoule. The system was filled with nitrogen, the ampoule detached from the apparatus and quickly stoppered.

A scratch was made at the constriction (Fig. 12a) with a glass-cutter, the ampoule broken open and quickly emptied, and the sample transferred either to a Parr bomb or tared crucible. The two pieces of the ampoule and the stopper were re-weighed to obtain the weight of the sample.

Note: If the metal was being determined by the oxide method, analysis was not affected by the decompositions which occurred when the sample was being transferred to the crucible. However, the samples for halogen determination were transferred to the bomb inside a nitrogen-filled glove box to avoid error due to loss of halogen, for example by solvolysis.

(ii) Samples to be stored: The ampoule (Fig. 12b) was fitted on to the filtration apparatus and the sample transferred into the ampoule as described above. With nitrogen running through the system, the ampoule was sealed at constriction 1 (Fig. 12b). To recover a sample from the sealed ampoule tube, the desired amount of the substance was transferred to one of the side tubes. The other side tubes were put into a Dewar flask containing liquid nitrogen and the tube with the desired amount of the sample was cut from the rest with a blow torch, e.g. at constriction 2 (Fig. 12b).

D.

PHYSICAL MEASUREMENTS

1. Infrared spectra:

(a) Instrumentation: Infrared spectra were recorded on a

Beckman Model IR20 Spectrophotometer. The instrument has the range $4000\text{--}250\text{ cm.}^{-1}$. Among the various accessories of the machine are gears which permit scale expansion by either four or ten times. The 4X scale expansion gears were usually used.

(b) Procedure:

(i) $4000\text{--}600\text{ cm.}^{-1}$ range: The samples were put on an agate mortar, thoroughly powdered and then mulled with Nujol. The mulls were held between two rock-salt discs and the spectra recorded.

(ii) $600\text{--}250\text{ cm.}^{-1}$ range: The samples were mixed with cesium iodide (as support) and pressed into discs as follows:-

Approximately 5-15 mg. of the sample whose far infrared spectrum was desired was mixed with 50-250 mg. of spectro-grade cesium iodide (Harshaw Chemical Co., Cleveland, Ohio) which had been dried at 180°C and cooled in an atmosphere of dry nitrogen in a dry box. The mixture was put in a steel cup, 2.5 cm. long and 9 mm. diameter, a steel ball 8 mm. diameter put in, the cup covered with a tightly fitting steel cover and the ingredients thoroughly mixed using an electric shaker (Crescent Dental Manufacturing Co.).

The mixture was put in a circular steel die and pressed into discs using pressure of $5,000\text{ lb. in.}^{-2}$. The disc, inside the die, was placed in the spectrophotometer which had been thoroughly purged with dry nitrogen and the spectrum was recorded.

(c) Calibration of peaks:

It was found that the calibration of the wavenumber drum corresponded very well with the markings on the chart paper. It was noticed, however, that when the instrument was set for high resolution, i.e. slit width kept at a minimum, the pen response was dependent on the slit opening. Spectra were, therefore, calibrated whenever possible against known peaks for polystyrene.

The procedure followed will be illustrated by assuming that the required peaks were in the spectral range 2000 cm.^{-1} to 1800 cm.^{-1} in which case the most convenient peak of the polystyrene film is that at 1601.8 cm.^{-1} . In other spectral regions, other peaks would have to be selected. The position of the 2000 cm.^{-1} wavenumber mark on the drum was set as accurately as possible and the pen set at a particular mark on the chart paper. The spectrum was scanned until about 1650 cm.^{-1} and the scanning stopped. The sample was removed from the optical path and the polystyrene film put in its place. Without adjusting the positions of either the wavelength on the drum or the pen on the chart paper, the scanning was continued until about 1550 cm.^{-1} . By using the peak at 1601.8 cm.^{-1} as the reference point, the positions of the peaks due to the sample were then marked.

(d) Scale expansion and accuracy of peaks:

Normally, a four-fold expansion of the wavelength scale was used in order to improve accuracy. This permitted a

spreading of 100 cm.^{-1} over a length of 51 mm. on the chart paper (for the spectral range $2000\text{-}250 \text{ cm.}^{-1}$). Hence, since one cm.^{-1} was then represented by a length of 0.51 mm., spectra in this range were precise to $\pm 1 \text{ cm.}^{-1}$.* For similar reasons, spectra in the spectral range $4000\text{-}2000 \text{ cm.}^{-1}$ were precise to $\pm 2 \text{ cm.}^{-1}$.

(e) Spectra in the range $260\text{-}200 \text{ cm.}^{-1}$

The spectra of the tungsten complexes WBr_3py_3 and WCl_3py_3 in the range $260\text{-}200 \text{ cm.}^{-1}$ were recorded on the Perkin-Elmer Model 225 spectrometer at Carleton University, through the courtesy of Dr. Michael Parris. The peaks in these spectra are probably accurate to within $\pm 0.5 \text{ cm.}^{-1}$.

2. Conductivity

Conductivity measurements were made using an Industrial Instruments conductivity bridge model RC-16B2. Solutions were held between two platinum electrodes in the conductivity cell shown in Fig. 13. The cell constant of this particular cell was 0.761. Conductivity measurements were carried out using non-aqueous ionizing solvents viz. acetonitrile, nitrobenzene and pyridine.

Procedure:

Solutions of known concentrations were prepared in a

* A length of 0.5 mm. can be read easily.

nitrogen-filled glove box. The solvent, which had been purified by one of the methods outlined earlier was degassed by blowing dry nitrogen through it. The conductance cell was rinsed with this solvent, then filled, stoppered and put in a water thermostat set at 25°C and left for at least half an hour. The conductance of the solvent was then determined.

The conductance cell was rinsed with the solution of the sample and then filled. The cell was stoppered and put in the thermostat for at least half an hour before measuring the conductance.

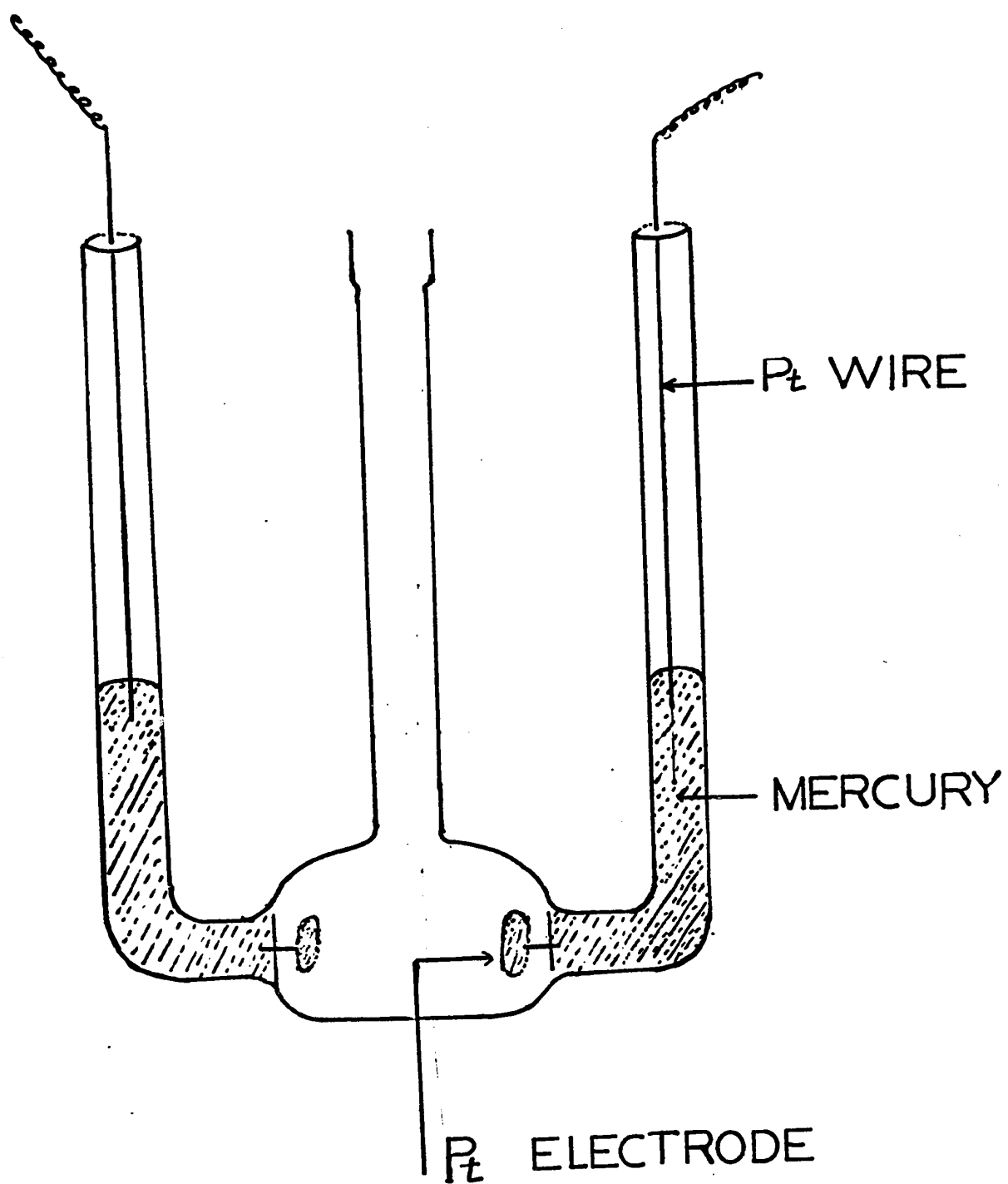
3. Nuclear magnetic resonance

Nuclear magnetic resonance spectra were recorded on a Varian Associates Model T-60 NMR spectrometer using tetramethylsilane (TMS) as a reference compound.

Procedure:

An NMR tube was put in the glove box and thoroughly flushed with nitrogen. A concentrated solution of the sample was dissolved in deuterated chloroform containing TMS and the tube filled to a depth of about 3 cm. with this solution and the tube capped. Air leakage into the solution was prevented by holding the cover against the tube with a cello-tape. Failure to seal the tube led to rapid oxidation of the sample.

FIGURE 13
Conductivity cell



4. Electronic spectra

Electronic spectra were recorded on a Beckman Model DK-2 spectrophotometer. According to the manufacturer's specifications, the lead sulphide detector was suitable for the range 2850-400 $m\mu$ and the photomultiplier suitable for the range 210-700 $m\mu$. In practice, however, it was found that when the lead sulphide detector was used outside the limits 650-2200 $m\mu$,

the slit opening was very wide and the peaks obtained were unreproducible. The lead sulphide cell was, therefore, used to cover the range 2000-625 $m\mu$ (i.e. 5000-16000 $cm.^{-1}$) and the photomultiplier was used for the region with wavelengths shorter than 650 $m\mu$. The instrument was allowed to warm up for at least one hour before use.

(a) Preparation of solutions:

In most cases, solutions of the compounds whose spectra were desired were made by dissolving the complex in the neutral ligand as a neat liquid. For example, a nitrile complex of the type $MoBr_3 \cdot 3NCR$ was dissolved in the parent nitrile, RCN . The pyridine complex, $WBr_3 \cdot py_3$, was dissolved in pyridine.

Solutions of 1,10-phenanthroline or 2,2'-bipyridyl complexes of molybdenum(III) were prepared in acetonitrile. Tetrahydrothiophene complexes of molybdenum(III) were dissolved in methylene chloride since tetrahydrothiophene has an obnoxious odour. Even solid complexes containing this ligand had a strong odour. Whenever the solubility permitted, concentrated solutions (10^{-2} - 10^{-3} M) of the complexes were

prepared since it was only with such concentrated solutions that it was possible to observe spin-forbidden bands.

(b) Procedure:

A sample of the compound under investigation was accurately weighed, put in the nitrogen-filled glove box and dissolved in the appropriate solvent. All the precautions mentioned earlier of minimizing chances of oxidation* (e.g. flushing the vessels with nitrogen) were taken. The well-dried one-cm. quartz cells were rinsed with the solvent used for making the solution, filled with the solvent, tightly capped with a teflon stopper, wiped dry with tissue paper, and put in the spectrophotometer.

The usual 100% and 0% transmittance adjustments were made after which an absorption spectrum was scanned. The cells were interchanged and the scanning process repeated. If the solvent was pure and the cells clean, this scanning gave an almost horizontal base line which was reproducible by interchanging the cells.

The cell in the sample compartment was removed, put in a dry box and emptied. It was rinsed several times with the standard solution, filled with the latter and tightly capped with the teflon stopper. It was then wiped clean with tissue paper

* Solutions of tungsten(III) compounds were extremely reactive towards oxygen, and probably, though not certainly, towards water. A white precipitate of WO_3 formed immediately if the solvent used contained dissolved oxygen.

which had been moistened with acetone or other suitable solvent, put back in the spectrophotometer and the spectrum recorded. During the scanning, the scanning was stopped at 25 cm.⁻¹ or 50 cm.⁻¹ intervals and the wavelength, as read on the drum, marked on the chart paper.

5. Magnetic susceptibility measurements (161, 162).

Magnetic susceptibility measurements were made using the Gouy Method (161, 162).

(a) Apparatus:

The balance used was a Sartorius-Werke Type MPR5 micro-balance of nominal accuracy 0.001 mg. The sample tube was a Pyrex tube of 4 mm. outside diameter, 2.5 mm. internal diameter and about 10 cm. long. One of its ends was sealed off square so that the sample had essentially a flat bottom. The open end was joined to a shorter pyrex tube 5 mm. outside diameter.

The sample tube was suspended from the left-hand pan by means of a brass stirrup, copper turnbuckle and a quartz fibre. It was protected from air drafts by means of a Pyrex tube jacket and wrapped with an asbestos tape. A copper tube was joined to the lower end of the glass tube. The temperature was measured by a Thermoelectric Minimate bridge (Thermo Electric Co. Inc., Saddle Brook, N. J.) using a copper-constantan thermocouple, one end of which was welded to the outer wall of the copper tube.

The electromagnet used had truncated poles, 1.9 cm. apart, and was mounted on a movable platform so that the magnet could be moved horizontally along either of two mutually perpendicular axes. The electromagnet was energized by means of a Hewlett-Packard No. 6433B, DC Power Supply. The current was measured by means of a Bach-Simpson Ltd., Model 9 Direct Current Ammeter which had a nominal full scale accuracy of 0.5%.

(b) Procedure:

(i) Calibration of the sample tube and field strengths

The sample tube was evacuated, sealed off, and fitted with a hook by means of which the tube could be suspended as shown in Fig. 14. After determining the sensitivity of the balance with respect to a one-mg. rider, the force changes for magnet currents of 2.5, 5.0, 7.5 and 10A were determined. The process was repeated for a series of lower temperatures attained by cooling the air around the copper tube with liquid nitrogen vapours. For each field strength, the force change due to the glass was plotted versus the absolute temperature.

The sample tube was sealed onto an evacuable tube, filled with $\text{HgCo}(\text{SNC})_4$ (203) to a depth of 7 cm. or more by adding the sample, a little at a time and gently tapping the tube on a wood surface for long periods to ensure uniform packing. After evacuating and sealing the tube, the force change due to the sample was measured at room temperature for magnet currents of 0, 2.5, 7.5 and 10A. A correction for the force change due to the glass was obtained from the force

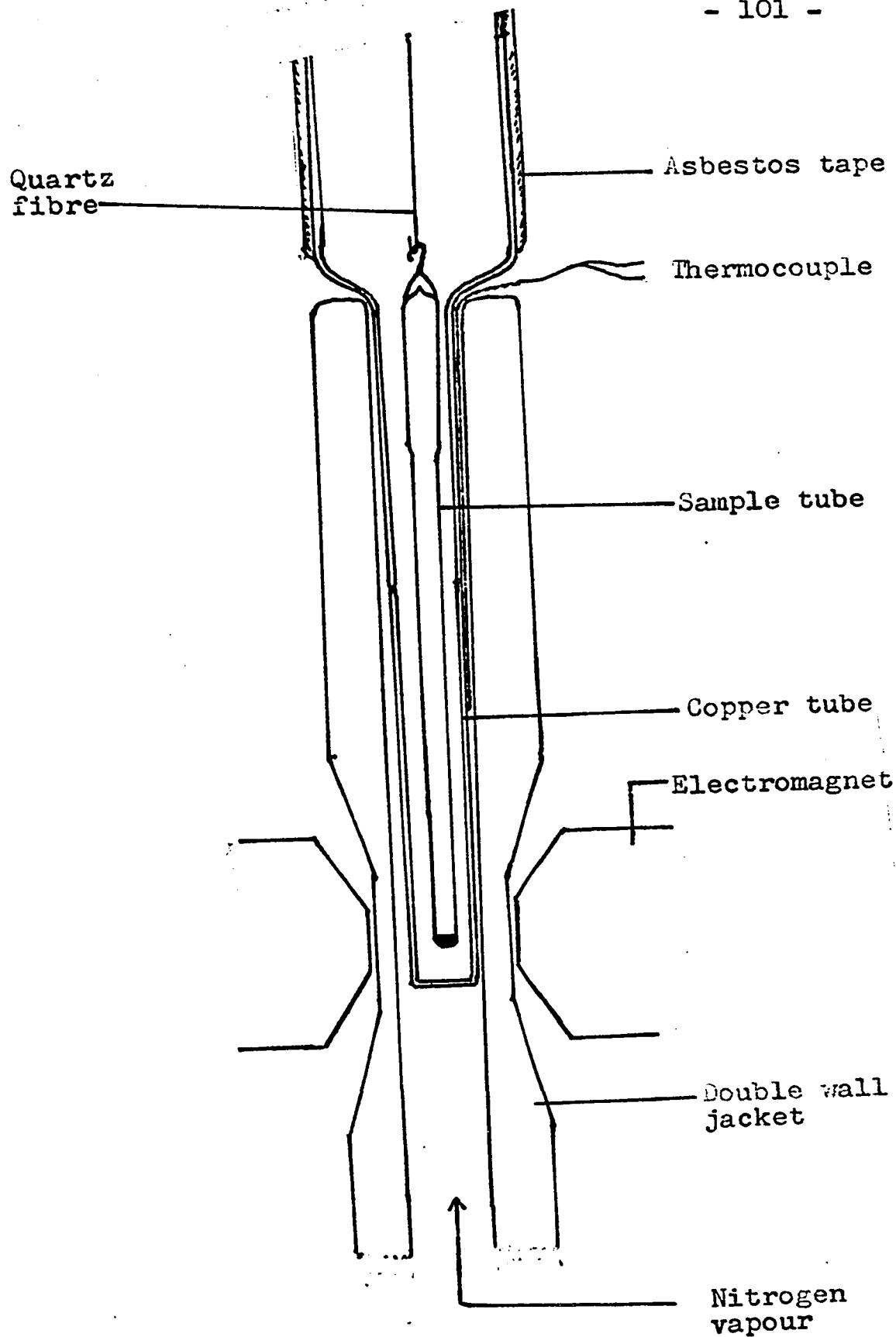


FIGURE 14

THE GOUY TUBE IN A MAGNETIC FIELD FOR MEASURE-
MET AT LOW TEMPERATURE.

change versus temperature graph. From the length and the weight of the sample, the field strengths produced by currents of 0, 2.5, 5.0, 7.5 and 10A were calculated, by means of equation 2-9 and found to be 0, 1420, 2790, 4140 and 5150 oersteds, respectively.

(ii) Susceptibility and effective moment of a sample

The measurements were made following the procedure used for $\text{HgCo}(\text{SNC})_4$, further details of which may be found elsewhere (204), and equation 2-9 used to calculate the gram susceptibility.* The molar susceptibility was obtained as explained in Chapter 2 and the correction due to diamagnetism of constituent ions or molecules made using published values (161, 162, 199). When such values were not available, they were estimated using Pascal's constants (163). The effective magnetic moments were then calculated using equation 2-10.

* Since the field was already known.

CHAPTER 4

PREPARATIVE WORK

Introduction: In this chapter, preparation of individual compounds or attempts to prepare specific compounds will be described. In order to avoid unnecessary repetitions, a general procedure will be described for those cases where two or more compounds can be made similarly with just a variation of reagents. The various procedures or attempted preparations are indicated with numerals, the first of which is 4 and indicates Chapter 4. The first procedure, for example, is 4.1; the second one is 4.2; and so on. All the preparations were done in an atmosphere of dry oxygen-free nitrogen or argon.

A. THE HALOCARBONYLS OF MOLYBDENUM(II) AND TUNGSTEN(II) (24, 25, 26)

The compounds $M(CO)_4X_2$ ($M = Mo, W$; $X = Cl, Br$) have been made following literature methods with some modifications. For example, instead of adding a few drops of bromine to $Mo(CO)_6$ to get $Mo(CO)_4Br_2$, the hexacarbonyl was treated with the stoichiometric amount of bromine.

4.1 Dichlorotetracarbonylmolybdenum(II), $Mo(CO)_4Cl_2$

Apparatus:

The apparatus used for preparation of the title compound

consisted of a Pyrex tube 30 cm. long and 21 mm. diameter (Figure 15). One end of this tube was closed and the other one was fitted with a No. 29/42 ground female joint. A Drechsel bottle top with a No. 29/42 male joint served as a stopper. The outlet and inlet tubes of the Drechsel bottle top were fitted with vacuum stop-cocks to permit easy evacuation of the system. The tube was cooled by means of a dry ice/acetone bath.

Procedure:

Two to six grams of well-powdered and dried molybdenum hexacarbonyl were put in the tube, the joints lightly greased, the tube stoppered and evacuated. It was next filled with nitrogen and cooled to -78°C . Dry chlorine was very slowly condensed on the hexacarbonyl until excess liquid chlorine was visible. The gas flow was stopped, stop-cocks A and B closed, the tube removed from the cold bath and allowed to warm up slowly while lightly holding the stopper. When some push was felt on the stopper, the latter was removed and the grease on the mouth of the tube wiped off with tissue which had been moistened with benzene or petroleum ether ($30-60^{\circ}\text{C}$). Care was taken not to let any organic solvent spill into the product.*

* In one such preparation, some ether fell into the product and the mixture caught fire.

FIGURE 15

Apparatus for preparation of $\text{Mo(CO)}_4\text{Cl}_2$

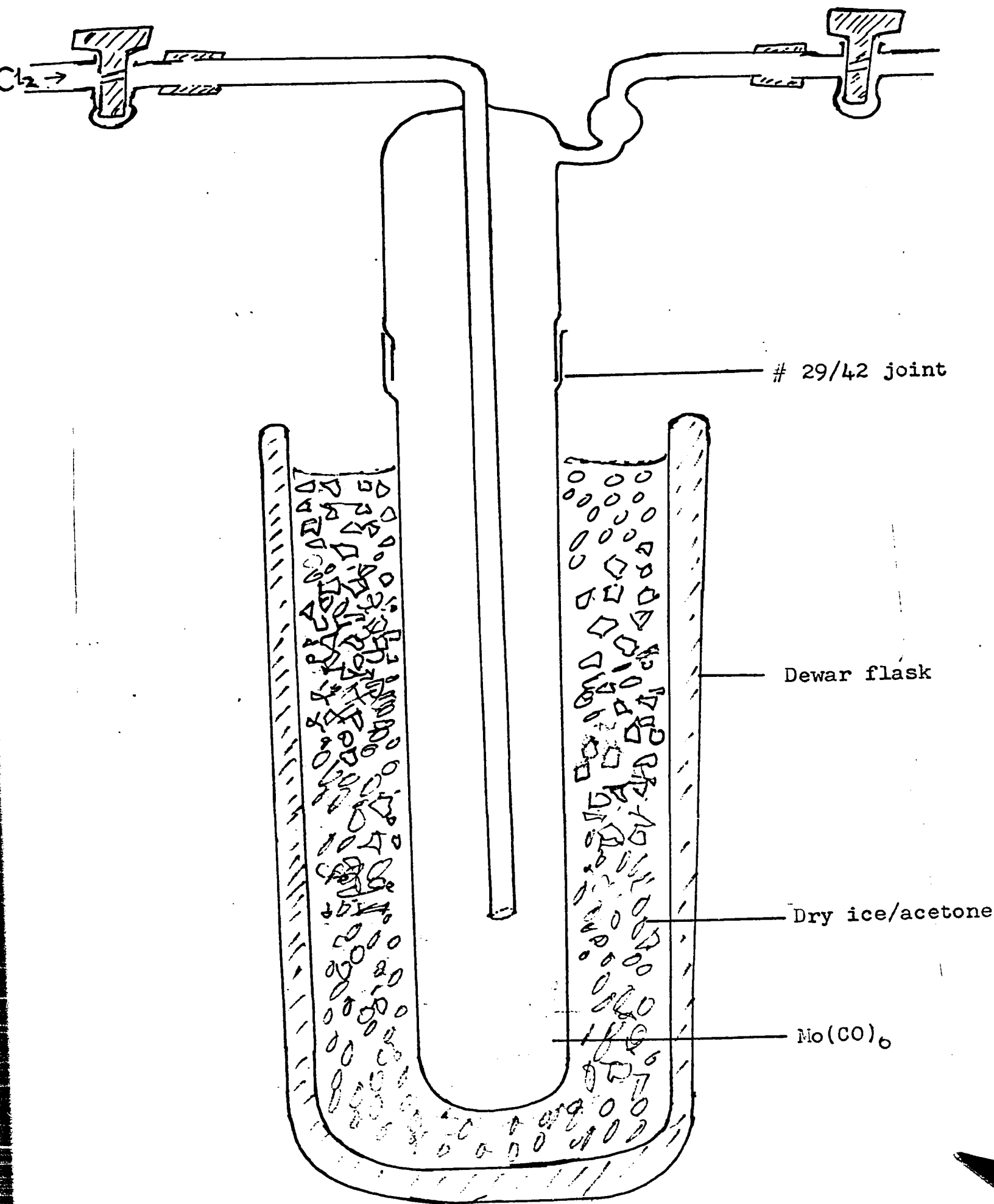
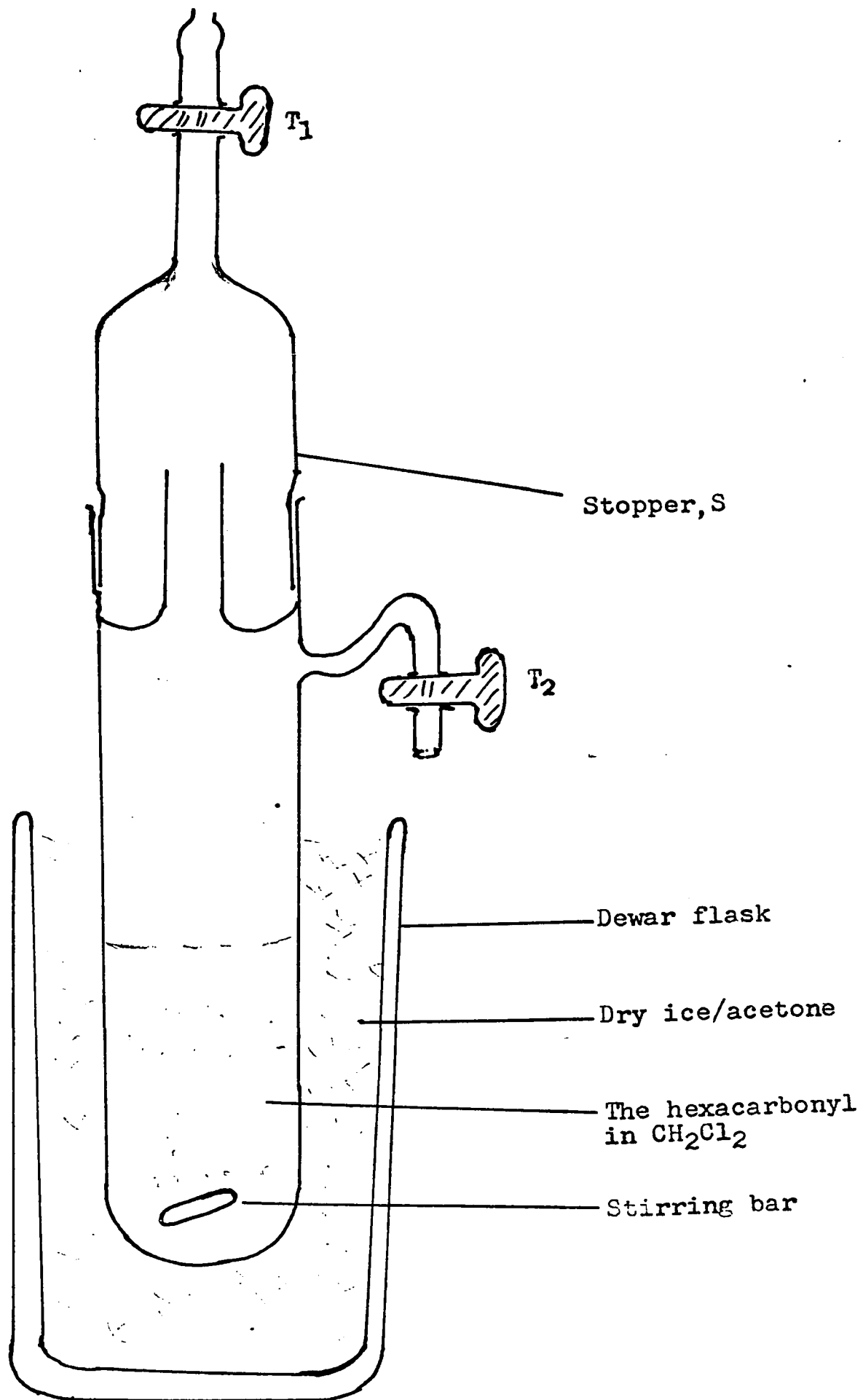


FIGURE 16

Apparatus for preparation of $\text{Mo}(\text{CO})_4\text{Br}_2$,
 $\text{W}(\text{CO})_4\text{Br}_2$ and $\text{W}(\text{CO})_4\text{Cl}_2$.



One end of a tube through which nitrogen was passing was put some centimeters inside the preparation tube but kept at least 10 cm. from the product. The excess chlorine was allowed to evaporate and the product was thoroughly flushed with dry oxygen-free nitrogen. The samples were taken immediately for analysis or for preparative work. For analysis, see Table 11.

4. Dibromotetracarbonylmolybdenum(II) and dibromotetracarbonyltungsten(II).

Apparatus:

A modified Schlenk tube, illustrated in Fig. 16, was used. The contents were stirred with a 1 1/2-inch teflon-covered stirring bar magnet.

Procedure:

The ground joints of the Schlenk tube and its stopper, S, were lightly greased with Apiezon Grease, N. The tube was connected to the vacuum line through stop-cock T_1 . Stop-cock T_2 was closed, stop-cock opened and the Schlenk tube thoroughly evacuated while being flamed out. Stop-cock T_1 was closed and the Schlenk tube filled with dry oxygen-free nitrogen through stop-cock T_2 .

As nitrogen was still passing through the system, a

suitable quantity (e.g. 2-6 gm.) of the metal carbonyl was accurately weighed and put into the tube. Approximately 50 ml. of freshly distilled methylene chloride were added, the Schlenk tube stoppered and the mixture degassed by evacuating the system for about a minute. The tube was re-filled with nitrogen and the mixture cooled to -78°C (see 4.1) for one hour.

The calculated amount of bromine was accurately measured with an all-glass syringe and dissolved in about 10 ml. of dry methylene chloride. The bromine solution was quickly added to the cold suspension of the hexacarbonyl, the tube quickly stoppered and removed from the cold bath. With stop-cock T_1 closed and stop-cock T_2 open to the nitrogen line, the mixture was stirred vigorously as the tube was allowed to warm up slowly. A vigorous reaction took place with evolution of gas to give an orange product, $(\text{Mo}(\text{CO})_4\text{Br}_2)$, or a dull-yellow product, $(\text{W}(\text{CO})_4\text{Br}_2)$. Either of the products could be recovered by one of two alternative methods as follows:-

4.2(a) When the gas evolution was complete, stop-cock T_2 was closed and the solvent removed completely by pumping off,

or (b) When the gas evolution was complete, stop-cock T_2 was closed and about two-thirds of the solvent pumped off. The Schlenk tube was filled with dry oxygen-free nitrogen, and with nitrogen flowing through the system, the bar magnet was removed.

Tube C in Fig. 11 was removed and the filtration apparatus fitted onto the Schlenk tube containing the $\text{Mo}(\text{CO})_4\text{Br}_2$ or $\text{W}(\text{CO})_4\text{Br}_2$. The apparatus was inverted so that the reaction mixture was emptied into the space above the fritted glass in tube B and filtered while still cold. The product was washed with a few ml. of methylene chloride and dried in vacuum for a few minutes. Unless otherwise specified, all the filtrations mentioned hereafter were done similarly.

4.2(a) gave products which had dark patches, but otherwise the products were sufficiently pure for preparative purposes.

4.3 Dichlorotetracarbonyltungsten(II).

The apparatus used for condensing chlorine is shown in Fig. 17. Essentially, this consisted of a pyrex tube, 19 mm. diameter and 12 cm. long, one end of which was sealed and the other fitted with a No. 19/38 male joint. Two thinner glass tubes were fixed on the sides of this tube as shown. The desired amount of liquid chlorine was measured with an all-glass syringe which had 0.01 ml. graduations.

Procedure:

The tube for collecting liquid chlorine and the all-glass syringe were set up as shown in Fig. 17 but with no grease on the ground joint. With clamp 2 open and clamps 1 and 3 closed, the system was thoroughly purged with dry

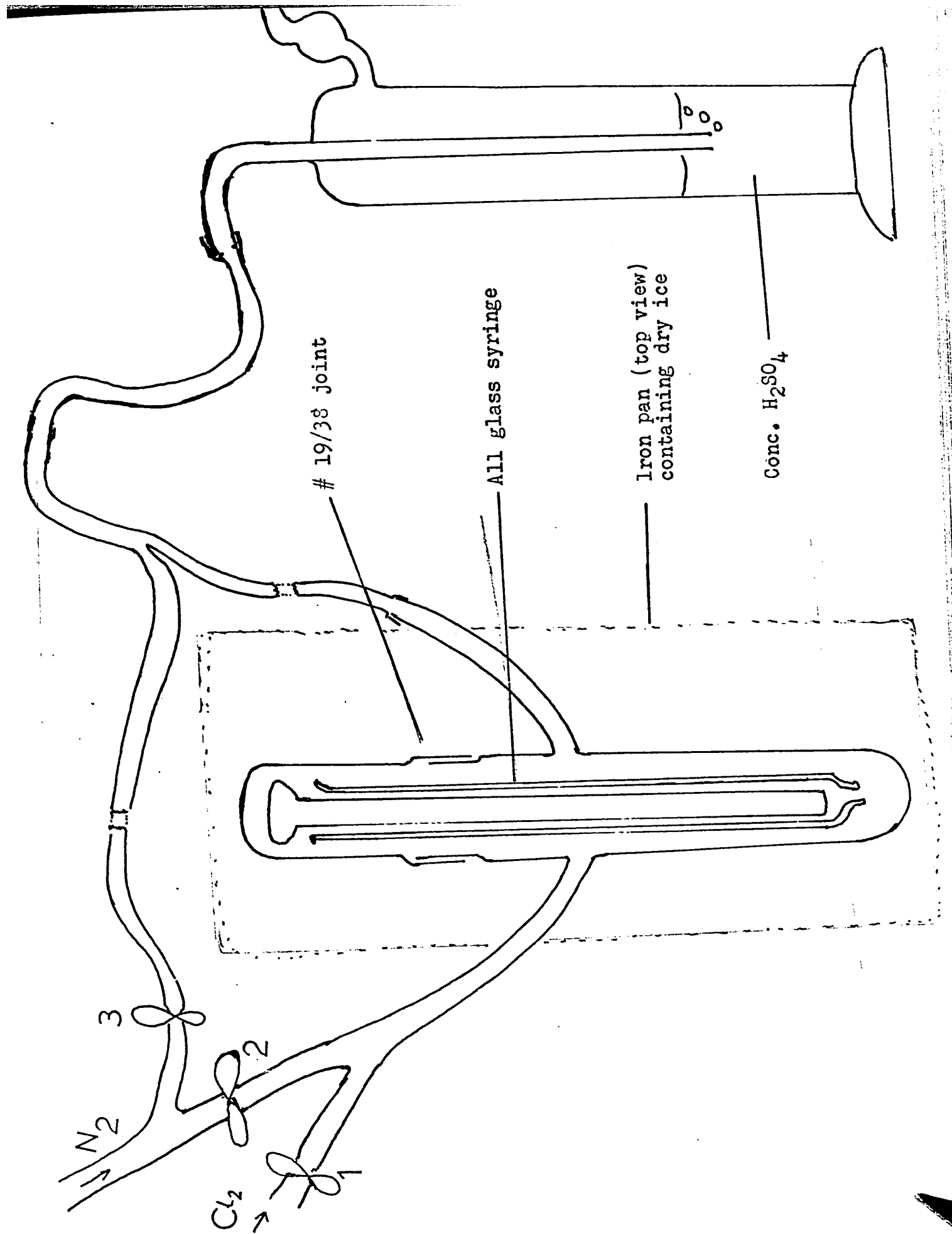
oxygen-free nitrogen for at least ten minutes. While nitrogen was still flowing, the tube for collecting chlorine was placed on some crushed dry ice in an open iron pan in a slanting position such that the open end of the tube, stoppered as shown in Fig. 17, was higher than the closed end. The tube was then covered with a thin layer of the crushed dry ice.

Clamps 1 and 3 were opened, and clamp 2 closed. The nitrogen flow was thus continued by by-passing the chlorine-condensing tube. At the same time, some chlorine was condensed in the tube without any danger of moist air sucking back. At the same time that chlorine was being condensed, some accurately weighed tungsten hexacarbonyl (2-6 gm.) suspended in methylene chloride was being cooled to -78°C , following the procedure described in 4.2. When sufficient chlorine had condensed, the chlorine flow was stopped but the nitrogen flow maintained. The tube was removed from the dry ice and, as quickly as possible, the amount of chlorine that would theoretically give $\text{W}(\text{CO})_4\text{Cl}_2$ on reacting with the amount of the hexacarbonyl that had been used was measured by means of the syringe and quickly added to the cold suspension of tungsten hexacarbonyl while a stream of nitrogen was being passed through the tube. The tube was then quickly stoppered.

There was no evidence of any reaction (no gas evolution observed) at the low temperature. The Schlenk tube was removed from the bath and allowed to warm up slowly in air as the mixture was vigorously stirred. The solution, which

FIGURE 17

Apparatus for condensing chlorine



was initially yellow, turned leaf green and then yellow. At the same time, a vigorous evolution of gas took place. The gas was swept away by passing a strong current of nitrogen through the tube. The rest of the procedure is as in 4.2.

B. SOME MOLYBDENUM COMPLEXES PREPARED BY REACTION OF
 $\text{Mo}(\text{CO})_4\text{Cl}_2$ OR $\text{Mo}(\text{CO})_4\text{Br}_2$ WITH π -BONDING LIGANDS

Introduction:

As will be recalled (see Chapter 1), ligands such as isocyanides capable of forming π -bonds with metal d-orbitals stabilize low oxidation states of transition metals. The attempted preparations described below were primarily aimed at establishing the degree of substitution which could be achieved in the reaction of $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with a large excess of such electron donors.

Basis for choosing liquid electron donors:

Liquid electron donors were chosen so that they could be used both as ligands and solvents. By dissolving the halocarbonyl in the electron donor, the maximum possible substitution is expected to occur more easily than when the ligand is dissolved in another solvent. This technique has not previously been used to study the reactions of the halocarbonyls of molybdenum(II) and tungsten(II) with various electron donors. It has been used, however, to study the reactions of the hexacarbonyls of these metals. For

TABLE 11

ANALYSES FOR THE HALOCARBONYL COMPOUNDS

$M(CO)_4X_2$ (M = Mo, W; X = Cl, Br).

<u>Compound</u>	<u>Found (%)</u>		<u>Calculated (%)</u>	
	<u>Mo or W</u>	<u>Cl or Br</u>	<u>Mo or W</u>	<u>Cl or Br</u>
1 $Mo(CO)_4Cl_2$	34.40	25.87	34.42	25.43
2 $Mo(CO)_4Br_2$	26.45	45.09	26.08	43.45
3 $W(CO)_4Cl_2$	49.00	20.01	50.12	19.45
4 $W(CO)_4Br_2$	39.83	34.32	40.34	35.06

example, ultraviolet irradiation of a mixture of acetonitrile and Mo(CO)_6 or W(CO)_6 in benzene gives products of the type $\text{M(CO)}_5(\text{NCCH}_3)$ and $\text{M(CO)}_4(\text{NCCH}_3)_2$ (205). On the other hand, higher substitution to give products of the type $\text{M(CO)}_3(\text{NCCH}_3)_3$ is achieved if the hexacarbonyls are irradiated using acetonitrile as the solvent (206).

Phenylisocyanide could not be used as the pure solvent for reasons discussed later.

4.4 Dichloromonocarbonyltris(phenylisocyanide)molybdenum(II)

0.997 gm. (3.53 mmoles) of $\text{Mo(CO)}_4\text{Cl}_2$ were dissolved in ether and filtered into a solution of 1.1 gm. (10.7 mmoles) of phenylisocyanide in about 20 ml. of ether. A vigorous reaction took place with evolution of gas to give a yellow solid. The reaction mixture was stirred for a further twelve-hour period in an atmosphere of nitrogen. The product was recovered by filtration, washed several times with ether and dried in vacuum at room temperature.

	Mo	Cl
Found:	18.58	14.07 %
$\text{C}_{22}\text{Cl}_2\text{H}_{15}\text{MoN}_3\text{O}$ requires	19.03	14.06 %

4.5 Dichloromonocarbonyltetrakis(phenylisocyanide)molybdenum(II)

The procedure was as described in 4.4. The only difference was that four millimoles of the ligand were used for

every millimole of $\text{Mo}(\text{CO})_4\text{Cl}_2$. The product was also obtained by adding the ligand to a suspension of $\text{Mo}(\text{CO})_4\text{Cl}_2$ in cyclohexane or an ether/cyclohexane mixture. The analysis for a typical preparation was as follows:-

	Mo	Cl
Found:	15.50	11.97 %
$\text{C}_{29}\text{Cl}_{12}\text{H}_{20}\text{MoN}_4\text{O}$ requires	15.80	11.67 %

4.6 Dichlorodicarbonyltris(trimethylphosphite)molybdenum(II)

6 gm. of dichlorotetracarbonylmolybdenum(II) were put in a nitrogen-filled Schlenk tube followed by freshly distilled trimethylphosphite (50 ml.). The mixture was stirred vigorously for a few minutes to ensure that all the solid had dissolved. The resulting yellow solution was quickly filtered to separate it from any solid products. After stirring the filtrate thus obtained for about five minutes, a bright yellow solid started crystallizing out. Stirring was continued for a further twelve-hour period to ensure completion of the reaction and the solid was separated by filtration. It was washed several times with methylene chloride and dry ether and dried at room temperature by evacuation. Elemental analysis showed that the product was $\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Cl}_2$.

	Cl	C	H	P
Found:	11.92	23.31	4.68	16.37 %
$\text{C}_{11}\text{Cl}_2\text{H}_{27}\text{MoO}_8\text{P}_3$ requires	12.02	22.20	4.57	15.62 %

4.7 Dibromodicarbonyltris(trimethylphosphite)molybdenum(II).

This compound was made following the procedure described for making the analogous compound (4.6).

	C	H	P	Br
Found:	17.92	3.98	12.09	23.26 %
$\text{Br}_2\text{C}_{11}\text{H}_{27}\text{MoO}_8\text{P}_3$ requires	19.32	3.98	13.58	21.36 %

The compound was unstable and decomposed on standing.

4.8 Reaction of dichlorotetracarbonylmolybdenum(II) with triethylarsine.

4.5 gm. of dichlorotetracarbonylmolybdenum(II) and 20 ml. of triethylarsine were used and the procedure of 4.6 followed. After stirring the filtrate overnight and concentrating it by pumping off most of the solvent, there was no significant amount of solid produced and, therefore, the yellow product was precipitated by addition of 50 ml. of ether. The product was not, however, sufficiently soluble in ether or benzene for re-crystallization from one solvent. The solid was hence re-dissolved in methylene chloride and re-precipitated by adding the minimum amount of ether.

The product was separated as usual, washed several times with ether and dried by evacuation for a few minutes at room temperature. The solid was transferred into a tube that could be heated in a water bath and the compound dried in vacuum at 50°C to remove any trapped methylene chloride.

	Cl	C	H	As
Found:	18.55	25.66	4.61	20.07 %
$\text{AsC}_8\text{Cl}_2\text{H}_{15}\text{MoO}_2$ requires	18.42	24.96	3.93	19.46 %

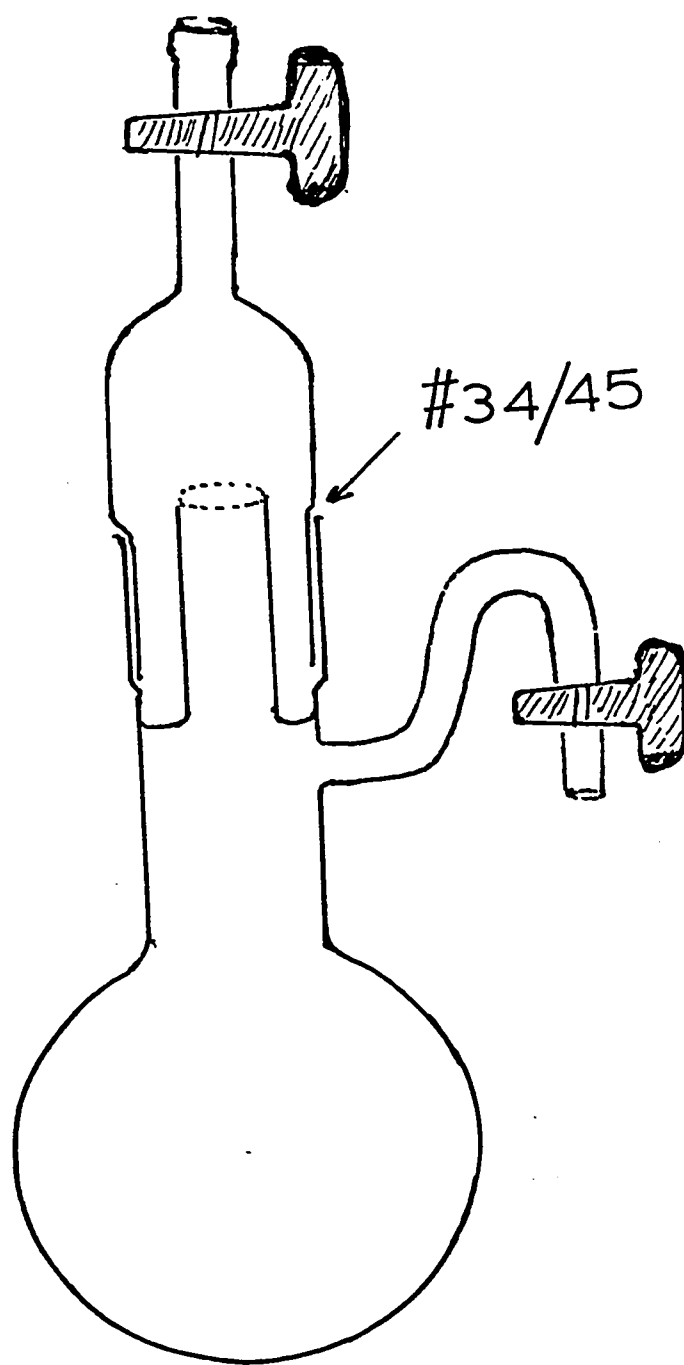
The compound darkened in bright light but retained the yellow colour when stored in a dark place. An infrared spectrum of the compound showed two CO groups. This was another indication of decomposition since the small amount of the product that was obtained by concentrating a large volume of ether solution showed three peaks in the CO region, suggesting the ether-soluble component was probably $\text{Mo(CO)}_3(\text{AsEt}_3)_2\text{Cl}_2$.

4.9 Dichlorotricarbonylbis(triethylphosphine)molybdenum(II)

3.0 gm. of dichlorotetracarbonylmolybdenum(II) were put on the frit of the filtering system (Fig. 11) under nitrogen, with the apparatus in a well-ventilated hood. About 8 ml. of triethylphosphine were added. A vigorous reaction occurred with evolution of gas to give a yellow solution. About 20 ml. of methylene chloride were added, the solution filtered and the filtrate concentrated to about 15 ml. After stirring the filtrate overnight, the product was precipitated once with ether, filtered, washed several times with the same solvent and dried in vacuum at room temperature for a few minutes.

FIGURE 18

Apparatus for crystallizing sparingly soluble
air-sensitive compounds.



	Mo	Cl	C	H	P
Found:	19.36	16.27	37.90	6.65	13.80 %
$C_{15}Cl_2H_{30}MoO_3P_3$ requires	19.21	14.55	36.98	6.21	12.72 %

C. SOME COMPLEXES OF MOLYBDENUM(II) WITH LOW OR POOR π -BONDING ABILITY.

4.10 Dichlorodicarbonylbis(pyridine)molybdenum(II)

6.0 gm. (21.5 mmoles) of dichlorotetracarbonylmolybdenum(II) were suspended in 40 ml. of dry oxygen-free ether in a Schlenk tube. 3.5 gm. (45.3 mmoles) of pyridine were dissolved in 20 ml. of dry ether and the solution slowly added to the halocarbonyl while vigorously stirring the latter and passing a current of dry nitrogen through the tube. When the addition was complete, the mixture was degassed, the tube filled with dry oxygen-free nitrogen and the mixture stirred for twelve hours. The product, an orange solid, was separated by filtration, washed several times with methylene chloride/ether (1:1) and the material re-crystallized from methylene chloride using the apparatus shown in Fig. 18 as follows:-

The apparatus, which was essentially a 500-ml. flask converted into a Schlenk vessel, was put in place of tube A (Fig. 11) while the solid was on the frit in B. The solid was dissolved in hot methylene chloride and the solution filtered into the 500-ml. flask, concentrated by pumping off most of the solvent and the dull-orange product isolated as usual. Elemental analysis showed that the product was $Mo(CO)_2py_2Cl_2$.

	Mo	Cl	C	H	N	O
Found:	24.50	18.82	37.87	2.99	8.39	7.24 %
$C_{12}Cl_2H_{10}MoN_2O_2$ requires	25.18	18.61	37.82	2.65	8.40	7.35 %

4.11 Dichloroacetoneitriletricarboxymolybdenum(II)

The procedure is as in 4.10 with the following slight differences: (1) Ether was used as the solvent and (2) the product was used without re-crystallization, because the compound was decomposing. A grey product was deposited when an ether solution (green) was being concentrated. In a typical preparation where 9.0 gm. (32.7 mmoles) of $Mo(CO)_4Cl_2$ were treated with 2.80 gm. (68.2 mmoles) of acetonitrile, the product obtained gave the following analysis:

	Mo	Cl
Found:	32.58	24.28
$C_5H_3Cl_2MoNO_3$ requires	32.86	25.39

The microanalytical data were unreliable because the compound decomposed on storing.

4.12 Attempted preparation of nitrile complexes of the type $Mo(CO)_3(NCPh)_2X_2$ (X = Cl, Br), using a large excess of the nitrile:

Procedure:

Attempts to make complexes of the above type were made following the procedures in 4.4 and 4.5 but instead of using a stoichiometric amount of benzonitrile, a very large excess of the ligand was used.

In a typical preparation where 1 gm. of $\text{Mo(CO)}_4\text{Br}_2$ was dissolved in ether (100 ml.) and the solution filtered into 20 ml. of benzonitrile in 20 ml. of ether, the green solid obtained gave the following analysis:

	Mo	Br	C	H	N	O
Found:	17.80	39.79	33.82	2.31	5.68	0.73 %
$\text{Br}_8\text{C}_{42}\text{H}_{30}\text{Mo}_3\text{N}_6$ requires	18.62	41.36	32.63	1.96	5.44	0.00 %

The ratio of Br:Mo in the compound obtained was 2.71:1. All compounds prepared by this method had halogen:molybdenum ratio between 2.5:1 and 3:1. Possible reasons for this ratio are discussed in Chapter 5.

4.13 Dichlorotricarbonyltriphenylphosphineoxidemolybdenum(II)

This compound was made following the procedure described in 4.4 with the following variations: The reactants were in a 1:1 mole ratio and a large quantity of ether was used because of low solubility of triphenylphosphine oxide in ether. The reaction mixture was stirred for twenty-four hours instead of just twelve hours. The light-yellow product obtained was found to be $\text{Mo(CO)}_3(\text{OPPh}_3)\text{Cl}_2$.

	Mo	Cl	C	P	H
Found:	18.21	13.36	51.1	6.60	3.45 %
$\text{C}_{21}\text{Cl}_2\text{H}_{15}\text{MoO}_4\text{P}$ requires	18.12	13.40	47.8	5.85	2.86 %

4.14 Tetrabromoheptacarbonyltriphenylphosphineoxidedimolybdenum(II)

A compound approximating the composition $\text{Mo}_2(\text{CO})_7(\text{OPPh}_3)\text{Br}_4$ was isolated in a preparation similar to that in 4.13. The reaction was allowed to proceed for just half an hour. The reactants were in a 1:1 mole ratio.

	Mo	Br
Found:	19.23	32.23 %
$\text{Mo}_2(\text{CO})_7(\text{OPPh}_3)\text{Br}_4$ requires	19.46	32.42 %

The ratio of Br:Mo was 2:1.

4.15 Tetrachlorotris(triphenylarsineoxide)hexacarbonyl-dimolybdenum(II)

2.30 gm. (8.2 mmoles) of $\text{Mo}(\text{CO})_4\text{Cl}_2$ were put into a suspension of 5.51 gm. (17.01 mmoles) of OAsPh_3 in 100 ml. of ether and the mixture stirred in an atmosphere of nitrogen for three days. The solid product (dull yellow) was recovered by filtration and the solid recrystallized from CH_2Cl_2 /ether. The solid was washed several times with CH_2Cl_2 /ether and dried in vacuum at 60°C .

	Mo	Cl	C	H	As
Found	13.05	9.95	49.54	3.83	14.07 %
$\text{Mo}_2(\text{CO})_6(\text{Ph}_3\text{AsO})_3\text{Cl}_4$ requires	13.07	9.66	51.52	3.08	15.31 %

D. SOME COMPLEXES OF MOLYBDENUM(III) FROM REACTIONS OF $\text{Mo}(\text{CO})_4\text{Cl}_2$ AND $\text{Mo}(\text{CO})_4\text{Br}_2$ WITH NEAT ELECTRON DONORS.

4.16 Nitrile complexes of Molybdenum(III)

General Procedure:

Two to six gm. of $\text{Mo(CO)}_4\text{Cl}_2$ or $\text{Mo(CO)}_4\text{Br}_2$ were treated with 20 - 40 ml. of freshly distilled nitrile following the procedure described in 4.6 with the following variations: The reaction mixture was stirred for at least twenty-four hours even when a precipitate formed within a short time. The solid products (yellow) were separated in one of the following ways:-

4.16 (a) Complexes of low-boiling nitriles were recovered as follows: After the end of the reaction, some of the nitrile was pumped off to leave 10-15 ml. of solution plus the solid. This was filtered and the yellow solid washed several times with nitrile/ether (1:5) and finally with ether and dried in vacuum at room temperature for several hours.

Complexes of high-boiling nitriles, e.g. phenylacetone nitrile were recovered in one of two ways:-

(b) After the end of the reaction, the product was isolated by filtration without attempting to concentrate the solution. The product was washed several times with ether.

or (c) After the completion of the reaction, the reaction mixture was diluted with about one-half of its volume of ether, the solid recovered by filtration and washed several times with ether. Provided care had been taken to avoid oxidation of the products, the products obtained by 4.16(c) were found to be analytically pure. Analyses for nitrile complexes prepared by this method are summarized in Table 12.

TABLE 12

Analyses for some nitrile complexes of molybdenum(III).

No.	Compound	Found (%)				Calculated (%)					
		Mo	Cl or Br	C	H	N	Mo	Cl or Br	C	H	N
I	MoCl ₃ .3NC-Ph	18.76	20.74	49.31	3.18	6.93	18.75	20.80	49.28	2.95	6.52
II	MoCl ₃ .3NCCH ₃	29.35	32.35				29.51	32.69	22.14	2.79	12.91
III	MoCl ₃ .4NCCH ₃	26.13	29.06	25.96	3.47	15.23	26.18	29.02	26.22	3.30	15.29
IV	MoCl ₃ .3NCCH ₂ Ph	17.18	19.03	52.82	3.8	7.48	17.21	19.06	52.06	3.82	7.59
V	MoCl ₃ .3NCCH ₂ CH ₃	26.01	28.97	29.19	3.99	11.27	26.11	28.94	29.40	4.09	11.43
VI	MoCl ₃ .3NC(CH ₂) ₂ CH ₃	23.41	26.05	35.54	5.34	10.36	23.43	25.99	35.19	5.19	10.26
VII	MoCl ₃ .3NCCH(CH ₃) ₂	23.12	26.01	35.30	5.29	10.13	23.43	25.99	35.19	5.19	10.26
VIII	MoCl ₃ .3NC(CH ₂) ₃ CH ₃	20.95	23.40	39.81	5.87	9.22	21.24	23.55	39.81	6.03	9.31
IX	MoBr ₃ .3NCPh	14.81	35.0	39.68	3.03	6.10	14.87	37.06	39.10	2.34	6.51
X	MoBr ₃ .3NCCH ₃	20.45	51.73	15.47	2.60	8.91	20.91	52.25	15.71	1.98	9.16
XI	MoBr ₃ .4NCCH ₃	19.18	47.78	18.38	2.35	10.04	19.19	47.96	19.22	2.42	11.21
XII	MoBr ₃ .3NCCH ₂ Ph	13.71	34.65	43.54	3.32	6.04	13.96	34.89	41.95	3.08	6.12
XIII	MoBr ₃ .3NCCH ₂ CH ₃	19.21	47.64	19.54	3.06	8.44	19.15	47.87	21.58	3.02	8.39
XIV	MoBr ₃ .3NC(CH ₂) ₂ CH ₃	17.54	44.20	26.81	3.54	7.85	17.67	44.5	26.54	3.90	7.74
XV	MoBr ₃ .3NCCH(CH ₃) ₂	17.50	44.22	26.68	3.81	7.91	17.67	44.5	26.54	3.90	7.74
XVI	MoBr ₃ .3NC(CH ₂) ₃ CH ₃	16.40	40.96	30.89	4.40	7.37	16.40	40.99	30.79	4.65	7.18

Ph = phenyl

4.17 Acetonitrile complexes $\text{MoCl}_3(\text{NCCH}_3)_4$ and $\text{MoBr}_3(\text{NCCH}_3)_4$

These compounds were prepared as in 4.16 but instead of drying the products in vacuum, a current of dry oxygen-free nitrogen was blown over the product. See Table 12 for analysis of the products. The complexes $\text{MoX}_3(\text{NCCH}_3)_3$ were obtained by drying $\text{MoX}_3(\text{NCCH}_3)_4$ compounds at 30°C . At 50°C , $\text{MoCl}_3(\text{NCCH}_3)_4$ decomposed to give a product of the composition $\text{MoCl}_3 \times \text{NCCH}_3$ $2 < x < 3$.

4.18 The nitrile complexes $\text{MoCl}_3(\text{NCCH}_3)_3$ and $\text{MoCl}_3(\text{NCCH}_3)_4$ obtained from the reaction of $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$ with neat acetonitrile.

The partially substituted nitrile complex, $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$, was prepared as in 4.11. 4 gm. of the material were put in a nitrogen-filled dry Schlenk tube which had been thoroughly dried by evacuating while flaming out 30 ml. of acetonitrile were added and after degassing the mixture to remove any traces of oxygen, the tube was refilled with nitrogen and the reactants stirred for three days. The dull green solid dissolved slowly to give a light purple solution from which a yellow solid crystallized out slowly. When the solid was recovered as in 4.17, the product was found to be $\text{MoCl}_3(\text{NCCH}_3)_4$, which lost a molecule of nitrile when dried in vacuo at 30°C to give $\text{MoCl}_3(\text{NCCH}_3)_3$.

4.19 The pyridine and 2,6-dimethylpyridine complexes of molybdenum(III)

The pyridine complex, MoCl_3py_4 , was prepared either as

TABLE 13

ANALYSES FOR SOME PYRIDINE AND 2,6-DIMETHYLPYRIDINE
COMPLEXES OF MOLYBDENUM(III).

<u>Compound</u>	<u>FOUND (%)</u>					<u>CALCULATED (%)</u>				
	Mo	Cl or Br	C	H	N	Mo	Cl or Br	C	H	N
MoCl ₃ py ₃	21.33	24.08	41.29	3.48	9.50	21.82	24.18	40.98	3.44	9.56
MoCl ₃ py ₄	18.58	20.77	44.86	3.79	10.88	18.49	20.65	46.30	3.89	10.88
MoBr ₃ py ₃	16.71	41.78	31.31	2.81	7.47	16.74	41.83	31.46	2.64	7.34
MoBr ₃ (lut) ₂	16.03	43.10	32.36	3.23	5.5	17.44	43.58	30.57	3.30	5.10

lut = 2,6-lutidine

in 4.17 from the reaction of $\text{Mo(CO)}_4\text{Cl}_2$ with pyridine or as in 4.18 from the reaction of $\text{Mo(CO)}_2\text{py}_2\text{Cl}_2$ (see 4.10) with pyridine. When the product was dried at 50°C in vacuum, the complex, MoCl_3py_3 , was obtained.

MoBr_3py_3 and $\text{MoBr}_3(2,6\text{-lutidine})_2$ were prepared following the procedure given in 4.16. The 2,6-lutidine complex was washed with chloroform. Analyses for these compounds are summarized in Table 13.

4.20 Tetrahydrofuran and tetrahydrothiophene complexes of molybdenum(III)

The tetrahydrofuran(THF) and tetrahydrothiophene(THT) complexes $\text{MoCl}_3(\text{THF})_3$, $\text{MoBr}_3(\text{THF})_3$, $\text{MoCl}_3(\text{THT})_3$ and $\text{MoBr}_3(\text{THT})_3$ were prepared following the procedure of 4.16. The bromo complex, $\text{MoBr}_3(\text{THT})_3$, was recovered as follows:-

After completion of the reaction (3 days), the solvent was concentrated to a small volume by pumping off. No solid was obtained. The sides of the Schlenk tube were scratched with a glass rod to induce crystallization upon which operation some brown solid was precipitated. More product was obtained by diluting the solution with about 50 ml. of dry ether, and the product isolated as usual by filtration. The analyses of the products obtained are summarized in Table 14.

4.21 Attempted preparation of a molybdenum(III) complex containing a secondary amine.

It was seen in Chapter 1 (Table 5) that the reaction of

TABLE 14

TETRAHYDROFURAN AND TETRAHYDROTHIOPHENE COMPLEXES
OF TRIVALENT MOLYBDENUM MADE FROM THE HALOCARBONYLS

<u>Compound</u>	<u>Found (%)</u>					<u>Calculated</u>				
	Mo	Cl or Br	C	H	O or S	Mo	Cl or Br	C	H	O or S
I $\text{MoCl}_3 \cdot 3 \text{ THF}$	23.33	25.30	34.28	5.84	11.21	22.97	25.41	34.43	5.78	11.47
II $\text{MoBr}_3 \cdot 3 \text{ THF}$	17.20	43.39	25.95	4.38	8.58	17.38	43.43	26.11	4.38	8.70
III $\text{MoCl}_3 \cdot 3 \text{ THT}$	20.00	22.38	31.08	5.34	20.22	20.53	22.79	30.90	5.24	20.61
IV $\text{MoBr}_3 \cdot 3 \text{ THT}$	16.00	39.94	23.88	4.08	16.00	16.7	39.94	24.01	4.03	16.03

THF = Tetrahydrofuran

THT = Tetrahydrothiophene

molybdenum trihalides with secondary amines is accompanied by solvolysis. It was of interest to see what type of product would be obtained from the reaction of $\text{Mo(CO)}_4\text{Br}_2$ with piperidine at room temperature.

Procedure

About 5 gm. of $\text{Mo(CO)}_4\text{Br}_2$ and 30 ml. of piperidine were used and the procedure 4.16(a) followed. A yellow solid was obtained after a few minutes. Stirring was continued for twelve hours and the solid separated as usual and washed several times with methylene chloride. Elemental analysis showed that the product was the zerovalent molybdenum complex, $\text{Mo(CO)}_4(\text{piperidine})_2$.

	C	H	N	O	Br	Mo
Found	44.27	5.93	7.40	16.89	0.00	25.36 %
$\text{C}_{14}\text{H}_{22}\text{MoN}_2\text{O}_4$ requires	44.46	5.86	7.40	16.92	0.00	25.34 %

4.22 Reactions of $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ with NNN'N'-tetramethylethylenediamine

The reactions of $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ with $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ($\equiv$ tmen) with the ligand acting as a solvent were attempted following the procedure described for making nitrile complexes (4.16). The products obtained (brown-pink) were found to contain very low percentages of molybdenum and gave unreliable analysis. For example, in a typical preparation, the reaction of $\text{Mo(CO)}_4\text{Cl}_2$ with neat $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ gave a product with percentage of Mo = 7.8 which did not correspond

to any simple complex of molybdenum.

The material was re-crystallized from methanol. Analysis suggested that the product was, in fact, mainly a salt of the base and that the molybdenum was present only as an impurity.*

	Mo	Cl	C	H	N
Found:	2.30	36.19	37.31	9.98	14.22 %
$C_6Cl_2H_{18}N_2$ requires	0.00	37.79	38.10	8.57	14.80 %

4.23 Zerovalent molybdenum complex from the reaction of $Mo(CO)_4Cl_2$ with neat $(CH_3)_2NCH_2CH_2N(CH_3)_2$.

Procedure:

The solvent, from the reaction of $Mo(CO)_4Cl_2$ with neat $(CH_3)_2NCH_2CH_2N(CH_3)_2$ as a solvent was pumped off, the yellow residue dissolved in ether and the products separated chromatographically on an alumina column. The main product was shown to be the zerovalent molybdenum complex, $Mo(CO)_4(tmen)$.

	Mo	C	H	N	O	Cl
Found:	29.59	37.55	5.66	10.74	20.69	0.00 %
$C_{10}H_{20}MoN_2O_4$ requires	29.59	37.03	4.97	8.64	19.74	0.00 %

4.24 Reaction of a $Mo(CO)_4Cl_2$ with phenylisocyanide as the solvent.

* A genuine molybdenum complex with this analysis would have a molecular weight of 4200 per molybdenum atom. This is meaningless in this particular case.

Introduction:

At room temperature, $\text{Mo(CO)}_4\text{Cl}_2$ reacted with liquid phenylisocyanide very exothermically* to give a black resinous material from which no crystalline product could be recovered. The preparation was attempted at lower temperature as follows:-

About 20 ml. of phenylisocyanide were put in a thoroughly dried Schlenk tube, the latter evacuated, refilled with nitrogen and the ligand frozen by cooling in a dry ice/acetone bath. With nitrogen flowing through the tube, 3.40 gm. of $\text{Mo(CO)}_4\text{Cl}_2$ were added, the tube stoppered and removed from the cold bath. It was allowed to warm up slowly. When the ligand melted, large lumps of unreacted material remained. Hence, the reaction mixture was diluted with about 15 ml. of methylene chloride, upon which all the material dissolved.

Most of the methylene chloride was pumped off and the reaction mixture stirred overnight in an atmosphere of dry nitrogen. The mixture was filtered and the light pink product washed several times with acetone, and finally with diethyl ether. It was dried at room temperature in vacuum. An infrared spectrum of the product did not show bands characteristic of carbonyl groups. Elemental analysis, however, showed that the product was not pure but was of approximate composition $\text{MoCl}_3(\text{CNPh})_4 \cdot 2\text{CH}_2\text{Cl}_2$.

* The heat of reaction made the lower part of the Schlenk tube too hot to hold with bare hands.

	Mo	Cl	C	H	N	
Found:	11.70	30.1	44.2	4.7	8.07	%
$C_{30}Cl_{17}H_{24}MoN_4$ requires	12.20	31.6	45.8	3.1	7.2	%

4.25 Reaction of $MoBr_3(NCPh)_3$ with hot benzene

The yellow molybdenum complex, $MoBr_3(NCPh)_3$, dissolved in hot benzene (70°) to give a green solution from which a solid of approximate composition $Br_8C_{42}H_{30}Mo_3N_6$ crystallized out on concentrating the solution. The product was separated as usual, washed with ether and dried in vacuum at room temperature. The compound contained only a negligible amount of oxygen and thus, the green colour was unlikely to be due to the presence of oxidized species.

	Mo	Br	C	H	N	O
Found:	18.72	41.37	27.56	1.79	5.29	0.12 %
$Br_8C_{42}H_{30}Mo_3N_6$ requires	18.62	41.36	32.63	1.96	5.44	0.00 %

The ratio Br:Mo in this compound was 2.67:1 (c.f. compound obtained in 4.12).

E. SOME COMPLEXES OF MOLYBDENUM DERIVED FROM MoI_3 OR COMPLEXES OF THE TYPE MoX_3L_3 .

4.26 Molybdenum triiodide:

Procedure: 5gm. of molybdenum hexacarbonyl were put in a Schlenk tube, followed by the stoichiometric amount of iodine calculated to give MoI_3 . 50 ml. of dry benzene/toluene mixture (1:1) were added, the mixture degassed by evacuating for a few seconds, the tube filled with nitrogen and put in a silicone

oil bath (Fig. 19).

With both stop-cocks T_1 and T_2 open, and nitrogen flowing through the system, the temperature of the bath was slowly raised to $100-110^{\circ}\text{C}$ while the reaction mixture was being stirred. Stop-cock T_1 was closed and this temperature maintained for about five hours after which time, there was negligible gas being evolved.

Stop-cock T_1 was opened to allow nitrogen to flow through the system and the Schlenk tube removed from the hot bath. When the tube was cool, the stirring bar magnet was removed from the Schlenk tube and the grey solid isolated by filtration. It was washed with benzene until it was free of iodine. The product was finally washed twice with ether, and dried in vacuum at room temperature.

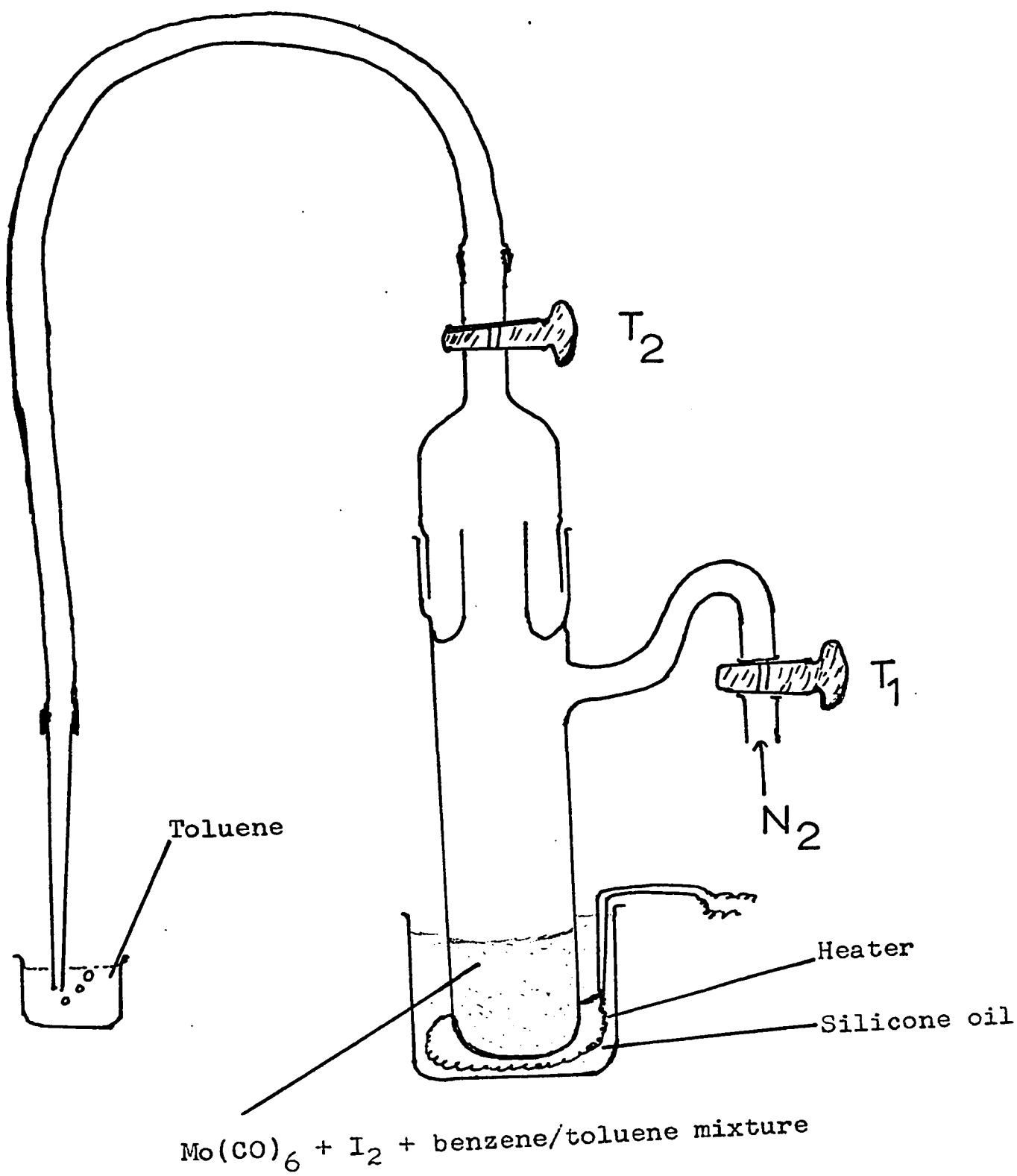
	Mo	I
Found:	19.50	80.00 %
Theory for MoI_3	20.13	79.87 %

4.27 Dibromobis(1,10-phenanthroline)molybdenum(III) bromide

Two to five gm. of a nitrile complex of the type $\text{MoBr}_3(\text{NCR})_3$ were put in a well dried Schlenk tube and the stoichiometric

FIGURE 19

Apparatus for preparation of molybdenum triiodide.



amount of 1,10-phenanthroline monohydrate added, followed by 50 ml. of tetralin. The tube was evacuated to remove oxygen and then filled with nitrogen and slowly heated to 160-170°C and the temperature maintained there for twenty-four hours while the mixture was stirred.

The tube was cooled, the product isolated by filtration, washed several times with benzene to remove any excess ligand and the product recrystallized from acetonitrile. The product was dried in vacuum at 50°C. For analysis, see Table 14.

4.27(a) Some complexes of molybdenum(III) prepared as in 4.27.

The iodo complexes, Mo(phen)I_3 , $(\text{Mo(phen)}_2\text{I}_2)\text{I}$ and $(\text{Mo(bipy)}_2\text{I}_2)\text{I}$ were prepared as in 4.27 from molybdenum triiodide with the stoichiometric amount of the ligand. Chloro and bromo complexes of empirical formulae $\text{MoCl}_3(\text{bipy})_{1.5}$ and $\text{MoBr}_3(\text{bipy})_{1.5}$ were also prepared as in 4.27 from the reaction of a complex of the type MoX_3L_3 ($\text{X} = \text{Cl, Br}$; $\text{L} = \text{a nitrile, tetrahydrofuran or tetrahydrothiophene}$) with two millimoles of 2,2'-bipyridine per millimole of the molybdenum complex. In the latter case, pure products were obtained without recrystallization. See Table 15 for analyses.

4.27(b) Reactions of complexes of molybdenum (III) with
1,10-phenanthroline and 2,2'-bipyridine in
phenylacetonitrile.

Introduction:

Phenylacetonitrile was chosen because it is an ionizing solvent and has a high boiling point.

Procedure:

As in 4.27, except in isolation of the products. These were recovered as follows:-

At the end of the reaction (two days), the solvent was pumped off at 100°C and the residue washed with a few ml. of acetonitrile, and the filtrate kept. The solids were further washed with benzene and ether. The solid products were $\text{Mo}(\text{phen})_2\text{Br}_3$ (compound 1, Table 15) and $\text{Mo}_2\text{Br}_6(\text{bipy})_3$ (compound 5, Table 15).

The analysis for the chloro compound was unsatisfactory in that, although the analysis suggested the product contained $(\text{Mo}(\text{phen})_2\text{Cl}_2)\text{Cl}$, both chlorine and nitrogen were poor, giving ratios of $\text{Cl}:\text{Mo} = 2.5:1$ and $\text{N}:\text{Mo} = 3.4:1$.

(c) Products from filtrates in 4.27(b)

The filtrate in the reaction of $\text{MoCl}_3(\text{NCR})_3$ with 1,10-phenanthroline (prep. 4.27(b)) was concentrated to a few ml. A little resinous material sticking to the sides of the

TABLE 15

SOME 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDYL
COMPLEXES OF MOLYBDENUM(III)

Compound	Mo	<u>FOUND (%)</u>				Br, Cl or I	Mo	<u>CALCULATED (%)</u>			
		Br, Cl or I	C	H	N			Br, Cl or I	C	H	N
1 $[\text{Mo}(\text{phen})_2\text{Br}_2]\text{Br}$	13.54	34.33	41.13	2.36	8.13	13.78	34.44	41.41	2.32	8.05	- 137 -
2 $[\text{Mo}(\text{phen})_2\text{I}_2]\text{I}$		44.35	35.05	2.14	6.43		45.48	34.44	1.93	6.69	
3 $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I} \cdot \text{NCCH}_3$		45.35	32.55	2.53	8.28		45.86	34.73	2.31	8.44	
4 $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{BPh}_4$		25.30	55.08	4.11	5.61		25.86	53.84	3.70	5.71	
5 $\text{Mo}_2\text{Br}_6(\text{bipy})_3$	16.98	42.27	31.46	1.96	7.50	16.83	42.07	31.60	2.12	7.37	
6 $\text{Mo}_2\text{Cl}_6(\text{bipy})_3$		24.29	41.13	3.13	9.45		24.36	41.26	2.77	9.62	
7 $\text{Mo}(\text{phen})\text{I}_3$	14.10	56.40	23.34	1.68	4.24	14.61	57.96	21.94	1.23	4.26	

tube was obtained. The solution (15 ml.) was filtered, and 10 ml. of ether added. The purple solid obtained was separated by filtration and washed several times with acetonitrile/ether (1:1). The product was dried in vacuum at 80°C. Analysis of the product suggested that it was $\text{Mo}(\text{phen})_3\text{Cl}_3$.

	Cl	C	H	N
Found:	14.90	57.65	3.68	9.94 %
$\text{C}_{36}\text{Cl}_3\text{H}_{24}\text{MoN}_6$ requires	14.32	58.20	3.26	11.31 %

4.27(d) Product in the filtrate from the reaction of $\text{MoBr}_3(\text{NCCH}_2\text{Ph})_3$ with 2,2'-bipyridine.

A small amount of red product was recovered as in 4.27(c). Elemental analysis suggested that the product was probably $\text{Mo}(\text{bipy})_3\text{Br}_3$.

	C	H	N
Found:	43.95	3.96	10.88 %
$\text{Br}_3\text{C}_{30}\text{H}_{24}\text{MoN}_6$ requires	44.80	3.11	10.45 %

4.28 Reaction of $\text{MoBr}_3(\text{C}_4\text{H}_8\text{S})_3$ with 1,10-phenanthroline in a 1:3 mole ratio.

Procedure:

The preparation was attempted following the procedure in 4.27(c). An orange product which was recovered after stirring the mixture at 170°C for three days was shown to be an impure material containing over 17% oxygen.

The filtrate (purple) was concentrated and the product recovered as in 4.27(c). Elemental analysis was as follows:-

	Br	C	H	N
Found:	25.27	48.20	3.30	9.19 %
$\text{Br}_2\text{C}_{24}\text{H}_{16}\text{MoN}_4$ requires	25.93	46.78	2.62	9.09 %

The ratio N:Br was 2.07:1.

It was unlikely that the material was $\text{Mo}(\text{phen})_3\text{Br}_3$, because of the low bromine content. (Calculated for $\text{Mo}(\text{phen})_3\text{Br}_3 = 27.34$).

4.29(a) Reaction of MoI_3 with 1,10-phenanthroline in benzonitrile in a 1:3 mole ratio.

Procedure:

As in 4.27(a) except that:-

1. The anhydrous ligand was used in order to avoid contamination of the products with oxygenated species, and
2. benzonitrile was used as the solvent. The purple product obtained after heating the reactants for three days at 170°C was thoroughly washed with hot acetonitrile and dried in vacuum at room temperature.

	Mo	I	C	H	N
Found:	13.09	36.44	38.92	2.30	8.01 %
$\text{C}_{24}\text{H}_{16}\text{I}_2\text{MoN}_4$ requires	13.51	35.74	40.59	2.27	7.89 %

The ratio of I:Mo (2.1:1) showed that the compound was a bivalent molybdenum complex. The N:Mo ratio (4.19:1) supports the above formulation. A similar conclusion was reached from

magnetic measurements.

4.29(b) Reaction of $\text{Mo}_2(\text{biny})_3\text{Br}_6$ with 2,2'-bipyridyl in a steel bomb.

Procedure:

1.5 gm. (1.32 mmoles) of $\text{Mo}_2(\text{bipy})_3\text{Br}_6$ and 1.5 gm. (9.6 mmoles) of 2,2'-bipyridyl were put in a steel bomb, the latter evacuated and refilled with dry oxygen-free nitrogen. 100 ml. of freshly distilled acetonitrile were added, the bomb evacuated and sealed. It was put in an electric oven and the temperature raised slowly to 180°C and maintained there for three days.

The bomb was cooled, filled with nitrogen, the red solution filtered, and concentrated by pumping off most of the solvent. No significant amount of solid had formed when about 20 ml. of the solution remained. The product was recovered as in 4.27(c).

For reasons which are not clear, the material left after oxidizing this compound with nitric acid and heating it to 600°C was brown-grey* and not the usual yellow molybdenum trioxide. As was frequently the case, the analysis for carbon was low but the nitrogen:bromine ratio (3.02:1) suggested that the product was $\text{Mo}(\text{bipy})_3\text{Br}_2$ rather than $\text{Mo}(\text{bipy})_3\text{Br}_3$.

	Br	C	H	N	
Found:	22.98	46.65	4.14	12.15	%
I $\text{Br}_2\text{C}_{30}\text{H}_{24}\text{MoN}_6$ requires	22.07	49.34	4.18	11.60	%
II $\text{Br}_3\text{C}_{30}\text{H}_{24}\text{MoN}_6$ requires	29.81	44.80	3.11	10.45	%

* Presumably iron impurities from the steel bomb. This is feasible if the iron reacted with bromine from the MoBr_3 complex to form FeBr_3 .

Furthermore, the room temperature magnetic moment (2 B.M.) indicated the presence of divalent molybdenum.

It was concluded that under these conditions, the trivalent molybdenum was reduced, presumably by the nitrile. The product was very soluble in water and acetonitrile.

F. SOME COMPLEXES OF TRIVALENT AND TETRAVALENT TUNGSTEN

4.31 Dichlorotricarbonylbis(pyridine)tungsten(II).

This compound was made by two different methods (see Table 16).

4.31(a) The halocarbonyl, $W(CO)_4Cl_2$, (see 4.3) was dissolved in methylene chloride and the solution filtered. A solution in methylene chloride containing the stoichiometric amount of pyridine was added, the reactants stirred for twelve hours and the resulting yellow solution filtered. The solution was concentrated to a few ml. by pumping off most of the solvent and the product precipitated by the addition of ether. The solid was isolated by filtration, washed several times with ether and dried in vacuum at $50^\circ C$. For analysis, see Table 17.

(b) Tetracarbonylbis(pyridine)tungsten(0) was made by heating tungsten hexacarbonyl in pyridine at $110^\circ C$. The apparatus of Fig. 19 was used, but with stop-cock T_2 closed and T_1 open to the nitrogen line. The orange product was isolated by filtration, washed with a few ml. of pyridine, ether and dried by evacuating at room temperature. Analysis: Found: $W = 40.18\%$ calculated for $W(CO)_4py_2$, $W = 40.49\%$. This material was used for preparation of $W(CO)_3py_2Cl_2$ as follows:-

TABLE 16

Routes to the tungsten complexes $W(CO)_3py_2X_2$ ($X = Cl, Br, I$).

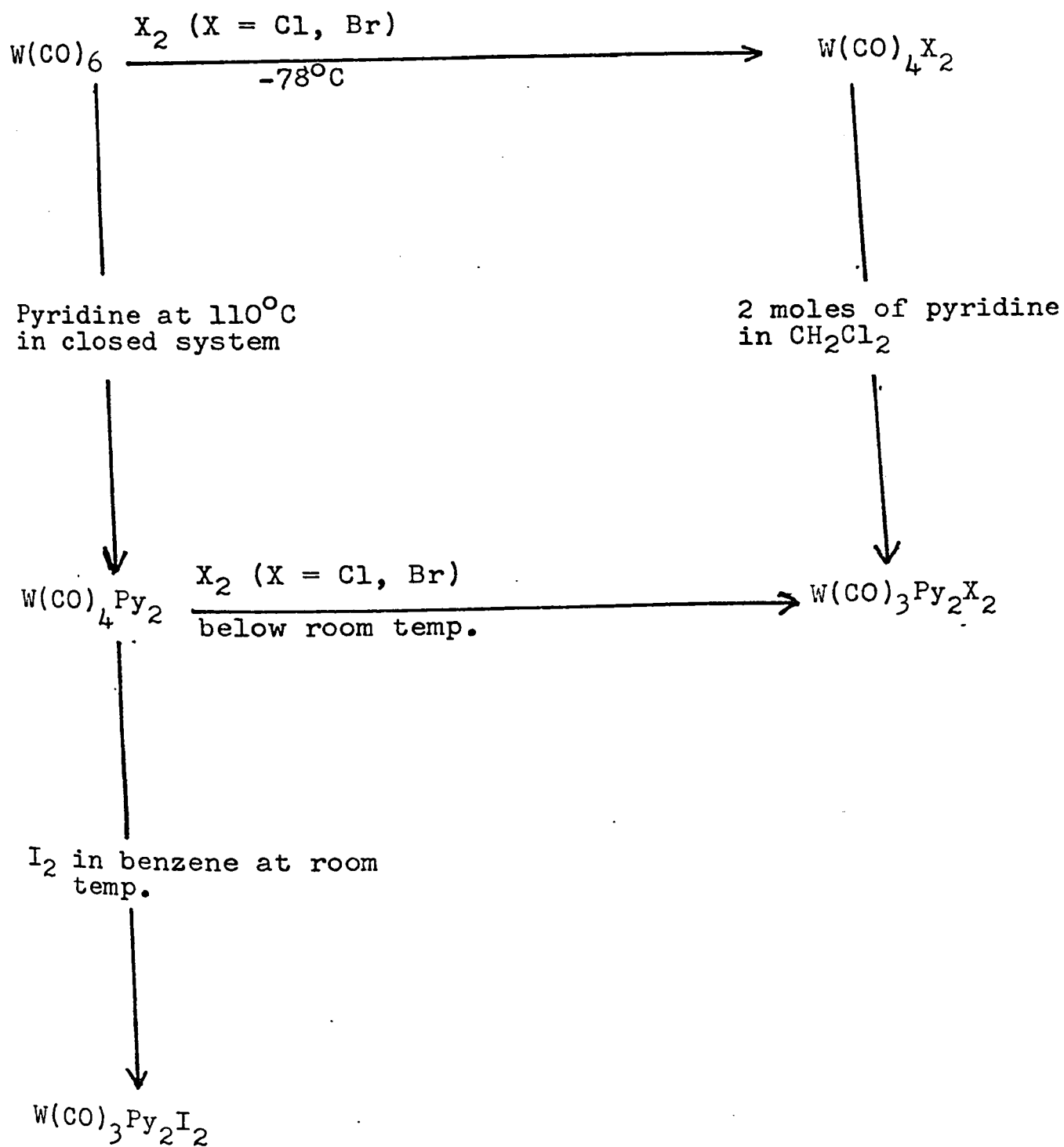


TABLE 17

ANALYSIS FOR THE TUNGSTEN COMPLEXES,

$W(CO)_3py_2X_2$ (X = Cl, Br, I).

Compound	Found (%)						Calculated (%)					
	W	X	C	H	N	O	W	X	C	H	N	O
1 $W(CO)_3py_2Cl_2$ (a)		14.11	31.29	2.17	5.72	9.45		14.27	31.42	2.03	56.4	9.66
(b)	36.70	14.27	29.66	2.36	5.66	9.86	36.99	14.27	31.42	2.03	5.64	9.66
2 $W(CO)_3py_2Br_2$	31.35	27.84	24.92	1.65	4.76	8.03	31.38	27.28	26.65	1.72	4.78	8.19
3 $W(CO)_3py_2I_2$	27.42	37.22	22.88	1.51	4.25	7.13	27.04	37.33	22.96	1.48	4.12	7.06

(a) From $W(CO)_4Cl_2$ + pyridine

(b) From $W(CO)_4py_2$ + chlorine

A convenient amount of $W(CO)_4py_2$ was put in a Schlenk tube and the preparation carried out following 4.3. The product was recovered following 4.31(a).

4.32 Dibromotricarbonylbis(pyridine)tungsten(II).

This compound was prepared exactly as its chloro analogue (from $W(CO)_4Br_2$ and pyridine or from $W(CO)_4py_2$ and bromine). See Table 17 for analytical data.

4.33 Di-iodotricarbonylbis(pyridine)tungsten(II).

Procedure:

Tetracarbonylbis(pyridine)tungsten(0) was prepared as in 4.31(b). 4 gm. of the orange product were put in the flask in Fig. 18. 50 ml. of freshly distilled benzene were added and after degassing the system and filling the flask with nitrogen, the stoichiometric* amount of powdered iodine was added.

The reddish-brown product obtained after stirring the reactants for twelve hours was isolated as usual, and washed with a few ml. of ether and dried at 50°C in vacuum. See Table 17 for analytical data.

4.34 Reaction of $W(CO)_4Cl_2$ with neat pyridine.

Procedure:

The halocarbonyl compound, $W(CO)_4Cl_2$ (see 4.3), was treated with neat pyridine following 4.16. Only a small amount of brown product had formed after stirring the filtrate overnight. An

* Calculated to give tungsten(II).

infrared spectrum of the compound showed weak carbonyl peaks identical to those of $W(CO)_3py_2Cl_2$. Elemental analysis showed that this material was essentially a tetravalent tungsten complex and the carbonyl compound was only an impurity.

	Cl	C	H	N	O	
Found:	29.38	24.74	2.15	5.67	1.32	%
$C_{10}Cl_4H_{10}WN_2$ requires	28.48	24.82	2.08	5.79	0	%

The filtrate was heated to $80^{\circ}C$ when more brown precipitate formed. The solution was cooled, the product isolated and dried at $50^{\circ}C$. Total elemental analysis confirmed that the product was a tungsten(IV) compound.

	W	Cl	C	H	N	
Found:	38.20	29.08	24.96	2.15	5.83	%
$C_{10}Cl_4H_{10}WN_2$ requires	38.00	28.48	24.82	2.08	5.79	%

Further evidence of valency of tungsten comes from magnetic measurements (see Table 20).

4.35 Trichlorotris(pyridine)tungsten(III).

Procedure:

3 gm. of WCl_4py_2 (4.34) were put in a Schlenk tube, 35 ml. of pyridine added and the mixture heated in an atmosphere of nitrogen while being stirred. At $120^{\circ}C$, the brown solid started dissolving visibly to give a red solution. The dissolution was complete at $140^{\circ}C$. The temperature was maintained

between 130°C and 140°C for twelve hours, the solution cooled to about 50°C, filtered and the solution concentrated to obtain a red solid which was recovered as usual.

When dried at room temperature in vacuum, this material appeared to be WCl_3py_4 . Found: $\text{W} = 31.53\%$. Calculated WCl_3py_4 $\text{W} = 30.4\%$. (c.f. MoCl_3py_4 in Table 13). The product was dried further at 80°C, to obtain WCl_3py_3 .

	W	Cl	C	H	N
Found:	34.27	19.77	34.43	3.11	7.70 %
$\text{C}_{15}\text{Cl}_3\text{WN}_3$ requires	34.85	20.16	34.15	2.87	7.97 %

In routine preparations, it was not necessary to isolate the intermediates. The $\text{W}(\text{CO})_4\text{Cl}_2$ was dissolved in pyridine, the filtered solution heated to 140°C and the product, WCl_3py_3 , isolated as described in 4.35.

4.36 Tribromotris(pyridine)tungsten(III).

Procedure:

$\text{W}(\text{CO})_4\text{Br}_2$ was dissolved in neat pyridine and the preparation carried out as in 4.35 without isolating intermediates. The product was recovered slightly differently as it was too soluble in pyridine to be simply crystallized.

After the reaction, all the pyridine was removed by pumping off. The residue was leached with freshly distilled methylene chloride and the product recovered after concentrating the solution. The product was dried at 80°C in vacuum.

	W	Br	C	H	N	
Found:	27.72	36.02	27.09	2.38	6.18	%
$\text{Br}_3\text{C}_{15}\text{H}_{15}\text{N}_3\text{W}$ requires	27.82	36.27	27.27	2.29	6.36	%

4.37. Attempted isolation of WBr_4py_2 .

An attempt to isolate the intermediate in the reaction of $\text{W(CO)}_4\text{Br}_2$ with neat pyridine was unsuccessful because the product obtained at room temperature was very soluble in pyridine. Hence, the product (pink) was precipitated by addition of a little ether. Unfortunately, this procedure also precipitated carbonyl compounds as impurities.

	W	Br	C	H	N	O
Found:	20.63	32.74	30.89	3.78	5.90	2.23 %

The Br:W ratio of 3.6:1 suggested that the product was predominantly a tungsten(IV) compound.

4.38 Reaction of tungsten hexacarbonyl with iodine in benzene/toluene mixture.

Procedure:

The procedure used is identical to that followed for preparation of molybdenum triiodide. At the end of the reaction (3 hours), it was noted that there was only a little black material whose analysis suggested that the product was a mixture of WI_4 and WI_3 .

Found: $\text{W} = 28.5\%$; theory for $\text{WI}_4 = 26.60\%$; theory for $\text{WI}_3 = 32.57\%$.

A pyridine derivative of this material gave further evidence that it was a tetravalent tungsten compound (see 4.40), and not

the desired compound.

4.39 Reaction of WI_x with acetonitrile at $80^\circ C$.

2 gm. of the material from 4.38 were dissolved in acetonitrile (25 ml.) and the solution heated to $80^\circ C$ for twelve hours during which time it turned yellow. A grey solid precipitated from the filtered solution by addition of ether and this was washed several times with the same solvent and dried under vacuum at room temperature.

	W	I	C	H	N
Found:	30.12	55.42	7.39	1.18	3.78 %
$C_{12}H_{18}I_8N_6W_3$ requires	30.41	55.99	7.95	1.00	4.64 %

(c.f. $Mo_3Br_8(NCPh)_6$ in 4.25). The colour of the solution was due to free iodine (thin layer chromatography).

4.40 Reaction of WI_x ($3 < x < 4$) with neat pyridine.

One gm. of the material obtained in 4.38 was dissolved in 20 ml. of freshly distilled pyridine and the reactants stirred at room temperature for twelve hours. On filtering, no solid was left and hence, the product was recovered as in 4.39.

	W	I	C	H	N
Found:	18.00	48.39	25.08	2.56	5.49 %
$C_{20}H_{20}I_4N_4W$ requires	18.23	50.37	23.83	2.00	5.56 %

The material was grey and had $I:W = 3.89$; $N:W = 4:1$; $C:W = 21.32:1$. This strongly suggested that it was a tungsten(IV) compound. A compound approximating this composition was

obtained in an independent method (4.43).

4.41 Triacetonitriletricarbonyltungsten(0).

This compound was made for use in interpreting the infrared spectra discussed in Chapter 5.

Procedure:

The compound was prepared following the procedure for making $W(CO)_4py_2$ (see 4.31(b)), except that the reaction was allowed to proceed for three days at 85-90°C. The solution was filtered hot, and on cooling, a yellow solid crystallized out. The latter was separated, washed with ether and dried in vacuum at room temperature.

	W	C	H	N	O
Found:	46.40	27.69	2.59	10.84	12.34 %
$C_{12}H_9N_3O_3W$ requires	47.02	27.64	2.32	10.75	12.27 %

The corresponding molybdenum compound was made similarly and identified by means of infrared spectroscopy. In the latter case, however, reaction was complete within six hours.

4.42 Attempted preparation of benzonitrile complexes of tungsten(III) of the type $WX_3(NCPh)_3$ ($X = Cl, Br$).

Procedure:

The procedure for preparation and isolation of WBr_3py_3 (see 4.36) was followed but no crystalline product could be obtained even after concentrating the solution to about 10 ml.

The products were therefore obtained by adding a large quantity of ether to the solution of the compounds in methylene chloride. The solids thus recovered were dried at 50°C in vacuum.

Except in a few cases where impurities in solution are negligible, this method of recovering products is undesirable for reasons discussed earlier (page 147). The analytical data obtained were, nevertheless, sufficiently good to show that the products obtained were complexes of bivalent tungsten. The halogen:tungsten ratio was 2.01:1 for the bromo compound and 1.84:1 for the chloro compound. For the complexes of the type WX_3L_3 , the ratio would be 3:1.

The data lead to the empirical formulae $WBr_2(NCPh)_2$ and $WCl_2(NCPh)_2$. These are more highly coordinated than the usual bivalent tungsten complexes of the type $W_6X_{12}L_2$ discussed in Chapter 1 (page 16).

	W	Br	C	H	N
Found:	33.88	29.32	28.32	2.19	4.04 %
$WBr_2(NCPh)_2$ requires	33.44	29.06	30.58	1.83	5.09 %
$W_6Br_{12}(NCPh)_2$ requires	48.63	42.28	7.41	0.4	1.24 %

	W	Cl	C	H	N
Found:	40.97	14.50	31.38	2.87	6.73 %
$WCl_2(NCPh)_2$ requires	39.88	15.38	36.47	2.19	6.08 %
$W_6Cl_{12}(NCPh)_2$ requires	63.59	24.52	9.69	0.58	1.61 %

4.43 Attempted preparations of WI_3Py_3 .

4.43(a) From the reaction of $W(CO)_3Py_2I_2$ with pyridine at 140°C.

Procedure:

$W(CO)_3py_2I_2$ was prepared as in 4.33. 2 gm. of this material were dissolved in 35 ml. of freshly distilled pyridine, the solution filtered and heated to $140^{\circ}C$ in an atmosphere of nitrogen for twelve hours. The solution was cooled, concentrated and filtered. The orange solid was washed with a few ml. of pyridine/ether and dried in vacuum at room temperature. An infrared spectrum showed two very strong peaks at 1747 cm.^{-1} and 1888 cm.^{-1} , showing that the product was probably $fac-W(CO)_3py_3$ which could be prepared from $W(CO)_6$ and pyridine.

Treatment of the filtrate:

To the filtrate (≈ 15 ml.), about 10 ml. of ether were added. A green product precipitated out. This was washed several times with methylene chloride and dried in vacuum at room temperature.

	W	I	C	H	N
Found:	17.34	49.56	24.75	2.60	5.55 %
$C_{20}H_{20}I_4N_4W$ requires	18.23	50.36	23.83	2.00	5.55 %

The I:W ratio = 4.14:1 (c.f. 4.40).

The analytical data show that the compound was not a trivalent tungsten complex such as obtained from the reactions of $W(CO)_3py_2Cl_2$ and $W(CO)_3py_2Br_2^*$ with neat pyridine at $140^{\circ}C$. The reasons for this are discussed in the next chapter.

* These are the initial products in the reaction of $W(CO)_4X_2$ ($X = Cl, Br$) with pyridine.

4.43(b) From the reaction of $W(CO)_3py_3$ with iodine.

Procedure:

Tricarbonyltripyridinetungsten(0) was prepared by the method of Hieber and Romberg (207). Found: $W = 36.26\%$; calculated for $C_{18}H_{15}N_3W$, $W = 36.39\%$. This material was used without further crystallization.

One gram (1.98 mmoles) of $W(CO)_3py_3$ was put in the flask shown in Fig. 18 followed by 50 ml. of freshly distilled benzene. After degassing the system and re-filling the flask with nitrogen, 0.761 gm. (3 mmoles) of iodine was added and the preparation completed, following the method for making $W(CO)_3py_2I_2$. The small amount of the product (grey) analysed as follows:-

	W	I	C	H	N	O
Found:	17.85	50.10	22.47	2.46	5.36	1.76 %
$C_{20}H_{20}I_4N_4W$ requires	18.24	50.15	23.83	2.00	5.56	0.00 %

The ratios $N:W = 3.94:1$, $I:W = 40.7:1$, $C:N = 4.9:1$ show that, despite the small amount of oxygen present (certainly in an impurity), the compound was not a trivalent tungsten compound but a tungsten(IV) complex. The product in the solution was not examined.

CHAPTER 5

RESULTS AND DISCUSSION

A. PREPARATIVE WORK:

(i) Reactions of $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ with donor molecules capable of stabilizing low oxidation states.

The main conclusion that can be drawn from the reactions of the halocarbonyls $\text{Mo(CO)}_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with electron donors capable of stabilizing low oxidation states is that such ligands generally stabilize bivalent molybdenum. This is well illustrated by the following examples:-

<u>Reactants</u>	<u>Reaction conditions</u>	<u>Product isolated</u>
$\text{Mo(CO)}_4\text{Cl}_2 + \text{PEt}_3$	Ligand as solvent	$\text{Mo(CO)}_3(\text{PEt}_3)_2\text{Cl}_2$
$\text{Mo(CO)}_4\text{Cl}_2 + \text{P(OCH}_3)_3$	Ligand as solvent	$\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Cl}_2$
$\text{Mo(CO)}_4\text{Cl}_2 + \text{PhNC}$	4 moles of ligand Ether as solvent	$\text{Mo(CO)(CNPh)}_4\text{Cl}_2$

$\left[(\text{c.f. } \text{Mo(CO)}_4\text{X}_2 + \text{excess isocyanide} \longrightarrow \text{Mo(CNR)}_5\text{X}_2 \text{ in Table 3}) \right]$

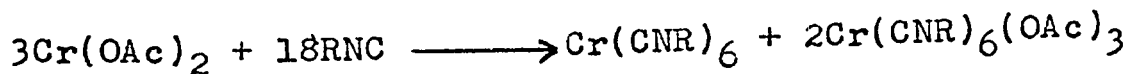
These examples show that the reactivity of these halocarbonyls toward electron donors of this type parallels the reactivity of Mo(CO)_6 toward such donors. In molybdenum hexacarbonyl, for example, the maximum substitution of CO

groups by electron donors of this type that has been achieved is as follows:-

<u>Type of electron donor, L.</u>	<u>Product with maximum number of ligands of the type L.</u>	<u>Reference</u>
Monodentate, alkyl or aryl phosphines	$\text{Mo}(\text{CO})_3\text{L}_3$	209, 210
Monodentate phosphites	$\text{Mo}(\text{CO})_2\text{L}_4$	208, 209
Isocyanides	MoL_6	13

An attempt to obtain increased substitution in $\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Br}_2$ by heating the compound with trimethylphosphite to 80°C gave a halogen-free product approximating the composition $\text{C}_4\text{H}_{15}\text{MoO}_{13}\text{P}_3$ (ratios of atoms) which did not, however, correspond to a substituted compound of the type $\text{Mo}(\text{CO})_{6-n}\text{L}_n$.

Formation of the trivalent molybdenum complex, $\text{Mo}(\text{NCPh})_4\text{Cl}_3$, from the reaction of $\text{Mo}(\text{CO})_4\text{Cl}_2$ with phenylisocyanide was surprising in that isocyanides are among the best known electron donors which stabilize low oxidation states of transition metal ions (131). It is of interest to note, however, that zerovalent chromium complexes of the type $\text{Cr}(\text{CNR})_6$ were obtained via a disproportionation reaction when chromium(II) acetate was treated with excess isocyanide (211). The authors suggest that the reactions proceed according to the general reaction



but also report that the trivalent complexes could not be isolated.

(ii) Reactions of $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ with electron donors that have no special ability to stabilize low oxidation states.

(a) Reactions in suitable organic solvents using stoichiometric amounts of the reactants:

It was found that the products of the type $\text{Mo(CO)}_x(\text{NCR})_y\text{X}_2$, e.g. $\text{Mo(CO)}_3(\text{NCCH}_3)\text{Cl}_2$ decomposed on standing. Furthermore, it was not possible to make complexes of the type $\text{Mo(CO)}_3(\text{NCR})_2\text{X}_2$ even when the reaction was allowed to proceed for several days. These observations indicate that nitriles are bound to molybdenum(II) less strongly than phosphines or arsines are because, in the latter case, stable complexes such as $\text{Mo(CO)}_3(\text{PPh}_3)_2\text{Cl}_2$ (21) and $\text{Mo(CO)}_3(\text{AsPh}_3)_2\text{Br}_2$ (22) are readily formed by treating the halocarbonyls $\text{Mo(CO)}_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with the appropriate ligand.

As will be recalled from the discussion in Chapter 1 (p.10), the halocarbonyl compounds of the type $\text{M(CO)}_4\text{X}_2$ are believed to be dimeric since they are diamagnetic (24). Further support for this formulation comes from the reactions of $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ with Ph_3PO and Ph_3AsO which gave compounds of the type $\text{Mo(CO)}_x\text{L}_y\text{X}_2$. As in the case of nitrile compounds, $y < 2$. Isolation of compounds with non-integral values of x and y in such compounds, e.g. $\text{Mo(CO)}_{3.5}(\text{OPPh}_3)_{0.5}\text{Br}_2$ and $\text{Mo(CO)}_3(\text{OAsPh}_3)_{1.5}\text{Cl}_2$

is interpreted as indicating that the compounds are dimeric. The two compounds just cited, for example, have been formulated as $\text{Mo}_2(\text{CO})_7(\text{OPPh}_3)\text{Br}_4$ (4.14) and $\text{Mo}_2(\text{CO})_6(\text{OAsPh}_3)_3\text{Cl}_2$ (4.15), respectively. The binuclear structures most probably drive from the starting materials.

(b) Reactions in which the neat ligands were used as the solvents.

1. Conclusion and evidence:

Conclusion: The main conclusion that can be drawn from the reactions of $\text{Mo}(\text{CO})_4\text{Cl}_2$ and $\text{Mo}(\text{CO})_4\text{Br}_2$ with neat electron donors of poor π -bonding capacity is that such ligands do not stabilize bivalent molybdenum. Consequently, when $\text{Mo}(\text{CO})_4\text{Cl}_2$ or $\text{Mo}(\text{CO})_4\text{Br}_2$ were dissolved in such electron donors, instead of recovering substituted halocarbonyl products of the type $\text{Mo}(\text{CO})_x\text{L}_y\text{X}_2$ which one obtains when electron donors such as phosphines are used, the bivalent molybdenum disproportionated into molybdenum(III) and molybdenum(0). This is the basis of the preparations described in 4.16-4.20 for making complexes of trivalent molybdenum from molybdenum(II).

Evidence: The reactions of $\text{Mo}(\text{CO})_4\text{Cl}_2$ with neat acetonitrile, benzonitrile and propionitrile were studied first. It was noted that molybdenum(III) complexes of the type $\text{Mo}(\text{CO})_3(\text{NCR})_3$ were isolated in much larger quantities than could be accounted for by assuming the presence of

molybdenum(III) impurities in the $\text{Mo}(\text{CO})_4\text{Cl}_2$. Furthermore, complexes of this type were recovered even when $\text{Mo}(\text{CO})_4\text{Cl}_2$ was shown (analytically) to be pure. An estimation of the yields showed that about two-thirds of the original molybdenum (which was in oxidation state +2) was recovered as trivalent molybdenum in accordance with the stoichiometry of the disproportionation reaction (equation 5-1).

(ii) As a reaction mixture was stirred, molybdenum hexacarbonyl crystallized on the sides of the reaction tube.

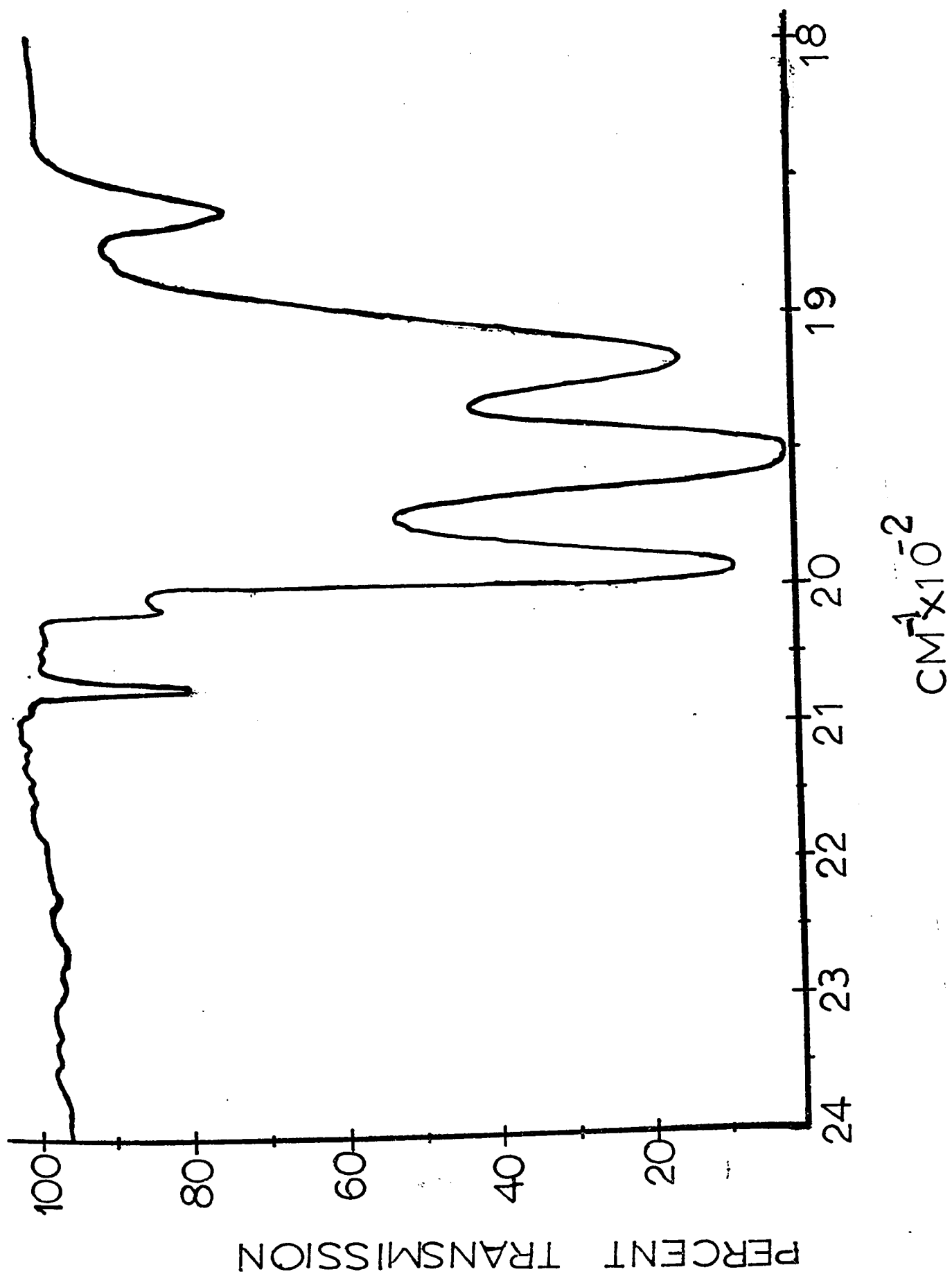
(iii) When the mother liquor in the reaction of $\text{Mo}(\text{CO})_4\text{Cl}_2$ with neat propionitrile was evaporated off, the residue extracted with ether and the products separated chromatographically on an alumina column, air-sensitive substituted carbonyls of the type $\text{Mo}(\text{CO})_{6-n}(\text{NCCH}_2\text{CH}_3)_n$ were recovered.

Infrared spectra in the carbonyl region showed that total separation of the products was not achieved. The carbon-nitrogen stretching frequencies were not sufficiently strong to show presence of the nitrile (Fig. 20). The reason for this is discussed in Section F. Qualitative tests showed the presence of molybdenum (α -benzoin oxime) and the absence of halogen.

(iv) When $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$ and $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$, both of which contained neither trivalent nor zerovalent molybdenum were dissolved in pyridine and acetonitrile, respectively, molybdenum(III) complexes (see 4.19 and 4.18) and molybdenum

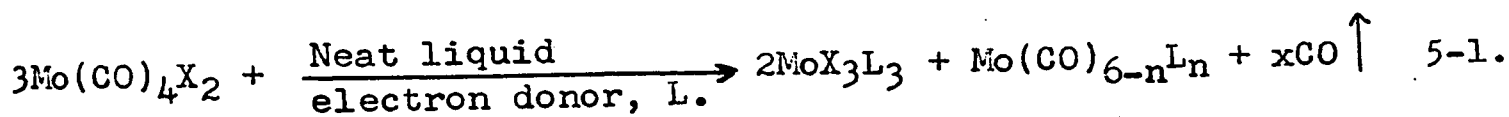
FIGURE 20

An infrared spectrum of halogen-free carbonyl compound from the reaction of $\text{Mo(CO)}_4\text{Cl}_2$ with neat propionitrile.



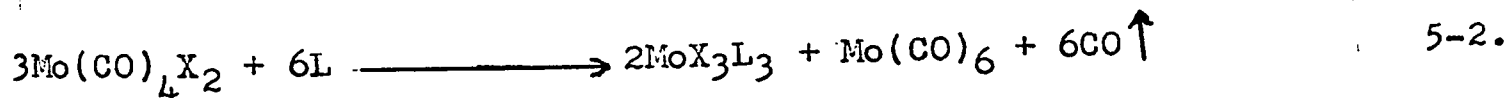
hexacarbonyl were recovered. Molybdenum hexacarbonyl was recovered from the filtrate in the reaction of $\text{Mo(CO)}_2\text{py}_2\text{Cl}_2$ with pyridine by acidifying the filtrate with sulphuric acid and steam distilling the hexacarbonyl.

Although the mechanisms by which various products are formed are not certain, the overall reaction can be represented, on the basis of the above observations, by equation 5-1.

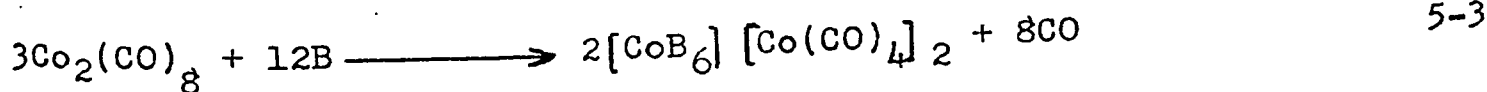


where $x = 6 + n$.

For the case when Mo(CO)_6 is the zerovalent product, (i.e. $n = 0$), we may write the simplified equation 5-2.

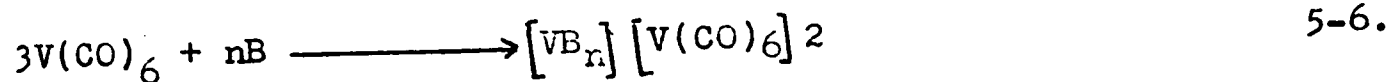
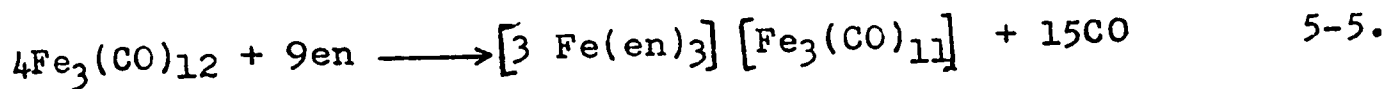
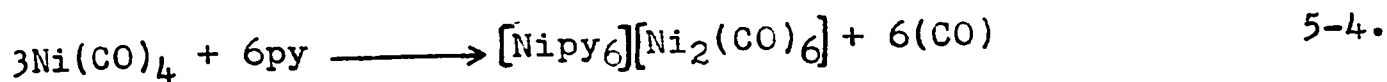


These are the first reported examples of disproportionation of bivalent molybdenum. It is of interest to note that chromium(II) (211) and manganese(III) (212, 213) both of which are, like molybdenum(II), d^4 systems, have been shown to undergo disproportionation reactions. However, reactions of this type are not by any means peculiar to d^4 systems. It is known, for instance, that several metal carbonyls undergo disproportionation reactions (214-219), a few of which are shown in equations 5-3—5-6.



In 5-3, $\text{B} = \text{NH}_3$ (214, 216), pyridine, methanol, ethanol

or t-butanol (218)..



In 5-6, B = a Lewis base such as pyridine, acetone, methanol or dioxane (219).

In these reactions, disproportionation occurs because the ligand displacing the CO groups is less effective in sustaining the low oxidation state than is carbon monoxide.

Molybdenum(III) complexes of the type MoX_3L_3 separated after a short reaction time were found to be contaminated with carbonyl impurities, showing two peaks around 2020-2050 cm^{-1} and 1950-2000 cm^{-1} . This suggested, but did not prove, that the product formed initially is of the type $\text{Mo}(\text{CO})_2\text{L}_n\text{X}_2$ and that such intermediates are stable as long as there are at least two CO groups present, as has been shown to be the case for $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$ (4.10).

In light of the results obtained when $\text{Mo}(\text{CO})_4\text{Cl}_2$ and $\text{Mo}(\text{CO})_4\text{Br}_2$ reacted with neat nitriles, it appeared that disproportionation of molybdenum(II) did occur to a certain extent when the reactions were carried out in other solvents using a large excess of the ligand. This would explain why the halogen:molybdenum ratio was always greater than 2:1 but less than 3:1. This implies that the products were mixtures of trivalent and bivalent molybdenum complexes.

2. Generality of the disproportionation reaction.

A wide range of electron donors was tested in order to find out which ones would react with $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ to give complexes of molybdenum(III). Dimethylsulphoxide (DMS) reacted with $\text{Mo(CO)}_4\text{Cl}_2$ to give a small amount* of a yellow product with no CO groups. All attempts to recover more solid product from the filtrate were unsuccessful; an oil was obtained instead. Dimethylsulphide apparently reacted with the halocarbonyls in the same manner as the nitriles but no solid could be recovered.

An attempt was made to examine whether steric effects could be of importance. When $\text{Mo(CO)}_4\text{Cl}_2$ was treated with triethylamine, the bulk of $\text{Mo(CO)}_4\text{Cl}_2$ did not dissolve. The initially formed product (yellow) was sparingly soluble in triethylamine and hence formed a protective layer on $\text{Mo(CO)}_4\text{Cl}_2$. 2,6-lutidine and $\text{Mo(CO)}_4\text{Br}_2$ (more soluble than $\text{Mo(CO)}_4\text{Cl}_2$) gave a complex of the type MoBr_3L_2 rather than the usual MoBr_3L_3 type of complexes obtained with monodentate ligands. This is to be attributed to a steric effect.

Although no trivalent molybdenum complexes were positively identified in the reactions of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ and piperidine with $\text{Mo(CO)}_4\text{Br}_2$, isolation of the zerovalent com-

* Most of the product was in solution.

plexes, $\text{Mo(CO)}_4(\text{tmen})$ and $\text{Mo(CO)}_4(\text{piperidine})_2$ strongly suggested that disproportionation did occur in these reactions. In the latter case, the possibility that the amine reduced $\text{Mo(CO)}_4\text{Br}_2$ could not be ruled out and further work is certainly required before any definite conclusion can be drawn.

3. Ligand field stabilization energy for the products

In order to be able to explain why $\text{Mo(CO)}_4\text{Cl}_2$ and $\text{Mo(CO)}_4\text{Br}_2$ react with ligands such as phosphines to give molybdenum(II) complexes but react with nitriles to give molybdenum(III) compounds, it is necessary to have a knowledge of all the energy changes that take place.

For a simple case such as that represented by equation 5-2, an estimation of the Ligand Field Stabilization Energy of the products showed that for a mole of $\text{Mo(CO)}_4\text{Br}_2$ which reacts in this way, the sum of Ligand Field Stabilization Energy (LFSE) and Pairing energy, P , for the products is of the order of -110 kcal. The $10Dq$ values for the nitrile complexes of the type $\text{MoBr}_3(\text{NCCR})_3$ were obtained from electronic spectra (see Section C). The $10Dq$ value for Mo(CO)_6 and the Racah parameters, B and C , used were those given by Beach and Gray (220). The pairing energy, P , for a d^6 ion was estimated using the method given by Griffith (221). i.e. $P = 2.5B + 4C$. Equation 5-2 is re-written below to indicate how the energy value of $\approx -110\text{kcal}$ was

arrived at.

Reaction:



$$\text{LFSE (kcal)} \qquad 2(-71.5) + (-220.5)$$

$$\text{P (kcal)} \longrightarrow \qquad 0 \qquad 3 \times (+45.90)$$

$$\text{LFSE} + \text{P} \qquad -143.0 + 0 + -174.6$$

For three moles of $\text{Mo}(\text{CO})_4\text{Br}_2$ which react as in equation 5-2, products have a (LFSE + P) equal to -317.6. Hence, from a mole of $\text{Mo}(\text{CO})_4\text{Br}_2$, the (LFSE + P) for the products is -105.9 kcal. A reliable estimate of what the ligand field stabilization energy of a hypothetical octahedral complex of the type $\text{Mo}(\text{NCR})_4\text{Br}_2$ is not possible since the necessary parameters are unknown. If the value of 400 cm.^{-1} is taken as the Racah parameter, B, as suggested by Lewis *et al.* (68) for molybdenum(II), and assumption made that (1) two of the four d-electrons would be paired, and (2) the $10Dq$ value for the hypothetical complex is about $17,000 \text{ cm.}^{-1}$, then (LFSE + P) for $\text{Mo}(\text{NCR})_4\text{Br}_2$ is approximately -48 kcal/mole. Hence, energetically, it is more favourable for $\text{Mo}(\text{CO})_4\text{Br}_2$ to react with nitriles with formation of $\text{MoBr}_3(\text{NCR})_3 + \text{Mo}(\text{CO})_6$ rather than $\text{Mo}(\text{NCR})_4\text{Br}_2$. Of course, there are many other factors involved in the detailed thermodynamics of these reactions.

(iii) Reactions of molybdenum hexacarbonyl with iodine in organic solvents.

If both Mo(CO)_6 and I_2 are heated together in an open system in the dry state, they sublime off before reacting. On the other hand, a benzene (or similar solvent) solution of the reactants could be heated in a test tube to about 90°C without any observable loss of either reactant (37). At this temperature, iodine reacts slowly with molybdenum hexacarbonyl but much faster if the temperature is raised to 110°C . This observation is the basis of the preparation of molybdenum triiodide as described in Chapter 4.

The amount of molybdenum triiodide that could be made was limited only by the sizes of the apparatus used whereas in the previous method of making MoI_3 from Mo(CO)_6 and I_2 , the high pressure built in the reaction tube limited the amount of MoI_3 that could be made in one preparation to one gram or less.

(iv) 2,2'-bipyridine and 1,10-phenanthroline complexes

Attempts to make the complexes $\text{Mo(bipy)}_2\text{Cl}_3$ and $\text{Mo(bipy)}_2\text{Br}_3$ were based on the assumption that since nitrile complexes such as $\text{MoBr}_3(\text{bipy})\text{NCCH}_3$ are readily made (97), further substitution of the nitrile might be achieved by heating $\text{MoX}_3(\text{bipy})\text{NCR}$ ($\text{X} = \text{Cl}, \text{Br}$) with more ligand at higher temperature. Contrary to this expectation, it was found that $\text{MoBr}_3(\text{NCCH}_3)_3$ reacted with bipyridyl at 80°C to give

$\text{MoBr}_3(\text{bipy})\text{NCCH}_3$. At 170°C , $\text{MoBr}_3(\text{bipy})\text{NCCH}_3$ and similar nitrile complexes of molybdenum(III) reacted with excess bipyridyl to give complexes of the type $\text{Mo}(\text{bipy})_{1.5}\text{X}_3$ which have been made previously in attempts to make complexes of the type $\text{Mo}(\text{bipy})_3\text{X}_3$ (103).

This indicates that, as was expected, bipyridyl does react with the nitrile complexes, $\text{Mo}(\text{bipy})(\text{NCR})\text{X}_3$, to form the cations $\text{Mo}(\text{bipy})_2\text{X}_2^+$. However, the halide ion, X^- , does not cling on to $\text{Mo}(\text{bipy})_2\text{X}_2^+$ but attacks another $\text{Mo}(\text{bipy})(\text{NCR})\text{X}_3$ molecule to form the anion $\text{Mo}(\text{bipy})\text{X}_4^-$. One, therefore, isolates the salts $[\text{Mo}(\text{bipy})_2\text{X}_2] [\text{Mo}(\text{bipy})\text{X}_4]$ in which both the cation and the anion are large, instead of compounds of the type $[\text{Mo}(\text{bipy})_2\text{X}_2]\text{X}$ in which the cation is large and the anion small.

A higher degree of substitution was achieved by treating the bromo salt, $[\text{Mo}(\text{bipy})_2\text{Br}_2] [\text{Mo}(\text{bipy})\text{Br}_4]$, with more bipyridyl and the reaction carried out in a steel bomb at 180°C using acetonitrile as a solvent. However, under these conditions, molybdenum was reduced to form $\text{Mo}(\text{bipy})_3\text{Br}_2$. The compound was very soluble in both water and acetonitrile. This made re-crystallization of the product from acetonitrile difficult. Since the purity of the compound was not certain, a molar conductivity value cannot be quoted. An estimated value, based on the above formulation, of $307 \text{ ohm}^{-1} \text{ cm}^2$ for a $4 \times 10^{-4}\text{M}$ solution at 25°C , shows that the compound can reasonably be formulated as a 2:1 electrolyte $[\text{Mo}(\text{bipy})_3]\text{Br}_2$ (c.f. the value for $\text{Cu}(\text{ClO}_4)_2$; a $2 \times 10^{-2}\text{M}$ solution has a molar

conductivity of 235 ohm.⁻¹ cm.² (224).

Unlike all the other molybdenum compounds encountered during this work, this compound was very resistant to destructive oxidation with nitric acid. With the dilute cold acid, there was no observable colour change. With the cold concentrated acid, the red colour changed very slowly to give a brown material (presumably molybdenum(III)). With hot acid, the colour changed to blue (presumably molybdenum(V), whereas under these conditions, molybdenum in other complexes was readily oxidized to the hexavalent state.

In attempts to make $\text{Mo(phen)}_3\text{Br}_3$ and $\text{Mo(phen)}_3\text{I}_3$, it was noted that trivalent molybdenum was somewhat reduced if nitriles were used and the reaction carried out at 170°-180°C. At least this is certain for the iodo complexes (see 4.29a). The nitrile appears to be responsible for the reduction because the iodo complex, $\text{Mo(phen)}_2\text{I}_3$, could be heated to 200°C in tetralin without appreciable effect.

All the 2,2'-bipyridine (brown) and 1,10-phenanthroline complexes (dark purple) of molybdenum(III) were more resistant to oxidation than complexes of the type MoX_3L_3 . Thus, in the former case, the compounds in the solid form (but not in solution) could be left exposed to air for several weeks without observable colour change whereas in the latter case, the compounds darkened within a few hours' exposure to air.

(v) Compounds in which the metals have apparently non-integral oxidation states.

As was noted in Chapter 4 (4.12), attempts to make sub-

stituted halocarbonyl complexes of the type $\text{Mo}(\text{CO})_3(\text{NCR})_2\text{X}_2$ by using a large excess of the nitrile gave green compounds in which the halogen:molybdenum ratios were between 2.5:1 and 2.7:1. This might be, as noted above, due to a mixture of compounds of trivalent and bivalent molybdenum. It should be noted, however, that nitrile complexes of molybdenum(III) are yellow. Initially, such compounds were of little interest for two reasons, viz.

1. Infrared spectra of the products showed the presence of CO groups, albeit very weak, and hence, the compounds thus obtained probably impure.

2. There was no obvious reason why any molybdenum(II) compound made from $\text{Mo}(\text{CO})_4\text{Cl}_2$ or $\text{Mo}(\text{CO})_4\text{Br}_2$ should give a halogen:molybdenum ratio greater than 2:1.

It was noted later, in a completely different experiment, that when $\text{MoBr}_3(\text{NPh})_3$ (yellow) was dissolved in hot benzene, a green diamagnetic compound of empirical composition $\text{Mo}_3\text{Br}_8(\text{NPh})_6$ ($\text{Br}:\text{Mo} = 2.67:1$) was obtained (see 4.25). The related grey diamagnetic tungsten compound, $\text{W}_3\text{I}_8(\text{NCH}_3)_6$, was obtained by heating tungsten tetraiodide with acetonitrile at 80°C (4.39). These compounds are interesting because they are derivatives of the unknown halides, M_3X_8 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$). For niobium, halides of this type, e.g. Nb_3Cl_8 , are well known (50). It would be of interest to find out whether there is any connection between the green compound obtained in the reaction of $\text{Mo}(\text{CO})_4\text{Br}_2$ with a large excess of benzonitrile in ether or benzene and the green

product obtained from the reaction of $\text{MoBr}_3(\text{NCPh})_3$ with hot benzene.

(vi) Tungsten compounds.

The preparative work with tungsten compounds illustrates two points:-

(a) The tendency of tungsten in low oxidation states to form tungsten-tungsten bonds.

(b) The tendency of tungsten to form compounds in oxidation state +4 rather than +3.

(a) Formation of tungsten-tungsten bonds.

The formation of complexes of the type $\text{WX}_2(\text{NCPh})_2$ rather than $\text{WX}_3(\text{NCPh})_3$ is to be attributed to the fact that tungsten has a high tendency to form tungsten-tungsten bonds. This is so because of the high heat of atomization of tungsten. The fact that the reactions of $\text{W(CO)}_4\text{Cl}_2$ and $\text{W(CO)}_4\text{Br}_2$ with neat pyridine lead to disproportionation whereas those with benzonitrile give tungsten(II) complexes is to be attributed to the weaker basicity of nitriles than that of pyridine. In the former case, the complexes formed are such that tungsten ions can interact sufficiently strongly to form tungsten-tungsten bonds. On the other hand, in the pyridine compound, pyridine molecules are bonded sufficiently strongly to stop tungsten atoms from forming tungsten-tungsten bonds. It is probably for similar reasons that tungsten(IV) iodide reacts

with acetonitrile to form the diamagnetic complex, $W_3I_8(NCCH_3)_6$, whereas pyridine forms a tungsten(IV) complex.

(b) Stability of oxidation states +3 and +4.

The tendency of tungsten to form tungsten(IV) complexes rather than those of tungsten(III) is exemplified by the following observation:-

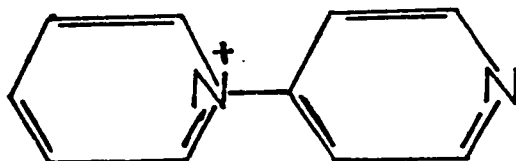
1. The reaction of $W(CO)_3py_3$ with iodine gives WI_4py_4 , a tungsten(IV) compound. This shows further that pyridine is not very effective in stabilizing low oxidation states since in $W(CO)_4$ (diars), oxidation with bromine or iodine does not proceed beyond the trivalent state (13).

2. The reaction of $W(CO)_4Cl_2$ with neat pyridine gave WCl_4py_2 and $W(O)$ complexes such as $W(CO)_3py_3$ (i.r.) (see 4.34). Although the corresponding bromo compound was not isolated pure, analytical data clearly showed that the product was unlikely to be a tungsten(III) compound ($Br:W = 3.6:1$).

The tungsten(III) complexes obtained, therefore, resulted from reduction of tungsten(IV) by pyridine. This has been shown to be the case for the chloro compound. The chloro and bromo complexes, WCl_3py_3 and WBr_3py_3 , both of which are red, are soluble in pyridine and methylene chloride. In solution, they were quickly oxidized by air to deposit white precipitates. The magnetic and spectral properties, to be discussed shortly, are typical of a $5d^3$ ion.

The oxidation products in the reaction of WCl_4py_2 with

pyridine at 140°C were not isolated. However, it has been shown by McCarley and co-workers (222) that Niobium penta-bromide is reduced by pyridine to NbBr_4 , whereas the pyridine is oxidized to 1-(4-pyridyl)pyridinium ion.



Presumably, pyridine reacts similarly with tungsten(IV).

Isolation of the tungsten(IV) complex, WI_4py_4 , from the reaction of $\text{W(CO)}_3\text{py}_2\text{I}_2$ may appear surprising since both $\text{W(CO)}_3\text{py}_2\text{Cl}_2$ and $\text{W(CO)}_3\text{py}_2\text{Br}_2$, which are the initial products when the halocarbonyls $\text{W(CO)}_4\text{X}_2$ are treated with neat pyridine, give WCl_3py_3 and WBr_3py_3 , respectively.

The following explanation appears probable. Niobium penta-iodide reacts with hot pyridine to give NbI_4py_2 and free iodine (222). The latter is recovered as a pyridine complex. The fact that the reaction of $\text{W(CO)}_3\text{py}_2\text{I}_2$ with pyridine at 140°C gives a zerovalent complex, $\text{W(CO)}_3\text{py}_3$ indicates that disproportionation of bivalent tungsten does occur. At 140°C , tungsten(IV) might have been reduced to tungsten(III). The free iodine produced would still be present at the end of the reaction as a pyridine complex. As has already been pointed out, tungsten(III) complexes are extremely sensitive to oxidation and so, as the reaction mixture was cooled, the iodine in the solution oxidized the tungsten(III) compound.

It was not possible, therefore, to recover the desired compound, WI_3py_3 , but a compound of empirical formula WI_4py_4 . This compound has been made in three different ways, albeit accidentally.

3. Under the same conditions that molybdenum triiodide was made, the reaction of $W(CO)_6$ with iodine gave a compound which was presumably WI_4 , since the derivative WI_4py_4 could be made from it (4.40).

B.

ELECTRICAL CONDUCTIVITY

RESULTS AND DISCUSSION

The measurement of electrical conductivity is a somewhat crude, though often informative, means of establishing the ionic constitution of a compound. For a solution of molarity, M , and specific conductance, L , the molar conductivity, Λ , is given by

$$\Lambda = \frac{1000L}{M} \text{ ohm.}^{-1} \text{ cm.}^2 \quad 5-7.$$

(i) Molybdenum compounds:

The molar conductivities of some complexes of molybdenum are summarized in Table 18. In acetonitrile, $1 \times 10^{-3}M$ solutions of typical 1:1 electrolytes have molar conductivities of 120-160 $\text{ohm.}^{-1} \text{ cm.}^2$ (223). On this basis, compounds II, III and IV in Table 18 are clearly 1:1 electrolytes. These compounds were, therefore, formulated as $[Mo(phen)_2Br_2]Br$,

TABLE 18

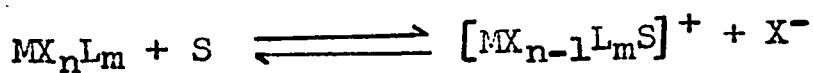
MOLAR CONDUCTIVITIES, Λ , OF SOME MOLYBDENUM COMPOUNDS AT 25°C

Compound (empirical formula)	Concentration (Moles/litre) $\times 10^4$	Solvent	Λ , ohm. ⁻¹ cm. ²
I MoBr ₃ (NCCH ₃) ₄	5.7	MeCN	40.7
II MoBr ₃ (phen) ₂	13.4 6.68	MeCN	119 127
III MoI ₃ (phen) ₂	39.4	MeCN	111
IV MoI ₃ (bipy) ₂	19.5 4.88	MeCN	122 142
V MoI ₂ (phen) ₂	11.3 5.64	MeCN	137 143
VI MoCl ₃ py ₄	7.3	py PhNo ₂	8.6 5

$[\text{Mo}(\text{phen})_2\text{I}_2]\text{I}$ and $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$, respectively.

When crystallized from acetonitrile, compound IV was solvated with one molecule of acetonitrile. Further evidence for this compound was obtained by precipitating the tetraphenylborate salt, $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{BPh}_4$, by adding acetonitrile solution of sodium tetraphenylborate to a solution of $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$ in the same solvent. The tetraphenylborate salt was not solvated.

The molar conductivity of the acetonitrile complex, $\text{MoBr}_3(\text{NCCH}_3)_4$, is too low for it to be a strong 1:1 electrolyte. The analogous chloro complex is not ionized (98a). Although the observed conductance ($40.7 \text{ ohm}^{-1} \text{ cm}^2$) (see Table 16) could arise due to hydrolysis (225), it seems likely that this is due to weak solvolysis of the molybdenum-halogen bonds. Molar conductivities of this order of magnitude have been observed when complexes of metal halides of the type MX_nL_m are dissolved in acetonitrile (103, 226). The results are interpreted as indicating weak solvolysis, viz.

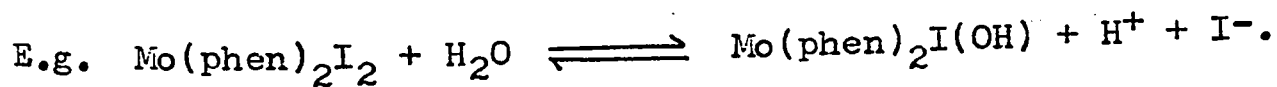


where S is the solvent. The low conductance of the acetonitrile complex shows that the compound is not a salt of the type $[\text{MoBr}_2(\text{NCCH}_3)_4]\text{Br}$ and the conductivity is to be attributed to solvolysis. The actual species present in the solution are not known but in the solid, the compound is probably best formulated as $[\text{MoBr}_3(\text{NCCH}_3)_3] \cdot \text{NCCH}_3$ for the following reasons:-

On co-ordination, the carbon-nitrogen stretching frequency of a nitrile increases over that of the free nitrile (Table 21). The increase is of the order of 20-30 cm^{-1} . In the acetonitrile compound, such an increase is observed but in addition to that, there is also a peak at 2257 cm^{-1} , 4 cm^{-1} higher than in the free acetonitrile, and is believed to be due to a nitrile which is not in the first co-ordination sphere. This peak is absent in the spectrum of $\text{MoBr}_3(\text{NCCH}_3)_3$.

The phenanthroline complex, $\text{Mo}(\text{phen})_2\text{I}_2$, is not expected to be ionized. The observed molar conductivity shows that in solution, this compound behaves as a strong 1:1 electrolyte. In this case, a high conductance could be observed for either of two reasons:-

(a) Hydrolysis: The concentrations of the solute are necessarily very low and so if there is some water in the solvent, hydrolysis of the metal-halogen bonds could occur and high conductance could be observed (225b).

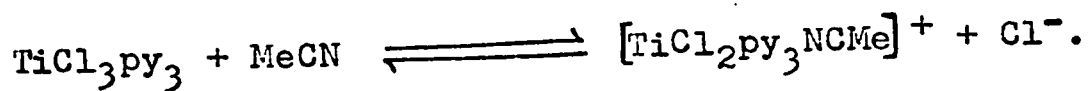


Hydrolysis should occur more readily for dilute solutions than for concentrated ones. Furthermore, it should also be significant in similar molybdenum compounds. The conductivity of $[\text{MoBr}_3(\text{NCCH}_3)_3] \text{NCCH}_3$ was measured on a more dilute solution than that used to measure the conductivity of $\text{Mo}(\text{phen})_2\text{I}_2$ and yet, in the former case, the conductivity was found to be very low. The conductivity of MoCl_3py_4 ($\Lambda = 8.6 \text{ ohm}^{-1} \text{ cm}^2$ for a $7.3 \times 10^{-4}\text{M}$ solution) was also very low. These observations

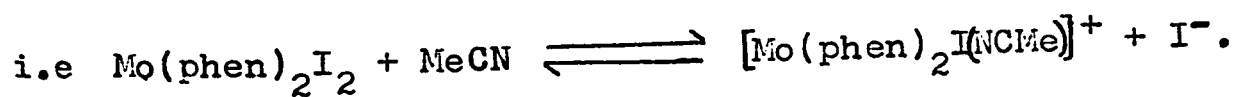
make it improbable that the conductivity of $\text{Mo(phen)}_2\text{I}_2$ was caused solely by hydrolysis.

(b) Solvolysis of molybdenum-halogen bonds by methylcyanide.

Fowles and Hoodless have observed that some complexes which are unionized in certain solvents, and are not expected to be, are typical 1:1 electrolytes in acetonitrile (226). The titanium complex, TiCl_3py_3 , was an example of such and the results were interpreted as indicating equilibria of the type



On this basis, it seems probable that the observed conductivity of $\text{Mo(phen)}_2\text{I}_2$ arises in the same way.



Trichlorotetrakis(pyridine)molybdenum(III).

This compound was largely unionized in pyridine and nitrobenzene. A $7.3 \times 10^{-4}\text{M}$ solution of this complex in pyridine had a molar conductivity of $8.6 \text{ ohm}^{-1} \text{ cm}^2$. $5 \times 10^{-4}\text{M}$ solutions of typical 1:1 electrolytes have molar conductivities of the order of $30\text{-}60 \text{ ohm}^{-1} \text{ cm}^2$ (227, 228) in this solvent.

A $5.5 \times 10^{-4}\text{M}$ solution of this complex in nitrobenzene had a molar conductivity $\approx 5 \text{ ohm}^{-1} \text{ cm}^2$. For solutions of this concentration, values in the range $20\text{-}40 \text{ ohm}^{-1} \text{ cm}^2$ are expected for 1:1 electrolytes (229). This complex was,

therefore, formulated as $[\text{MoCl}_3\text{py}_3]\text{py}$.

(ii) Tungsten compounds.

The tungsten compound with empirical formula WI_4py_4 gave an abnormally high conductivity ($\Lambda = 540 \text{ ohm}^{-1} \text{ cm}^2$ at 25°C for a $1.74 \times 10^{-4}\text{M}$ solution) in acetonitrile. The abnormally high conductivity could arise because of:-

1. Solvolysis of the tungsten-iodine bonds by acetonitrile.
2. Hydrolysis of the tungsten(IV) compound, and
3. Oxidation of the tungsten(IV) compound by atmospheric oxygen (which was impossible to exclude completely) followed by solvolysis or hydrolysis of the resulting product.

In contrast to this, the carbonyl compound, $\text{W}(\text{CO})_3\text{py}_2\text{I}_2$, was a non-conductor in acetonitrile. For example, a $5.9 \times 10^{-3}\text{M}$ solution had a molar conductivity of $4.2 \text{ ohm}^{-1} \text{ cm}^2$ at 25°C .

C.

ELECTRONIC SPECTRA

RESULTS AND DISCUSSION

(a) General: Electronic spectra of complexes of the type MoX_3L_3 or WX_3L_3 can be conveniently considered by comparing the spectra of the hexahaloanions MoX_6^{3-} or WX_6^{3-} . Unfortunately, no such anions are known for tungsten except WF_6^{3-} for which no spectral data are available (118). The spectra of

molybdenum and tungsten complexes of the type MX_3L_3 are, however, expected to be very similar since molybdenum(III) and tungsten(III) are both d^3 ions. Bands in electronic spectra of these complexes are expected to show structure because of low symmetry or the combined effect of low symmetry and spin-orbit coupling. This is well illustrated by the electronic spectra of such complexes which will be discussed below.

The intensities of spin-allowed bands and charge transfer bands are several orders of magnitude larger than intensities of spin-forbidden bands. Consequently, solutions of the order of 10^{-2} - 10^{-3}M were necessary in order to see the weak bands due to spin-forbidden transitions. For such concentrated solutions, bands due to spin-allowed transitions were off the scale. It was not possible, therefore, to record a spectrum that would show both spin-allowed and spin-forbidden bands using a solution of the same concentration. For the chloro complexes, $\text{MoCl}_3(\text{NCR})_3$, it was not possible to see any bands of lower energy than 13000 cm^{-1} because of the low solubility of the compounds. In the tetrahydrofuran (THF) and tetrahydrothiophene complexes, $\text{MoCl}_3(\text{THF})_3$ and $\text{MoCl}_3(\text{THT})_3$, respectively, the bands were observed at lower energies but in these cases they did not show structure. The possible reasons for these observations will be discussed later.

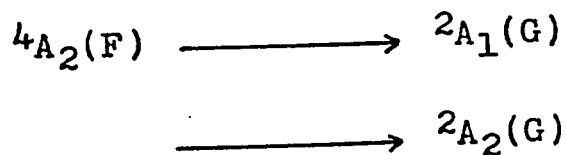
The chromophores in the complexes $[\text{Mo}(\text{phen})_2\text{Br}_2]\text{Br}$ and $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$ are the cations $[\text{Mo}(\text{phen})_2\text{Br}_2]^+$ and $[\text{Mo}(\text{bipy})_2\text{I}_2]^+$, respectively. These cations may have trans (D_{4h}) or cis (C_{2v}) symmetries. Since spin orbit coupling in

D_{4h} transforms as the irreducible representation, $\Gamma_g = (A_{2g} + E_g)$, arguments similar to those in Chapter 2, page 42, show that E-terms are split by spin orbit coupling in D_{4h} . Hence, whichever structure the complexes $Mo(phen)_2Br_2^+$ and $Mo(bipy)_2I_2^+$ may have, their electronic spectra are expected to qualitatively resemble those of complexes of the type MoX_3L_3 . The resolution of bands in spectra of the phenanthroline and bipyridyl complexes was, however, very poor.

(b) Bands and their assignments.

(i) The assignments: In order to avoid unnecessary repetitions in discussion of the electronic spectra, the band absorption maxima are summarized in Table 19. The table is divided into six columns, I-VI, each of which contains bands assigned to a particular transition. The entries in the columns are as follows:-

Column I: contains bands arising from the transitions



In many complexes, the two bands are not resolved. Whether the bands are resolved or not, the two transitions will be loosely referred to as the ${}^2E(G)$ -band manifold since, in an octahedral complex, the band would appear as one arising from the transition

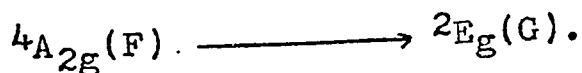


TABLE 19

ABSORPTION BANDS IN SOME MOLYBDENUM(III) AND
TUNGSTEN(III) COMPLEXES IN SOLUTION.

Compound	Band energy $\text{cm.}^{-1} \times 10^{-3}$					VI
	$\frac{2E(G)}{I}$	$\frac{2T_1(G)}{II}$	$\frac{2T_2(G)}{III}$	$\frac{4T_2(G)}{IV}$	$\frac{4T_1(G)}{V}$	
I $\text{MoCl}_3(\text{NCCH}_2\text{Ph})_3$			13.5, 14.3, 15.9		27.5	
II $\text{MoCl}_3(\text{NCCH}_2\text{CH}_3)_3$			14	22 sh.	27.5	
III $\text{MoCl}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$			13.2, 14.1, 15.9	22 sh.	27	
IV $\text{MoCl}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$			14.3	19.3 (?)	27.3	
V $\text{MoBr}_3(\text{NCCH}_2\text{Ph})_3$	6.8 b	8.0, 8.5 9.0	12.8, 13.7, 16.9	20.8 sh.		28
VI $\text{MoBr}_3[\text{NCCH}_2\text{CH}_3]_3$	7.0 br	8.0, 8.5 9.0	12.8, 13.8, 15	20.8 sh.	24, 26.5 sh.	
VII $\text{MoBr}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$	6.8 br	8.0, 8.5 9.0	12.8, 13.4, 15	20.8 sh.	24.1	28.2 sh.
VIII $\text{MoBr}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$	6.8	8.0, 8.5 9.0	14, 15.4	20.8		

TABLE 19 cont.

Compound	Band energy $\text{cm.}^{-1} \times 10^{-3}$				
	$\frac{2T_1(G)}{I}$	$\frac{2T_2(G)}{II}$	$\frac{2T_2(G)}{III}$	$\frac{4T_2(G)}{IV}$	$\frac{4T_1(G)}{V}$
IX $\text{MoCl}_3(\text{C}_4\text{H}_8\text{O})_3$	5.8	9.9	12.8 (?), 14.8	19.4	24.45, 28.2, 30.4
X $\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3^*$	5.7, 5.9	8.5, 12.2	14.1, 15.4, 17.2	21.3	30.0
XI $\text{MoBr}_3(\text{C}_4\text{H}_8\text{O})_3$	5.8	9.5	12.9, 15.8	19.2	23.8, 31.4
XII $\text{MoBr}_3(\text{C}_4\text{H}_8\text{S})_3$	5.8, 5.9	8.4, 9.9	14	21	26.3, 30.1
XIII $[\text{Mo}(\text{phen})_2\text{Br}_2]^{**}$	5.3 ?		14 (?)		21.7 ? 23.6, 26.3
XIV $[\text{Mo}(\text{bipy})_2\text{I}_2]^{**}$		7.0, 8.3	12 (?)		22, 25
XV WCl_3py_3	5.2, 5.4	7.1, 7.8, 8.0	12.6, 13.5		22.0 30.8 ? 33.4
XVI WBr_3py_3	5.8, 6.0	7.1, 7.7, 8.1	12.4, 13.3, 14.7		22.6 24.7 ? 33.3

* in CH_2Cl_2

** in acetonitrile

br = broad

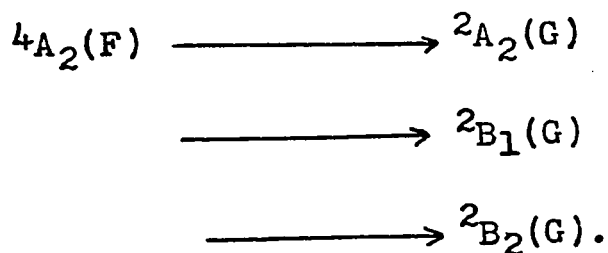
(?) = uncertain assignment

sh. = shoulder

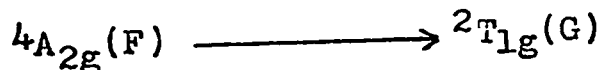
1 180 1

As will be recalled from the discussion in Chapter 2, the energies of the ${}^2E_g(G)$ - and ${}^2T_{1g}(G)$ -terms in an octahedral environment are accidentally degenerate. This degeneracy is lifted in environments of symmetries lower than O_h and consequently, the E-band must be discussed separately.

Column II: contains bands arising from the transitions

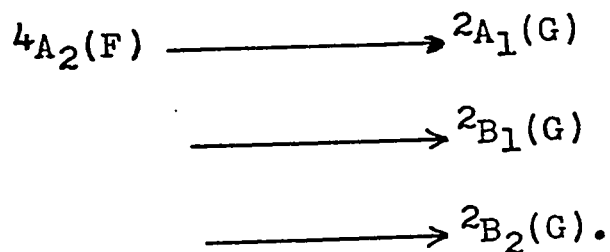


The three bands, which correspond to the transition



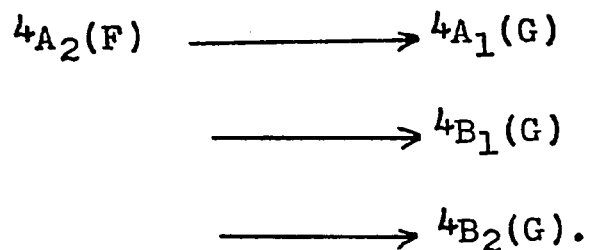
in octahedral complex, will be referred to loosely as the ${}^2T_1(G)$ -band manifold.

Column III: contains bands arising from the transitions

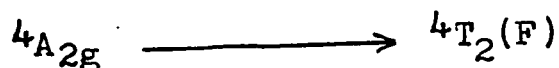


These transitions will be referred to loosely as the ${}^2T_2(G)$ -band manifold for similar reasons to those discussed above.

Column IV: contains bands arising from the transitions

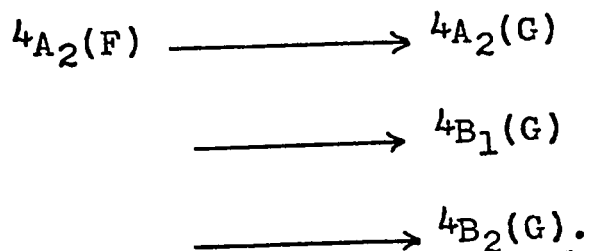


The corresponding band in octahedral complexes,



is the lowest energy spin-allowed band and 10Dq values cited later are obtained from the energy of absorption of this band. We refer in this case to the 4T_2 manifold.

Column V: contains bands assigned to the transitions



These transitions give the ${}^4A_{2g}(F) \longrightarrow {}^4T_{1g}(F)$ band in octahedral complexes and, therefore, constitute the ${}^4T_1(F)$ manifold.

Column VI: contains other band energies. A (?) signifies a band of uncertain origin.

(c) Basis for band assignments:

1. The ${}^2E(G)$ - and ${}^2T_1(G)$ -bands: The nitrile complexes

of the type $\text{MoBr}_3(\text{NCR})_3$ exhibit a band centered around 7000 cm.^{-1} which does not show structure and another one centered around $8000\text{--}8500 \text{ cm.}^{-1}$ which shows structure (Figs 21-23). Although the resolution of the lower energy band is not good, in the tungsten(III) complexes, WCl_3py_3 (Fig. 24) and WBr_3py_3 (Fig. 25), this band shows two components whereas the higher energy band shows three. The higher energy band, therefore, is not an E-band since according to the theory outlined in Chapter 2, an E-band can show a maximum of two components.

2. $^2T_2(\text{G})$ -band: Since this band is around $15,000 \text{ cm.}^{-1}$ (128) in the spectrum of MoCl_6^{-3} and band splitting normally separates components such that some have lower energy whereas the others have higher energy relative to the parent band (231), it seems reasonable to assign the band around $15,000 \text{ cm.}^{-1}$ to the $^2T_2(\text{G})$ -band manifold.

3. $^4T_2(\text{G})$ -band: The band at $19,000\text{--}22,000 \text{ cm.}^{-1}$ in molybdenum(III) complexes with nitriles, tetrahydrofuran and tetrahydrothiophene is assigned to the first spin-allowed transition because it is the lowest energy band with intensity in the range expected for spin-allowed d-d transitions. Furthermore, $10Dq$ values for molybdenum(III) complexes are expected to be about $20,000 \text{ cm.}^{-1}$ (127). The rule of average environment (232) was used as a further test for the correctness of this assignment. The rule states that if $\sigma(\text{MA}_6)$ and $\sigma(\text{MB}_6)$ are the wavenumbers of an absorption band in the octahedral complexes, MA_6 and MB_6 , respectively, then the wavenumber for

the corresponding band for the partially substituted complex, $(MA_{6-n}B_n)$, is given by

$$\sigma(MA_{6-n}B_n) = \frac{n}{6}\sigma(MA_6) + \frac{6-n}{6}\sigma(MB_6) \quad 5-8.$$

Literature values of $10Dq$ for $MoBr_6^{3-}$ (96) and $MoCl_6^{3-}$ (230a) were used and the bands at $19,000 \text{ cm.}^{-1}$ and $21,000 \text{ cm.}^{-1}$ in the spectra of $MoCl_3(C_4H_8O)_3$ and $MoCl_3(C_4H_8S)_3$ respectively, assumed to be due to the first spin-allowed transitions. The $10Dq$ values of the unknown cations $Mo(C_4H_8O)_6^{3+}$ and $Mo(C_4H_8S)_6^{3+}$ were thus estimated to be $19,650$ and $23,450 \text{ cm.}^{-1}$, respectively. Using these values and the $10Dq$ value of $18,300 \text{ cm.}^{-1}$ for $MoBr_6^{3-}$, the positions of the first spin-allowed bands in the bromo complexes, $MoBr_3(C_4H_8O)_3$ and $MoBr_3(C_4H_8S)_3$, are as indicated below:-

	<u>Band energy (cm.⁻¹)</u>	
	<u>Calculated</u>	<u>Observed</u>
$MoBr_3(SC_4H_8)_3$	20,900	21,000
$MoBr_3(OC_4H_8)_3$	19,000	19,200

4. $4T_1(G)$ -band: The assignments of some components to the $4A_2(F) \longrightarrow 4T_1(G)$ band are not certain for many complexes. Those given in Table 17 are suggested since they appear most reasonable. It should be noted here that some bands around $27,000 \text{ cm.}^{-1}$ in nitrile complexes of the type

$\text{MoCl}_3(\text{NCR})_3$ have been attributed by other workers to the first spin-allowed transitions (98b).

5. Charge transfer bands:

To a first approximation, the energy of a charge transfer band, ΔU , is given by

$$\Delta U = -\Delta I + I_L + \Delta A \quad 5-9$$

where ΔI is the difference between the n th and $(n-1)$ th ionization potentials of the central ion; I_L is the ionization potential of the ligand and ΔA is the difference between the electrostatic heats of formation of the complex in the ground state (charge n) and in the excited state (charge $(n-1)$ (233). For anionic ligands such as Cl^- , I_L is replaced by the electron affinity of the ligand (234-236). The quantity, ΔA is, unfortunately, difficult to calculate even for simple compounds such as the alkali metal halides. Bands of the charge transfer type may, however, still be deduced from intensities since the latter are much higher than intensities of the bands resulting from $d-d$ transitions. On this basis, bands around $30,000 \text{ cm}^{-1}$ in molybdenum(III) complexes appear to be of the charge transfer type. Not many complexes were examined in this region.

The bands at $22,600$ and $22,000 \text{ cm}^{-1}$ in the tungsten

complexes WBr_3py_3 and WCl_3py_3 , respectively, are probably of the charge transfer type since the extinction coefficients are of the order of 3,000. It is unlikely that these bands are due to spin-allowed d-d transitions since the band in chloro complex has a somewhat lower energy than the corresponding band in the bromide (Table 19) which would conflict with the spectrochemical series. Moreover, the first spin-allowed band in the molybdenum complex, MoCl_3py_3 , occurs at energy

$> 25,000 \text{ cm}^{-1}$ (96, 96a)* and it is not likely that the band would occur at lower energy in the analogous tungsten(III) complex, WCl_3py_3 . Since the difference between the third and fourth ionization potentials of tungsten is 11.3 eV (237) whereas the ionization potential of pyridine is 9.3 eV (199), presumably the bands arise from electron transfer from pyridine to the tungsten d-orbitals.

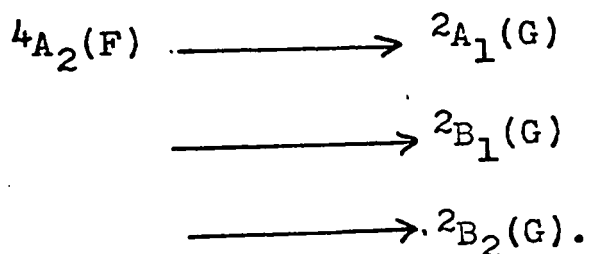
The bands around $22,000 \text{ cm}^{-1}$ in the electronic spectra of $\text{Mo(phen)}_2\text{Br}_3$ and $\text{Mo(bipy)}_2\text{I}_3$ have extinction coefficients of about 1300 and 2600, respectively. While these bands may be of the charge transfer type, the assignment is less certain

* 96a H. L. Schlafer and E. Konig; Z. phys. Chem. (Frankfurt) 30, 145 (1961); E. Konig and H. L. Schlafer ibid. 26, 371 (1960).

since spin-allowed d-d bands may have extinction coefficient of about 1,000 due to intensity stealing (Table 6).

(d) Splitting of bands:

1. Spin-forbidden bands: The bands that do not show structure in octahedral complexes show structure when the symmetry is lowered (see Figs. 21-25). The reasons for this band splitting have already been given in Chapter 2 and will not be repeated. The only point that should be noted is that it is not possible to tell, without some elaborate calculations (231), which of the three components in the ${}^2T_2(G)$ band, for example, arise from one of the transitions



2. Bands due to spin-allowed transitions.

According to the theory (Chapter 2), spin-allowed bands in complexes of the type MoX_3L_3 or WX_3py_3 should show structure. In practice, however, such bands, when they could be observed were either just shoulders or broad bands whose wavelength positions were difficult to determine accurately (Fig. 26). Tetrahydrofuran and tetrahydrothiophene complexes gave fairly sharp spin-allowed bands but there was little evidence of band

FIGURE 21

Spin-forbidden absorption bands in nitrile complexes of Mo(III). Parent nitrile was used as solvent.

- (a) $\text{MoBr}_3(\text{NCCH}_3)_3$, 0.059M.
- (b) $\text{MoBr}_3(\text{NCCH}_2\text{Ph})_3$, 0.080M.

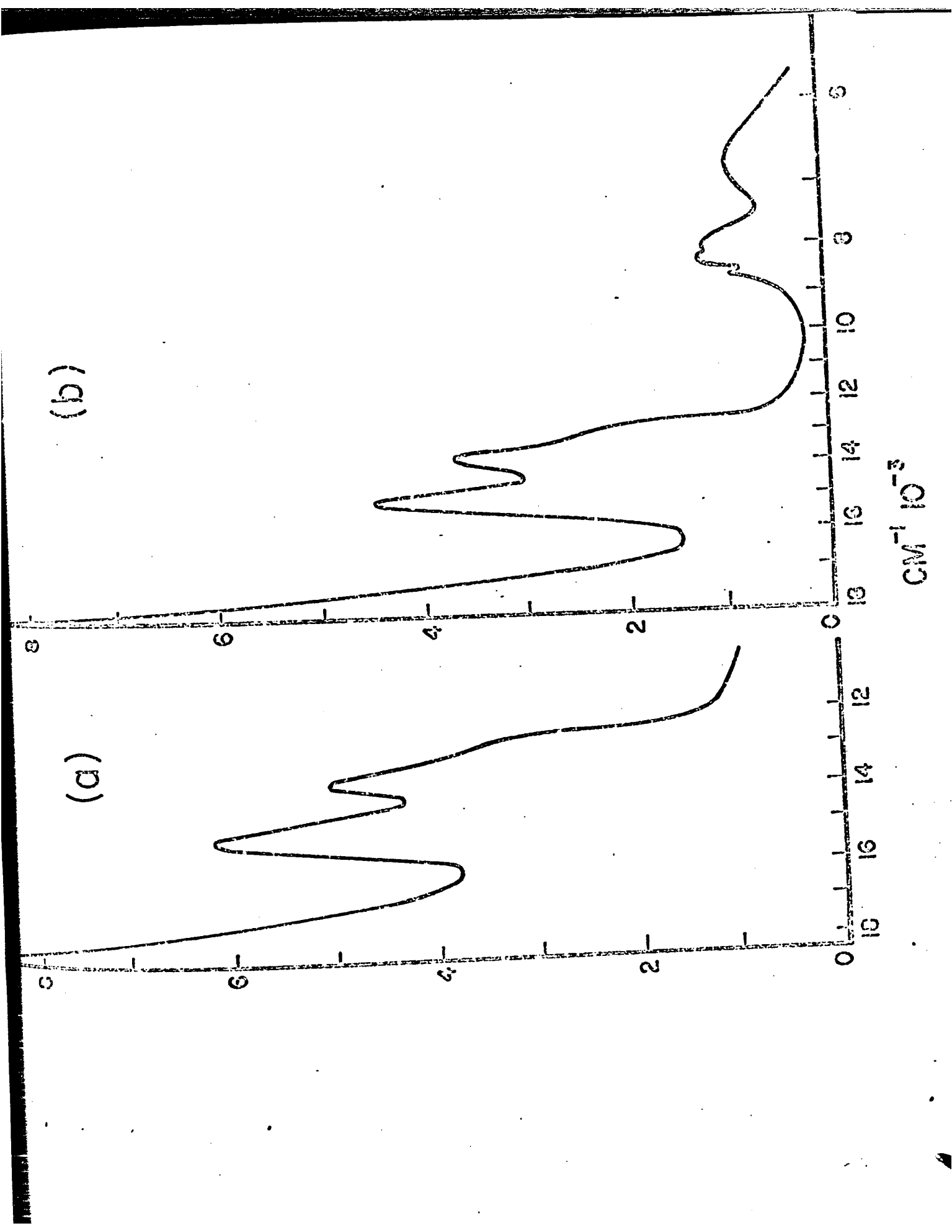


FIGURE 22

Spin-forbidden absorption bands in the valeronitrile complex $\text{MoBr}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$.

Solvent = valeronitrile

Conc. = 0.108M

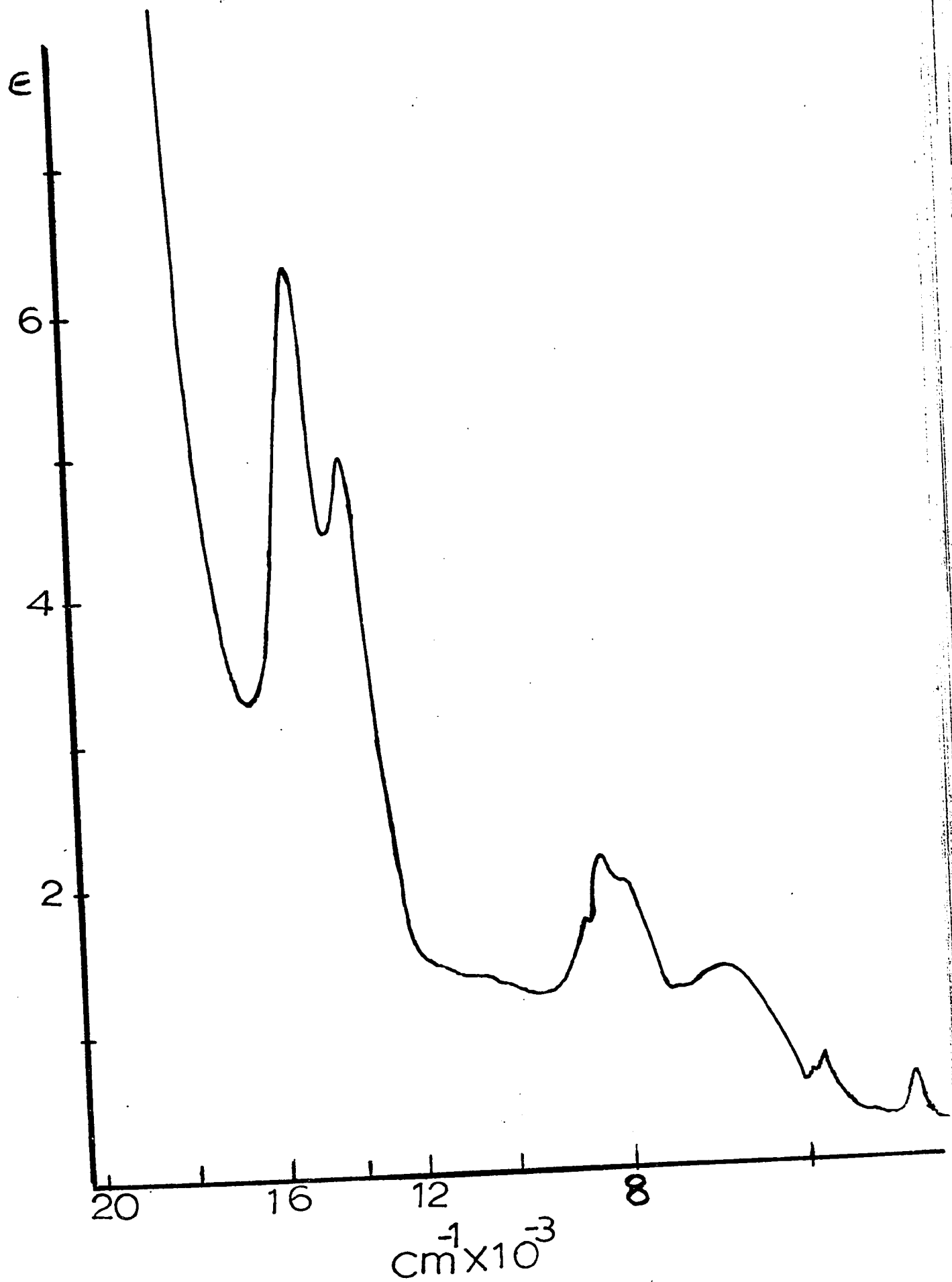


FIGURE 23

Spin-forbidden absorption bands in the butyronitrile complex, $\text{MoBr}_3(\text{NCCH}_2\text{CH}_2\text{CH}_3)_3$.

Solvent = butyronitrile

Conc. = 0.0754M.

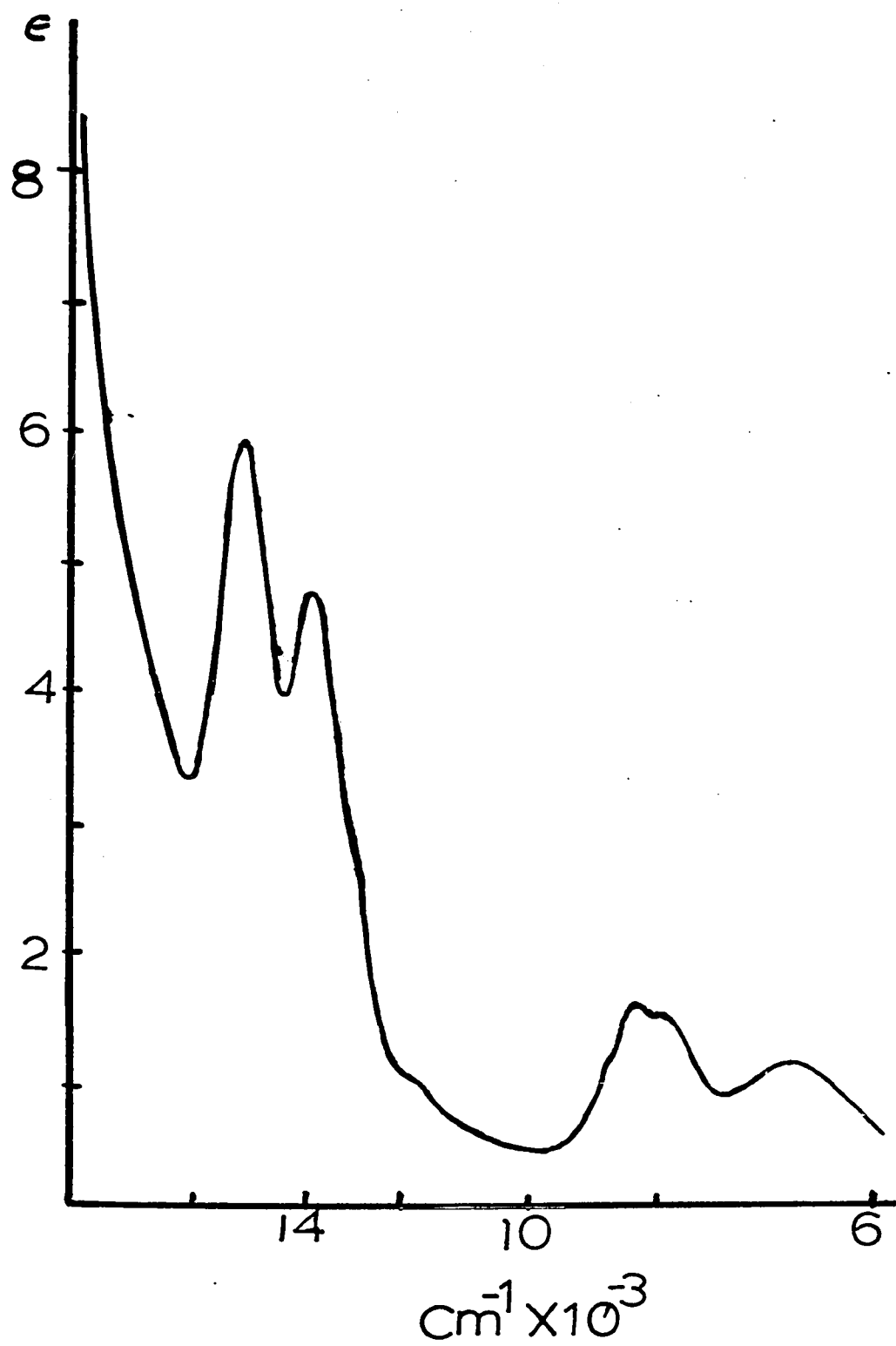


FIGURE 24

Spin-forbidden absorption bands in the electronic spectrum of the tungsten(III) complex, WCl_3py_3 .

Solvent = pyridine

Conc. = 0.0795M.

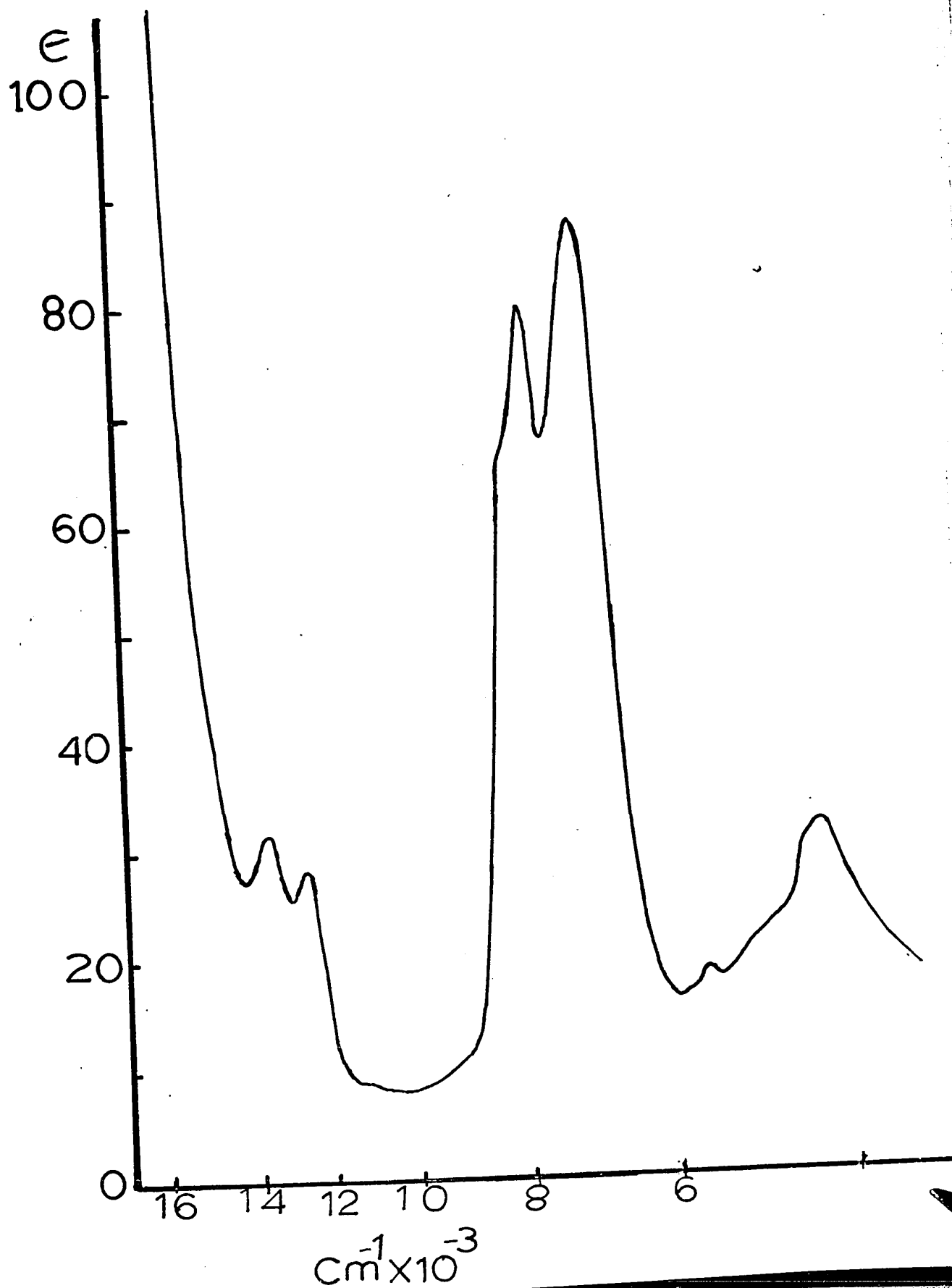


FIGURE 25

Spin-forbidden absorption bands in the electronic spectrum of WBr_3py_3 .

Solvent = pyridine

Conc. = 0.0106M.

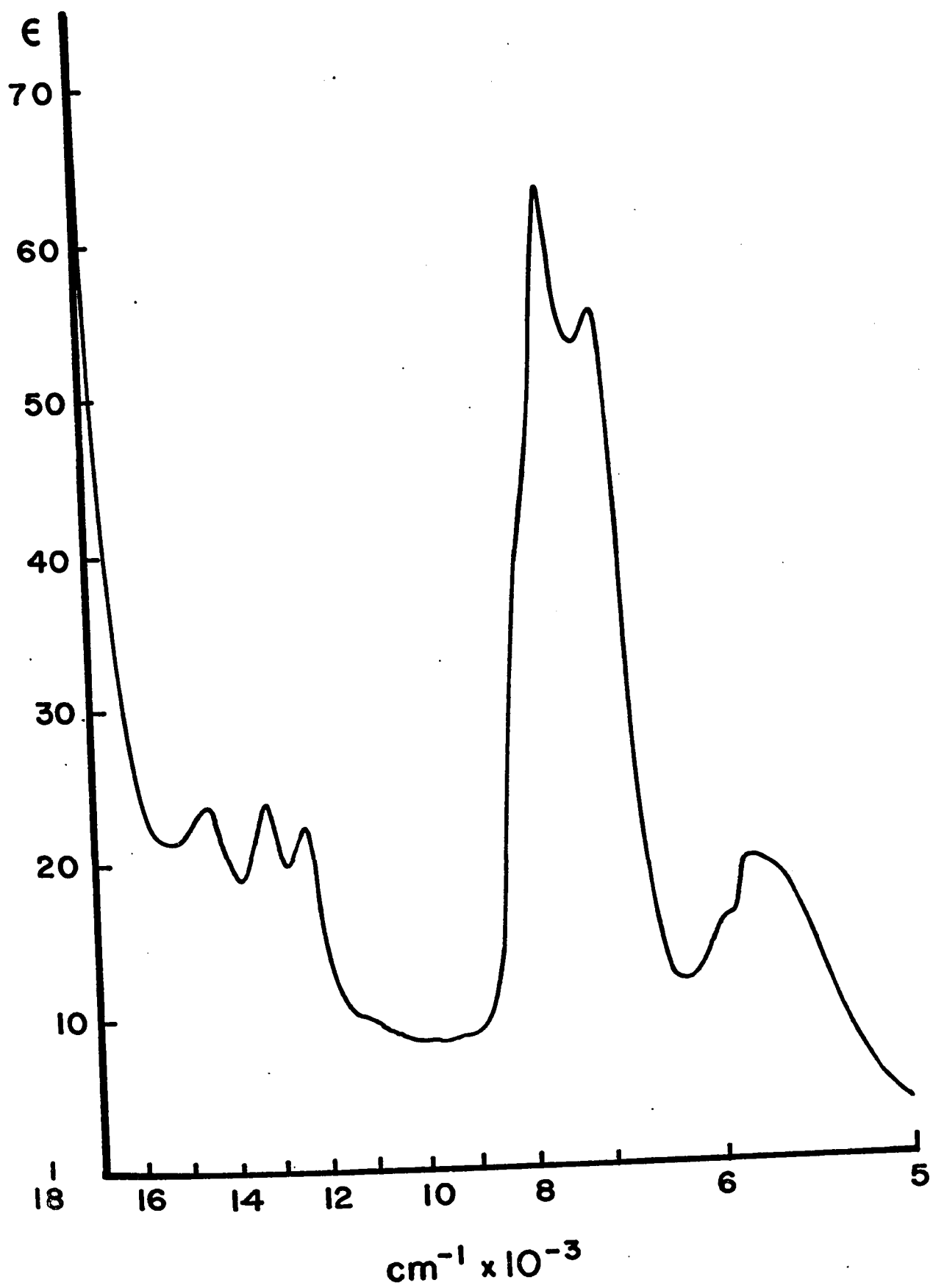


FIGURE 26

Some spin-allowed absorption bands in the spectrum
of the molybdenum(III) complex, $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$.

Solvent = propionitrile

Conc. = 0.00802M

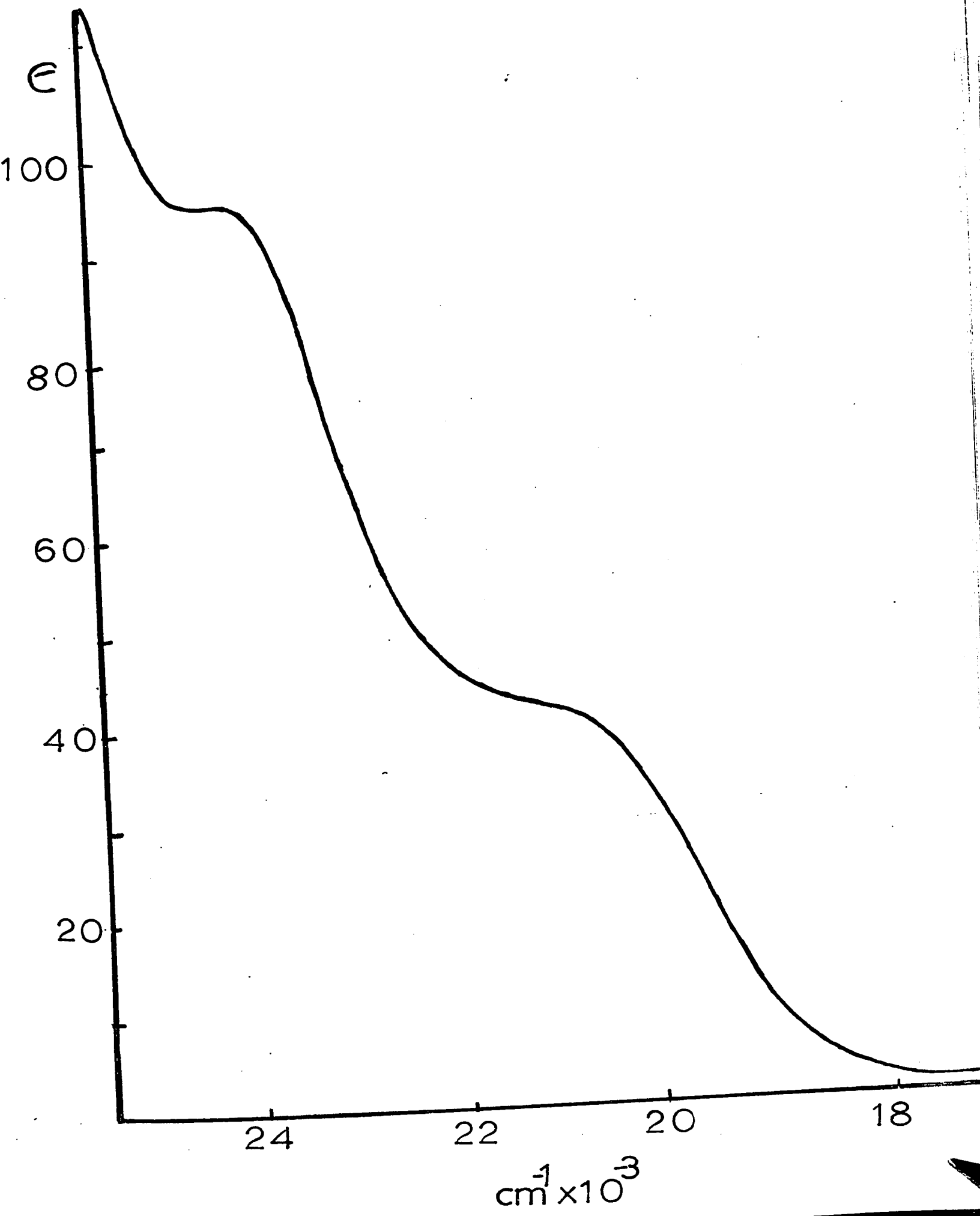


FIGURE 27

Part of the absorption electronic spectrum of
the tetrahydrothiophene complex, $\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3$.

Solvent = methylene dichloride

Conc. = 0.00344M.

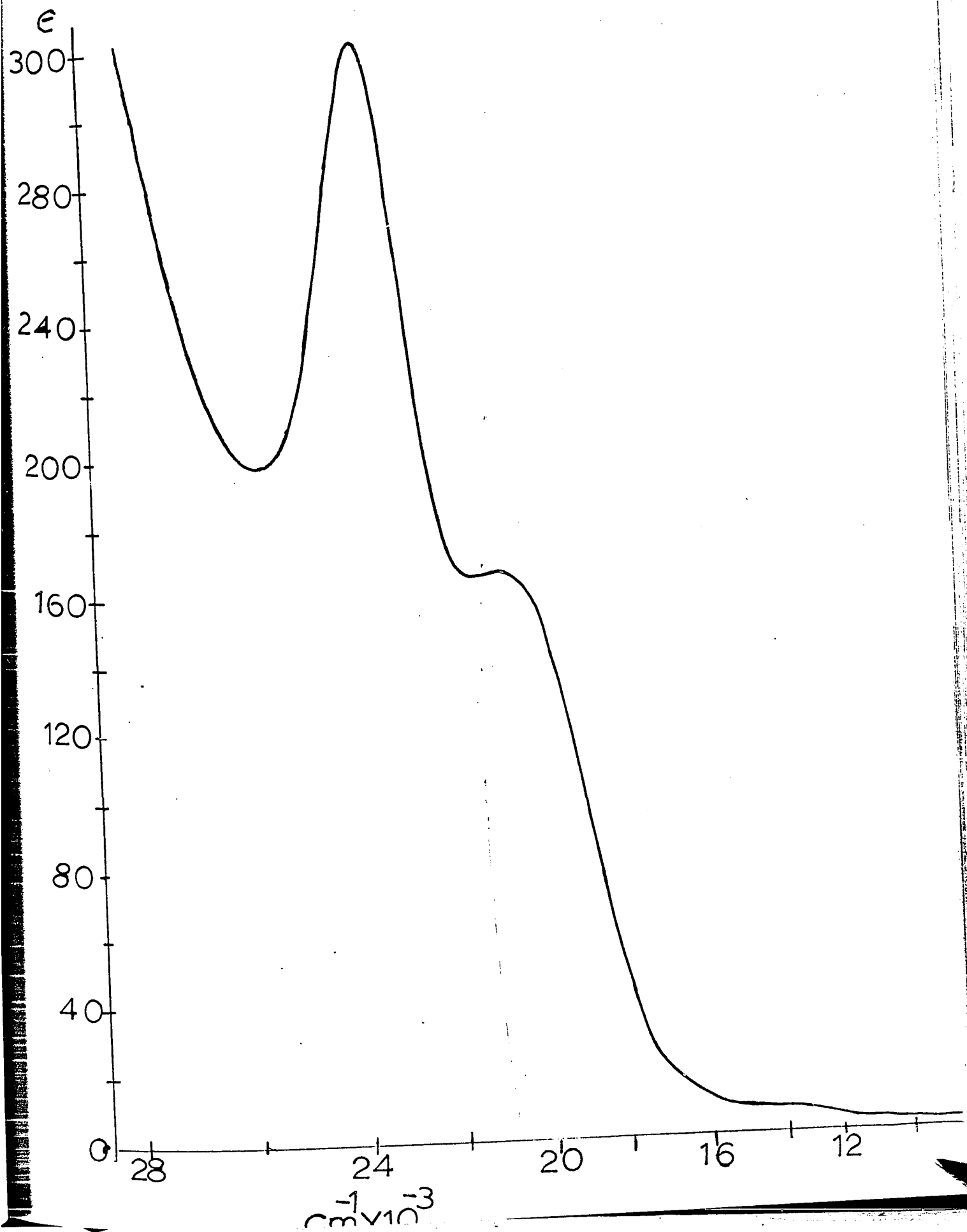


FIGURE 28

Part of the electronic spectrum of WBr_3py_3 .

Solvent = pyridine

Conc. = 0.000106M.

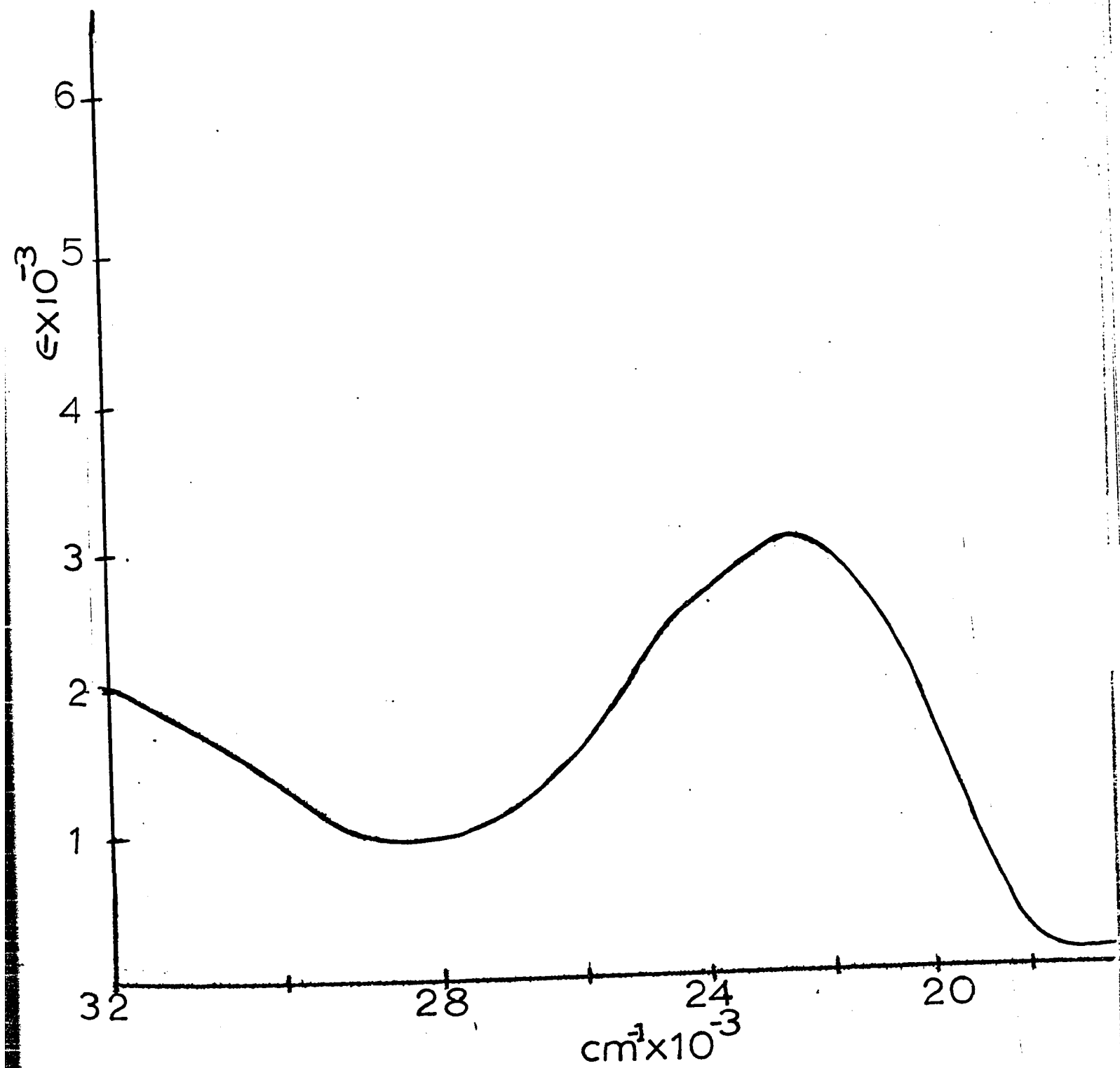


FIGURE 29

Part of the electronic spectrum of $[\text{Mo}(\text{phen})_2\text{Br}_2]\text{Br}$

Solvent = acetonitrile

Conc. = 0.000372M.

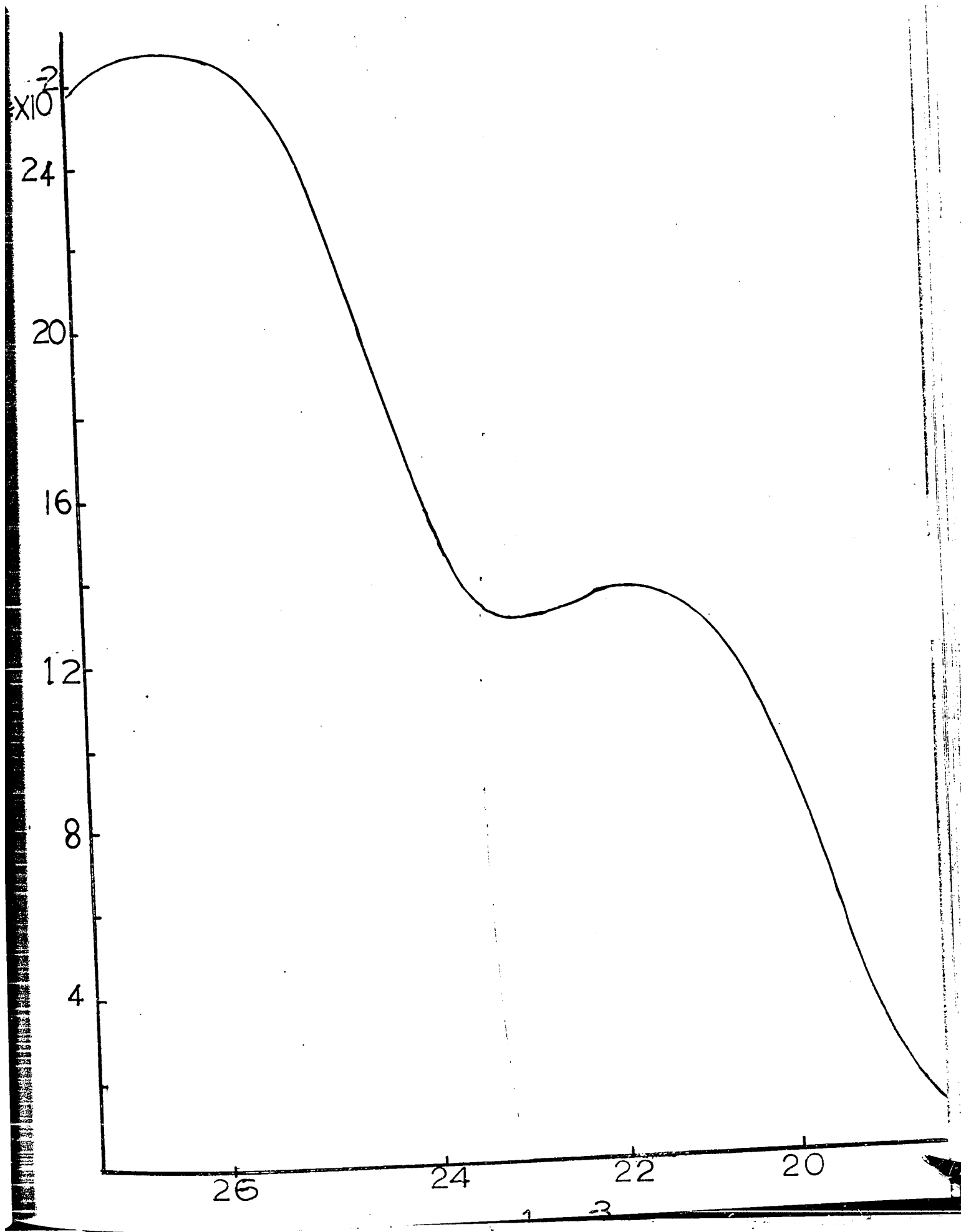


FIGURE 30

Part of the electronic spectrum of $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$.

Solvent = acetonitrile

Conc. = 0.000123M.

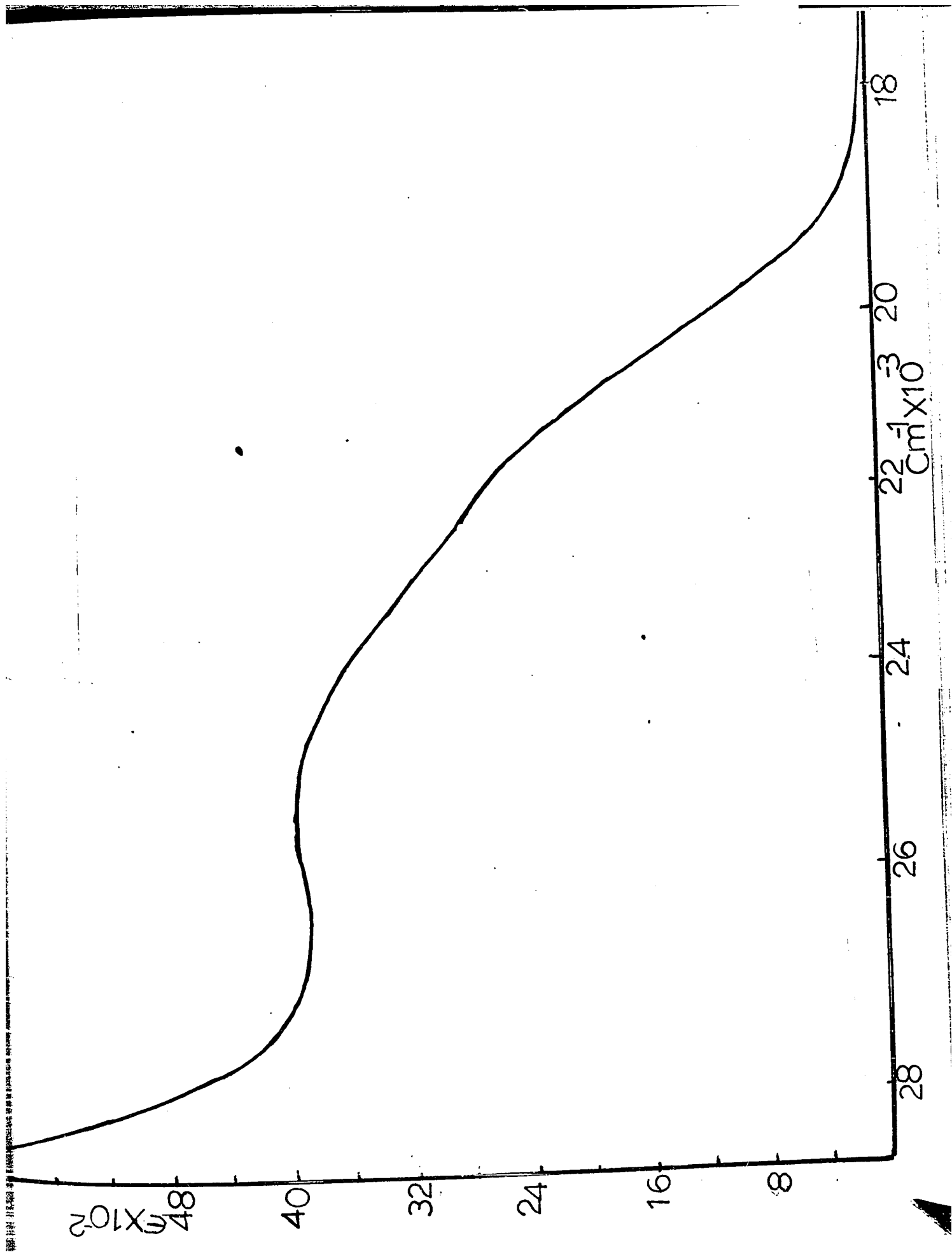


FIGURE 31

Spin-forbidden bands in the absorption spectra
of molybdenum complexes (a) $[\text{Mo}(\text{phen})_2\text{Br}_2] \text{Br}$

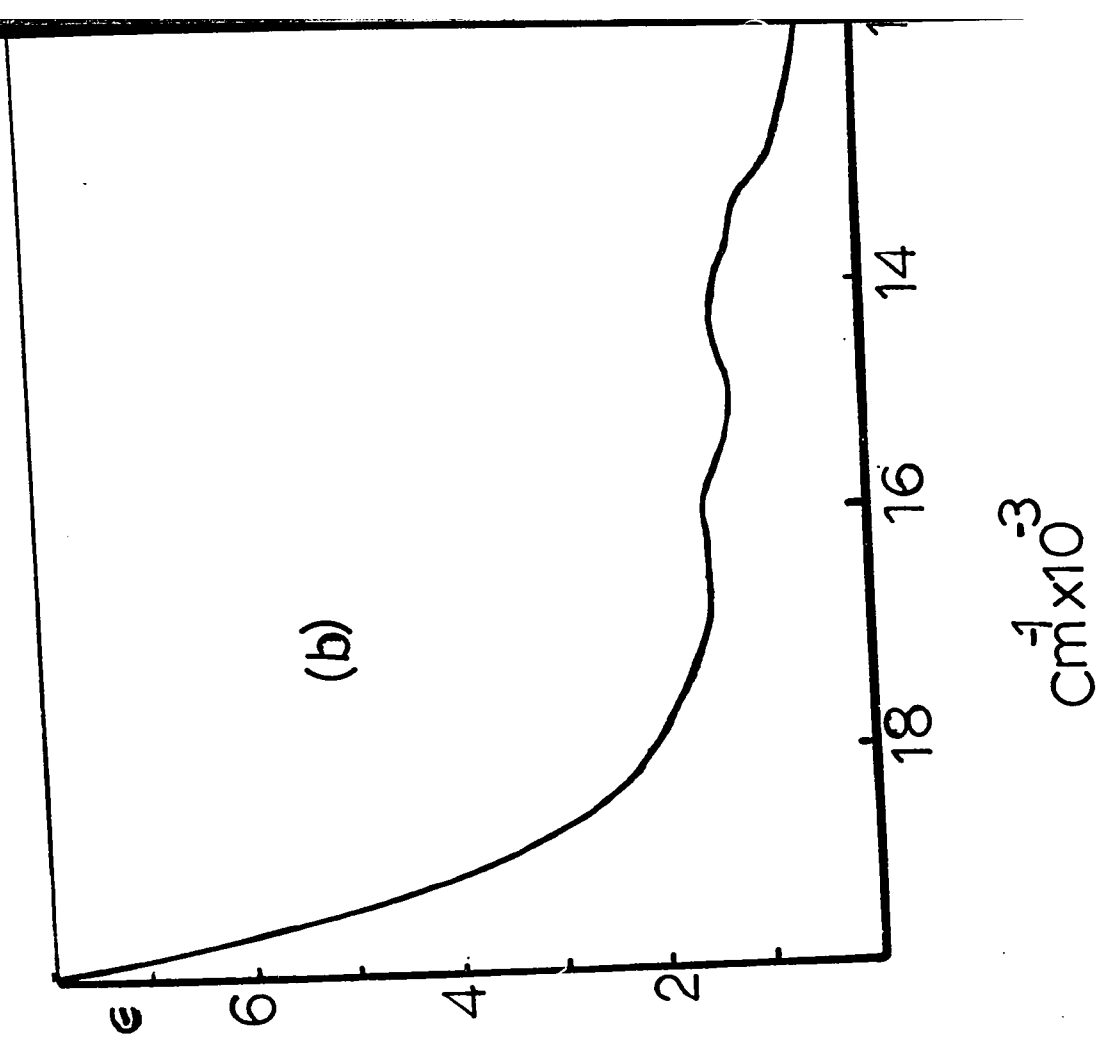
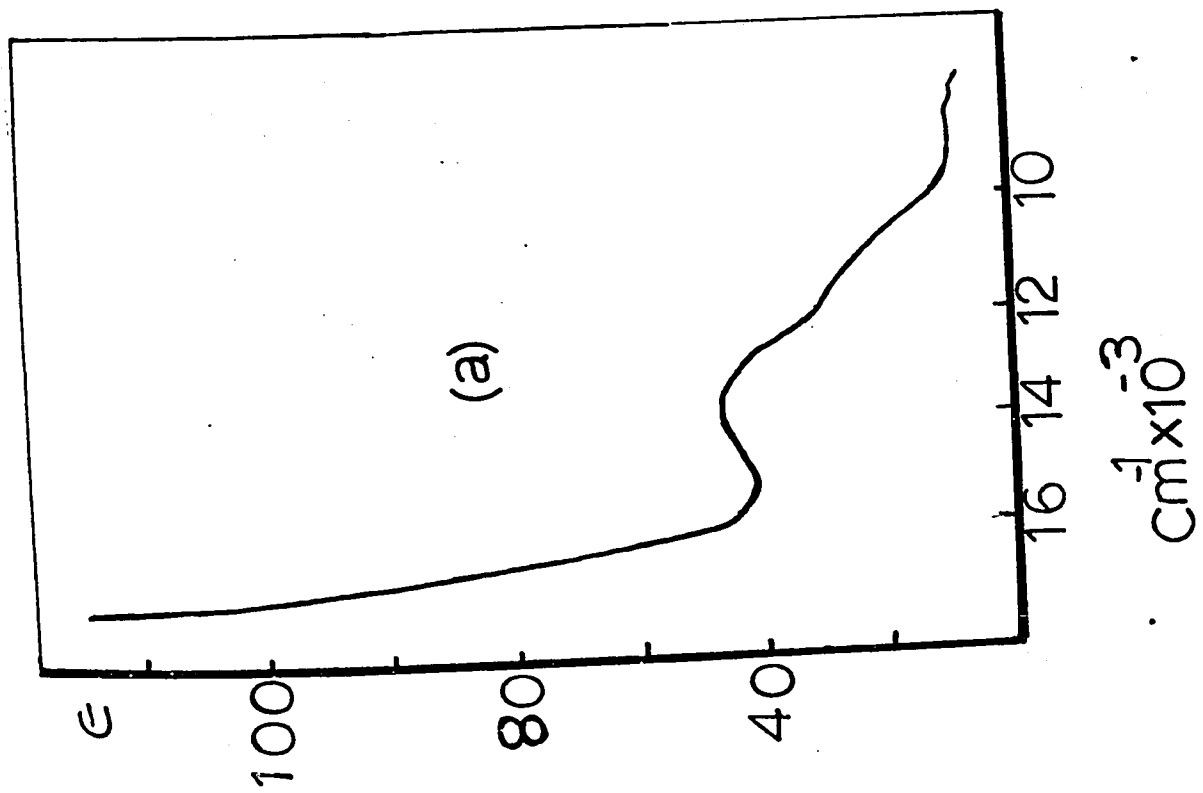
Solvent = acetonitrile

Conc. = 0.00289M

(b) $\text{MoCl}_3(\text{NCCH}_2\text{CH}_2\text{CH}_3)_3$

Solvent = butyronitrile

Conc. = 0.0471M



splittings (Figure 27). The reasons for this can be seen by considering the Tanabe-Sugano diagram for a d^3 ion given in Fig. 2.

An absorption band is expected to be sharper the less sensitive the transition energy, E , is to changes in the ligand field strength.

i.e. if $\frac{\partial E}{\partial Dq}$ is small (239).

It is clear from Fig. 2 that the energies of the $^2E(G)$, $^2T_1(G)$ and $^2T_2(G)$ -terms vary only slightly with ligand field strength. On the other hand, the energies of the $^4T_2(F)$ and $^4T_1(F)$ terms vary considerably with ligand field strength. It, therefore, follows that the multiplets of the spin-allowed bands will not be observed unless the resolution is very high. On the other hand, the spin-forbidden bands are expected to show structure as is actually observed experimentally.

(e) Intensities of spin-forbidden bands.

The intensity of spin-forbidden bands of molybdenum(III) and tungsten(III) complexes of the type MX_3L_3 is about one to two orders of magnitude greater than expected (Table 6). This is primarily due to spin-orbit coupling (Equation 2-2) and this is shown by the fact that the bands in tungsten(III) complexes are much more intense than those in the molybdenum(III) complexes. This is reasonable since tungsten(III) is expected to have a larger spin-orbit coupling than molybdenum(III) (127).

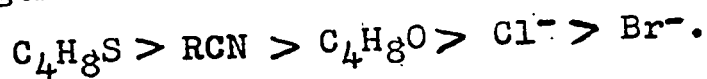
A notable feature of the spin-forbidden bands is that in molybdenum(III) complexes, the intensity of the band centered around $15,000 \text{ cm}^{-1}$ ($^2T_2(\text{G})$ -band) is greater than that of the band centered around $7,000 \text{ cm}^{-1}$ ($^2T_1(\text{G})$ -band) (Figs. 21-23). In the tungsten(III) complexes, the $^2T_1(\text{G})$ -band is more intense than the $^2T_2(\text{G})$ -band (Figs. 24, 25). The reason for this is not clear.

(f) Accuracy of band energies: We may note the following:-

- (i) Sharp components are accurate to $\pm 100 \text{ cm}^{-1}$.
- (ii) Broad components, particularly those of energies higher than $18,000 \text{ cm}^{-1}$, are probably precise to $\pm 200 \text{ cm}^{-1}$.
- (iii) Components occurring as shoulders are less accurately determined; they may be in error by as much as $\pm 300 \text{ cm}^{-1}$.

(g) Order of ligand field strengths of $\text{C}_4\text{H}_8\text{S}$, $\text{C}_4\text{H}_8\text{O}$, RCN , Cl^- and Br^- .

The use of the experimental data in conjunction with published work indicates the following order of decreasing ligand field strengths:



For nitriles, tetrahydrofuran, chloride and bromide, similar conclusions have been drawn by other workers (240, 241).

D.

MAGNETIC MEASUREMENTS

RESULTS AND DISCUSSION

The magnetic moments of some molybdenum and tungsten compounds are summarized in Table 20. As noted in Chapter 3, the measurements were made at four different magnetic field strengths in order to detect and make correction for impurities. With the exception of the molybdenum complex, $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$, susceptibilities were independent of field strengths, within experimental error.

1. Molybdenum complexes.

(a) Complexes of molybdenum(III): The magnetic moments of the trivalent molybdenum complexes vary between 3.5 and 3.9 B.M. These values fall in the expected range for compounds containing three unpaired electrons per molybdenum ion. This provided a further confirmation, in addition to elemental analysis, that the halocarbonyl compounds, $\text{Mo}(\text{CO})_4\text{Cl}_2$ and $\text{Mo}(\text{CO})_4\text{Br}_2$, react with neat electron donors, L, to give complexes of trivalent molybdenum.

Magnetic moments of such molybdenum(III) complexes are expected to remain nearly constant as the temperature varies (242). This was verified, by studies over a wide temperature range, for acetonitrile, benzonitrile and pyridine complexes. The results for the last two are summarized in Table 21.

(i) Octahedral and quasi-octahedral complexes. From the

work of Runciman and Schroeder, the spin-orbit coupling, λ , for Mo^{3+} is 183 cm.^{-1} (128). The $10Dq$ values of molybdenum(III) are expected to be of the order of $20,000 \text{ cm.}^{-1}$ (127). From equation 2-13, octahedral complexes of molybdenum(III) are, therefore, expected to exhibit magnetic moments of about 3.7 B.M.

Many complexes of molybdenum(III) have magnetic moments of about this value and may, therefore, be treated as octahedral or quasi-octahedral.

(ii) Distortion effects:

Complexes with mixed ligands, e.g. trivalent molybdenum compounds of the type MoX_3L_3 , will have distorted octahedral fields. The degree of distortion will depend upon the difference in ligand field strength of the two types of ligands. On this basis, bromo complexes of the type $\text{MoBr}_3(\text{NCR})_3$ should have more distorted fields than the corresponding chloro complexes. Most of the bromo complexes have magnetic moments close to the spin-only value and this is in accord with the theory which states that the spin-only value is approached more closely as distortion is increased (167).

(iii) High and low magnetic moments that may arise from dilution effects.

The magnetic moments of most of the compounds listed in Table 18 can be accounted for by considering the effects of distortion. It is clear, however, that the low magnetic moments

TABLE 20

MAGNETIC MOMENTS OF SOME COMPLEXES
OF MOLYBDENUM AND TUNGSTEN.

<u>Compound</u>	<u>μ_{eff}</u>	<u>Temp. ($^{\circ}\text{K}$)</u>
1 $\text{MoCl}_3 \cdot 3\text{NCPh}$	3.76	300
2 $\text{MoCl}_3 \cdot 3\text{NCCH}_3$	3.68	296
3 $\text{MoCl}_3 \cdot 4\text{NCCH}_3$	3.87	303
4 $\text{MoCl}_3 \cdot 3\text{NCCH}_2\text{Ph}$	3.61	301
5 $\text{MoCl}_3 \cdot 3\text{NCCH}_2\text{CH}_3$	3.67	301
6 $\text{MoCl}_3 \cdot 3\text{NC}(\text{CH}_2)_2\text{CH}_3$	3.80	303
7 $\text{MoCl}_3 \cdot 3\text{NCCH}(\text{CH}_3)_2$	3.71	300
8 $\text{MoCl}_3 \cdot 3\text{NC}(\text{CH}_2)_3\text{CH}_3$	3.78	301
9 $\text{MoBr}_3 \cdot 3\text{NCPh}$	3.74	301
10 $\text{MoBr}_3 \cdot 3\text{NCCH}_3$	3.65	299
11 $\text{MoBr}_3 \cdot 4\text{NCCH}_3$	3.87	299
12 $\text{MoBr}_3 \cdot 3\text{NCPh}$	3.90	300
13 $\text{MoBr}_3 \cdot 3\text{NCCH}_2\text{CH}_3$	3.82	300

TABLE 20 cont.

<u>Compound</u>	<u>μ_{eff}</u>	<u>Temp. ($^{\circ}\text{K}$)</u>
14 $\text{MoBr}_3 \cdot 3\text{NC}(\text{CH}_2)_2\text{CH}_3$	3.81	299
15 $\text{MoBr}_3 \cdot 3\text{NCCH}(\text{CH}_3)_2$	3.81	299
16 $\text{MoBr}_3 \cdot 3\text{NC}(\text{CH}_2)_2\text{CH}_3$	3.90	301
17 MoCl_3py_3	3.61	298.5
18 MoCl_3py_4	3.88	298.0
19 MoBr_3py_3	3.81	299
20 $\text{MoBr}_3(\text{lut})_2$	3.2	299
21 $\text{MoCl}_3(\text{THF})_3$	3.35	299
22 $\text{MoBr}_3(\text{THF})_3$	3.45	298
23 $\text{MoBr}_3(\text{phen})_2$	3.60	297
24 $\text{MoI}_3(\text{phen})$	2.98	300
25 $\text{MoI}_3(\text{phen})_2$	3.64	293
26 $\text{MoI}_3(\text{bipy})_2$	3.76	293
27 $\text{MoBr}_3(\text{THT})_3$	3.77	298

TABLE 2C cont.

<u>Compound</u>	<u>μ_{eff}</u>	<u>Temp. ($^{\circ}\text{K}$)</u>
28 $\text{MoCl}_3(\text{THT})_3$	3.54	300
29 $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$	2.73	300
30 $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$	2.04	299
31 WI_4py_4	1.02	300
32 WCl_4py_2	1.84	298
33 WCl_3py_3	3.39	299
34 WBr_3py_3	3.40	300

TABLE 21

MOLAR SUSCEPTIBILITIES AND EFFECTIVE MAGNETIC
MOMENTS OF $\text{MoCl}_3(\text{NPh}_3)$ AND $[\text{MoCl}_3\text{py}_3]\text{py}$ AT
VARIOUS TEMPERATURES.

$\text{MoCl}_3 \cdot 3\text{NPh}_3$	$\chi'_M \times 10^{-6} \text{ (cgs)}$	$\mu_{\text{eff}} \text{ (B.M.)}$	Temperature ($^{\circ}\text{K}$)
	5889.8	3.76	300
	6383.2	3.75	276
	7134.2	3.75	246
	8221.2	3.75	213.4
	9635.9	3.75	182.3
	11165.3	3.75	157.4
	14740.0	3.73	117.8
MoCl_3py_4	6330.6	3.89	298
	7467.8	3.89	253
	9062.6	3.89	208.4
	11945.6	3.89	158.3
	18922.4	3.88	99.1

of the complexes Mo(phen)I_3 (2.98 B.M. at 300°K) and $\text{MoBr}_3(2,6\text{-lutidine})_2$ do not necessarily imply that the ligand fields about the central metal ion are not distorted from octahedral. A possible reason for low magnetic moments is that there is not sufficient magnetic dilution in these compounds.

Detailed studies by other workers have shown that in the rhenium(IV) complexes, M_2ReX_6 , the susceptibility increases as the sizes of the cation, M, and the halogen, X, are increased (126). Thus, whereas the magnetic moment of K_2ReCl_6 at 300°C was only 2.65 B.M., that for the quinolinium salt, $(\text{QH})_2\text{ReCl}_6$, was close to 3.6 B.M. The difference was shown to be due to the fact that magnetic exchange was lower in the quinolinium salt than in the potassium salt. It is probable that the low magnetic moments in the complexes Mo(phen)I_3 and $\text{MoBr}_3(2,6\text{-lut})_2$ arise in the same way. This seems reasonable because, when the compound, Mo(phen)I_3 , is treated with more phenanthroline, the product, $\text{Mo(phen)}_2\text{I}_3$, has a higher magnetic moment (3.64 B.M. at 293°K).

(iv) Tetrahydrofuran and tetrahydrothiophene complexes of molybdenum(III).

Apart from the tetrahydrothiophene complex, $\text{MoBr}_3(\text{THT})_3$, the other compounds have rather low magnetic moments (3.35-3.54 B.M.). The figures probably indicate that the ligand fields about the central atom are only a little distorted from octahedral which agrees with the observation mentioned

earlier that the spin-forbidden bands in such complexes are not well resolved. The distortions in bromo complexes should be higher than those in the chloro complexes for reasons discussed earlier and this is probably why the former have higher magnetic moments.

(b) Complexes of molybdenum(II): The iodo complex, $\text{Mo(phen)}_2\text{I}_2$, had a very low corrected molar susceptibility, $\chi'_M = +130 \times 10^{-6}$ cgs. at 300°K . Such a low value may be explained by assuming that the complex has a trans structure (D_{4h}). Since the ligand field strength of phenanthroline is approximately twice that of the iodide (232), the result of a tetragonal distortion is to make the energy of two d-orbitals (d_{xz} and d_{yz}) much lower than the energy of the next orbital (d_{xy}) (166) so that the four d-electrons of molybdenum(II) would be paired.

Apart from the pyridine complex, $\text{Mo(CO)}_2\text{py}_2\text{Cl}_2$, which had a room temperature magnetic moment of 2.73 B.M. (Table 20), other paramagnetic molybdenum(II) complexes examined had magnetic moments of about 2 B.M. Such a moment was found for the bipyridyl complex, tentatively formulated as $\text{Mo(bipy)}_3\text{Br}_2$ and acetonitrile complexes of the type $\text{Mo(CO)}_x(\text{NCCH}_3)\text{Cl}_2$.

As expected, the molybdenum(II) complex, $\text{Mo(CO)}_2[\text{P(OCH}_3)_3]_3\text{Cl}_2$, was found to have a very low positive susceptibility ($\chi'_M = 42 \times 10^{-6}$ cgs. units at 300°K). The molecular weight of the compound (Table 26) shows that the complex is seven-coordinate.

2. Tungsten compounds:

Octahedral complexes of tungsten(III) are expected to exhibit magnetic moments of about 3.4 B.M. whereas tungsten(III) ion is expected to have a spin-orbit coupling of $\approx 600 \text{ cm.}^{-1}$. Unfortunately, the highest magnetic moment reported for any tungsten(III) compound is only that of tungsten triiodide and in this case, the susceptibility was field-dependent (47).

The pyridine complexes, WBr_3py_3 and WCl_3py_3 , though not octahedral, exhibit magnetic moments in the expected range for octahedral tungsten(III) compounds (Table 18) and are, in this respect, quasi-octahedral. The electronic spectrum of the bromo complex, WBr_3py_3 , has a shoulder at $24,7000 \text{ cm.}^{-1}$ which is probably due to the first spin allowed transition (Fig. 28).

If the energy of this band be taken as equal to the $10Dq$ value, and the compound treated to a first approximation as octahedral, a spin orbit coupling, λ , for tungsten(III) is estimated to be 766 cm.^{-1} . This is very reasonable since the exact position of an absorption band occurring as a shoulder is difficult to determine accurately.

The tungsten complex, WI_x ($3 < x < 4$), made from the reaction of W(CO)_6 with iodine had, on the basis of tungsten analysis, a magnetic moment of 1.30 B.M. per tungsten atom. This is further evidence that the compound was a tungsten(IV) complex rather than tungsten triiodide since μ_{eff} for WI_3 is about 4 B.M. (47).

The magnetic moments of the complexes WCl_4py_2 and WI_4py_4 are rather low for two unpaired electrons (Table 20). Such values have been observed in other tungsten(IV) compounds (230).

3. Accuracy of magnetic data.

An analysis of the measured quantities of equation 2-9 is tabulated below to show the possible sources of error.

<u>Quantity</u>	<u>Value</u>	<u>Possible error</u>	<u>% error</u>
l	7.0 cm.	0.2 cm.	2.86
H^2	2×10^6 (oe) ²		1.00
Weight, w	200 mg.	0.3 mg.	0.15
Temperature, T	300°K	0.1°K	0.03

An error of 0.2 cm. in the measurement of the length of a sample does not arise from limitations of the measuring instruments but from the difficulty of packing a sample uniformly, especially if the latter is in powder form. An error of 1% arises in the measurement of H^2 because the current was measured with an accuracy of $\pm 0.5\%$. The field strength, H , varies approximately directly with the current (p. 102).

From this data, it is evident that the corrected molar susceptibility was known with an accuracy of $\pm 4\%$. Hence, since the effective magnetic moment is directly proportional to $(\chi'_M)^{\frac{1}{2}}$, the magnetic moments quoted are accurate to $\pm 2\%$. It should be noted that if the sample is not uniformly packed, errors of up to 5% may result (162).

E. NUCLEAR MAGNETIC RESONANCE

RESULTS AND DISCUSSION

(a) Introduction: Structures of molybdenum complexes of the type MoX_3L_3 ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} =$ a neutral electron donor) are not known. On the basis of the electronic spectrum of the pyridine complex, MoCl_3py_3 , König has suggested that the compound has the trans (meridional) structure (238). This assignment is of questionable validity, however, because it can be shown that the cis compound exhibits the same qualitative splitting as a result of the combined effect of spin orbit coupling and low symmetry (231). (See also page 42).

NMR spectra of complexes of the type $\text{MoX}_3(\text{NCR})_3$ should provide information about the stereochemistry because:-

(i) The spectrum of the facial isomer should, qualitatively, resemble that of the parent nitrile.

(ii) The spectrum of the meridional isomer should be more complex because only two of the ligands are equivalent. The third one is unique in lying on the molecular axis.

On this basis, the structure of the complex $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$, discussed shortly, is believed to have the latter structure. Two difficulties prevented a full exploitation of this technique.

1. The compounds were very insoluble in deuterated chloroform. The chloro compounds were not sufficiently soluble to permit observation of any peaks. The possibility of ligand exchange did not, however, permit the use of the better sol-

vent, $(D_3C)_2SO$.

2. The compounds were paramagnetic and, therefore, the peaks were badly broadened. Even for the case cited above, there was no resolution in the peaks. The other compounds tested gave almost featureless tracks (for the concentrations used).

(b) Tribromotris(propionitrile)molybdenum.

The spectrum of this compound is given in Fig. 32. Tests on thin layer plates did not reveal the presence of different isomers.

Apart from a spinning sideband related to the TMS peak, there are unresolved peaks at 1.3, 2.2 and 4.p p.m. downfield from TMS. The intensity ratios are 28:66:67 which is close to 3:6:6. This corresponds to an assignment in the meridional configuration in which the high field peak is due to a methyl group on the molecular axis. The peak at 2.2 p.p.m. is due to the two equivalent methyl groups while the low field peak is due to the methylene protons in all the three co-ordinated groups. The unique methyl group is practically unshifted relative to TMS from its position in the pure nitrile.

F.

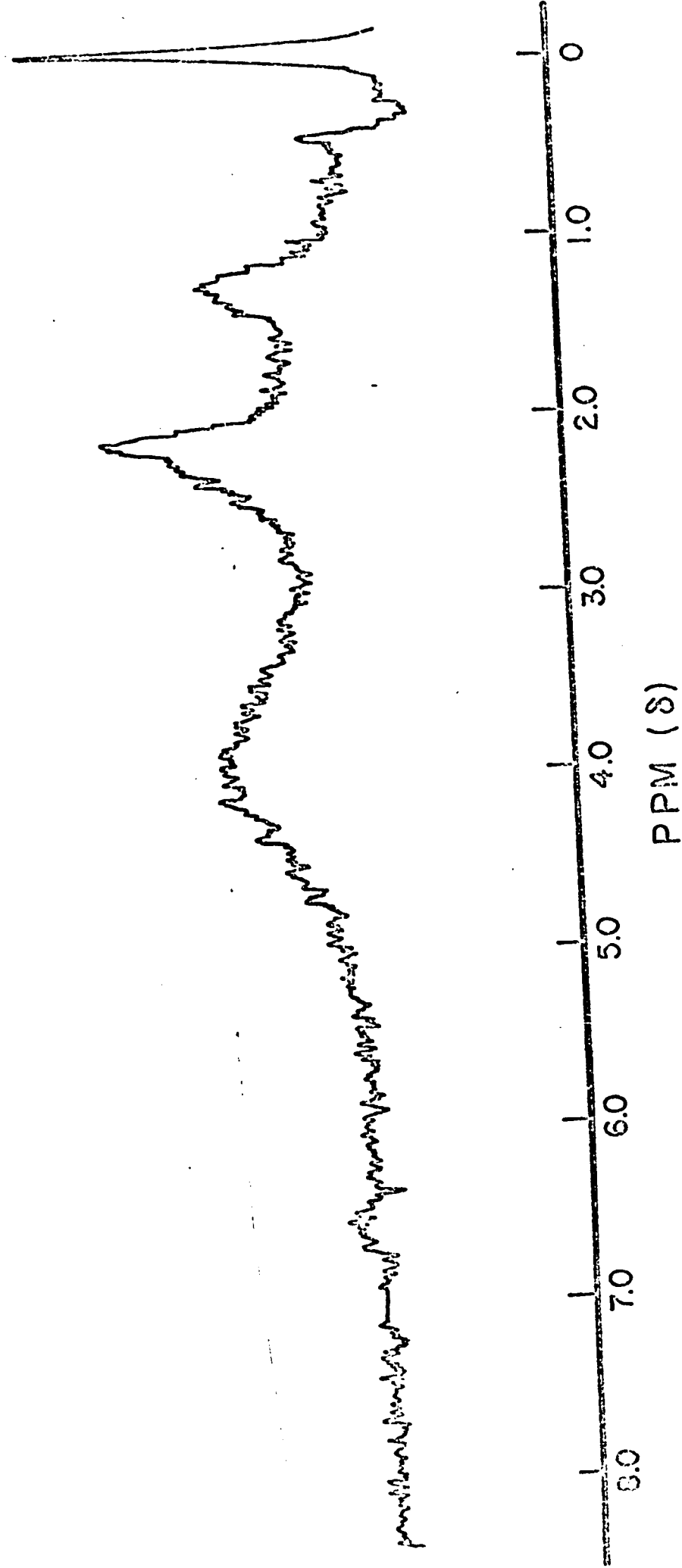
INFRARED SPECTRA

RESULTS AND DISCUSSION

1. Carbonyl complexes: The absorption energies for carbon-oxygen stretching frequencies in some carbonyl complexes are

FIGURE 32

Proton magnetic resonance of $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$.



given in Table 22. The data are typical and require no comment except in one case. For reasons which are not clear, the intensities of the bands in the complexes $\text{Mo}(\text{CO})_3(\text{Ph}_3\text{PO})\text{Cl}_2$ and $\text{Mo}_2(\text{CO})_6(\text{Ph}_3\text{AsO})_3\text{Cl}_4$ were very low.

2. Carbon-nitrogen stretching frequencies, $\nu(\text{CN})$, in nitrile complexes.

The carbon-nitrogen stretching frequencies, $\nu(\text{CN})$, of various complexes are summarized in Table 23. The main features of interest are the following:-

(a) Increase in carbon-nitrogen stretching frequency when the nitrile is co-ordinated.

As is clear from Table 23, the carbon-nitrogen stretching frequency, $\nu(\text{C-N})$, is some 20-30 cm^{-1} higher in the co-ordinated nitrile than in the free ligand.

With a few exceptions such as the complexes $\text{CoH}(\text{CNCH}_3)(\text{PPh}_3)_3$ (243), $[\text{Ru}(\text{NH}_3)_5(\text{NCPH})]^{2+}$ (244, 245) or the manganese and rhenium complexes, $\text{M}(\text{CO})_3(\text{NCCH}_2\text{CN})\text{X}$ ($\text{M} = \text{Mn, Re}$; $\text{X} = \text{Cl, Br, I}$) (246), in which a decrease in the $\nu(\text{C-N})$ vibration is observed when the nitriles are co-ordinated, an increase in the

$\nu(\text{C-N})$ when the nitrile is co-ordinated has been observed in nitrile complexes of other metal ions (223). The increase is interpreted as indicative of co-ordination of the nitrile to the Lewis acid via the lone pair on the nitrogen rather than via the C-N π -electrons (247). Various suggestions as to the

TABLE 22

CARBON-OXYGEN STRETCHING FREQUENCIES FOR SOME
CARBONYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN*

<u>Compound</u>	<u>$\nu(\text{C-O})$ (cm^{-1})</u>	<u>Medium</u>
1 $\text{Mo}(\text{CO})_4\text{Cl}_2$	2120s, 2070s, 2035sh	CH_2Cl_2
2 $\text{Mo}(\text{CO})_4\text{Br}_2$	2105s, 2045s, 1977s, 1971s 2170s, 2070s, 1985s, 1955w	CH_2Cl_2 Nujol
3 $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$	1940sh, 1920s, 1858s, 1800s	Nujol
4 $\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Cl}_2$	1973m, 1892s	Nujol
5 $\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Br}_2$	1978m, 1885s	Nujol
6 $[\text{Mo}(\text{CO})_2(\text{AsEt}_3)\text{Cl}_2]_x$	1932m, 1845s	Nujol
7 $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$	2240m, 1924s	Nujol
8 $\text{Mo}(\text{CO})_3(\text{Ph}_3\text{PO})\text{Cl}_2$	2030w, 1950w, 1890s	Nujol
9 $\text{Mo}_2(\text{CO})_7(\text{Ph}_3\text{PO})\text{Br}_2$	2080w, 2020m, 1935s, 1900sh	Nujol
10 $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$	2040s, 1970s, 1890m	Nujol
11 $\text{Mo}(\text{CO})(\text{CNPh})_3\text{Cl}_2$	1940m	Nujol

* Carbonyl compounds which were not recovered or were
not recovered pure have been excluded from this Table.

TABLE 22 (cont.)

<u>Compound</u>	<u>$\nu(\text{C-O})$ (cm.⁻¹)</u>	<u>Medium</u>
12 $\text{Mo}(\text{CO})(\text{NCPPh})_4\text{Cl}_2$	2000m	Nujol
13 $\text{W}(\text{CO})_4\text{Cl}_2$	2100m, 2010s, 1975s, 1945sh	CH_2Cl_2
14 $\text{W}(\text{CO})_4\text{Br}_2$	2100s, 2012s, 1988s, 1962s	Nujol
15 $\text{W}(\text{CO})_3\text{py}_2\text{Cl}_2$	2020s, 1977sh, 1890br	Nujol
16 $\text{W}(\text{CO})_3\text{py}_2\text{Br}_2$	2020s, 1940s, 1912s	Nujol
17 $\text{W}(\text{CO})_3\text{py}_2\text{I}_2$	2070m, 2010s, 1820s	Nujol
18 $\text{W}(\text{CO})_3(\text{NCCH}_3)_3$	1905s, 1780s	Nujol
19 $\text{W}(\text{CO})_3\text{py}_3$	1888s, 1747s	Nujol

m = medium

s = strong

w = weak

sh = shoulder

TABLE 23

CARBON-NITROGEN STRETCHING FREQUENCIES (cm.⁻¹) OF
NITRILE COMPLEXES OF MOLYBDENUM AND TUNGSTEN.

<u>Compound</u>	<u>C-N Stretching Frequency in Coordinated Nitrile</u>	<u>C-N Stretching Frequency in Uncoordinated Nitrile</u>	<u>Difference</u>
1 $\text{MoCl}_3(\text{NCPh})_3$	2238	2238	10
2 $\text{MoCl}_3(\text{NCCH}_3)_4$	2275, 2255*	2253	22, 2*
3 $\text{MoCl}_3(\text{NCCH}_2\text{Ph})_3$	2275	2244	31
4 $\text{MoCl}_3(\text{NCCH}_2\text{CH}_3)_3$	2268	2243	25
5 $\text{MoCl}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$	2273	2243	30
6 $\text{MoCl}_3[\text{NCCH}(\text{CH}_3)_2]_3$	2273	2252	21
7 $\text{MoCl}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$	2277	2242	35
8 $\text{MoBr}_3(\text{NCPh})_3$	2238	2228	10

* One of the four nitrile groups is apparently not coordinated strongly.

TABLE 23 (cont.)

Compound	C-N Stretching Frequency in Coordinated Nitrile	C-N Stretching Frequency in Uncoordinated Nitrile	Difference
9 $\text{MoBr}_3(\text{NCCH}_3)_4$	2277, 2257*	2253	24, 4*
10 $\text{MoBr}_3(\text{NCCH}_2\text{Ph})_3$	2275	2244	31
11 $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$	2268	2243	25
12 $\text{MoBr}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$	2268	2243	25
13 $\text{MoBr}_3[\text{NCCH}(\text{CH}_3)_2]_3$	2273	2252	21
14 $\text{MoBr}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$	2277	2242	35
15 $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$	2275m	2253	22
16 $\text{MoBr}_3(\text{bipy})\text{NCCH}_3$	2273	2253	20
17 $[\text{Mo}(\text{bipy})_2\text{I}_2]\cdot\text{I}\cdot\text{NCCH}_3$	2266	2253	13
18 $\text{W}_3\text{I}_8(\text{NCCH}_3)_6$	2280m	2253	27
19 $\text{WBr}_2(\text{NCPh})_2$	2266	2228	38
20 $\text{WCl}_2(\text{NCPh})_2$	2266	2228	38

reasons for the increase have been made (248-251).

Results of co-ordinate analyses by various workers show that there is some coupling of the C-N and N-M vibrations in a metal complex containing the linear system R-C-N-M (R = alkyl or aryl group; M = metal ion) (248, 249, 251). Gerrard et. al. (250), however, suggest that in view of the large differences in C-N and N-M stretching frequencies, kinematic coupling is less likely to be the cause of the increase in $\nu(\text{C-N})$. They suggested that the bond order (and hence the force constant) of the C-N bond increased when the nitrile was co-ordinated.

Beattie and Gilson suggest that both kinematic coupling and the increase in force constant of the C-N link should be taken into account (251). According to these workers, the rise in the C-N bond order might be due to repulsion of electrons from the nitrogen by the other atoms bonded to the Lewis acid into the C-N link.

Presumably, the change in the electronegativity difference between carbon and nitrogen causes a shortening of the C-N bond. The extreme case is that of a nitrile oxidized to a nitriloxide. The carbon-nitrogen stretching frequency in the nitriloxide is higher than in the nitrile by about 70 cm.^{-1} (252).

(b) The number of C-N stretching frequencies.

In substituted carbonyl complexes of the type $\text{Mo}(\text{CO})_3\text{L}_3$, the structures of the complexes can be deduced from the observed carbon-oxygen frequencies (208-210). Analogously, it

might be expected that the structures of nitrile complexes of the type $\text{Mo}(\text{NCR})_3\text{X}_3$ might be deduced from the carbon-nitrogen stretching frequencies. Apart from the complexes $[\text{MoCl}_3\text{NCCH}_3] \cdot \text{NCCH}_3$ and $[\text{MoBr}_3(\text{NCCH}_3)_3] \cdot \text{NCCH}_3$ whose spectra showed two $\nu(\text{C-N})$ peaks, each of the other nitrile complexes had only one peak which could unambiguously be associated with a C-N stretching mode. In the acetonitrile complexes cited, the increase in one of the $\nu(\text{C-N})$ vibrations was only slight (see Table 23), and was certainly due to the weakly co-ordinated nitrile. The peak disappeared when the nitrile was exposed to vacuum for prolonged periods.

It should be noted, however, that some workers have reported observing more than one $\nu(\text{C-N})$ band in nitrile complexes (253, 254). In one case, however, the band at 2311 cm.^{-1} , which the present author has also observed in complexes such as $\text{MoBr}_3(\text{NCCH}_3)_3$, is a combination band made of the C-C stretching mode and the symmetric CH_3 bending mode (255, 256).

(c) The intensity of $\nu(\text{C-N})$ bands appears to be related to the oxidation state of the Lewis acid.

When nitriles are either dissolved in solvents capable of hydrogen bonding (257) or co-ordinated to Lewis acids (256, 258), the intensity of the carbon-nitrogen stretching frequency is higher than it is in the free nitrile. According to observations during this work, the increase in intensity

appears to be greater the higher the oxidation state of the metal ion onto which the nitrile is co-ordinated.

This was the reason why the C-N stretching modes were not seen (Fig. 20) in zerovalent complexes of the type $\text{Mo}(\text{CO})_{6-n}(\text{NCR})_n$ which were isolated from the reactions of $\text{Mo}(\text{CO})_4\text{Br}_2$ or $\text{Mo}(\text{CO})_4\text{Cl}_2$ with neat nitriles. The zerovalent molybdenum and tungsten complexes $\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2$, $\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$ and $\text{W}(\text{CO})_3(\text{NCCH}_3)_3$ showed strong carbonyl bands. On the other hand, it was difficult without a previous knowledge of what the compound was, to associate any bands with C-N stretching modes because, in these complexes, the intensity of the band due to the C-N stretching mode was much lower than it was in complexes of the type $\text{MoX}_3(\text{NCR})_3$ ($\text{X} = \text{Cl}, \text{Br}$) (Fig. 33). It was, therefore, concluded that the intensity of a band due to a carbon-nitrogen stretching frequency is a function of the oxidation state of the Lewis acid onto which the nitrile is co-ordinated. If the oxidation state is high, the intensity is also high.

A similar observation has also been made by Zecchina *et al.* (259) who found that the intensity of the $\nu(\text{C-N})$ band of propionitrile adsorbed on a reduced chromia-silica catalyst was lower than that for one adsorbed on the oxidized form of the catalyst. In the reduced and oxidized forms, chromium is known to be present in oxidation states +3 and +6, respectively (260).

3. Pyridine complexes: The infrared (261-263) and Raman

TABLE 24

SOME PYRIDINE RING ABSORPTION BANDS (cm^{-1}).

<u>Compound</u>	<u>Absorption bands (cm^{-1})</u>		
$\text{C}_5\text{H}_5\text{N}$	1578m	605	405
MoCl_3py_3	1605m	634w	440m
MoBr_3py_3	1605m	635w	440m
WCl_3py_3	1608m	638m	445m
WBr_3py_3	1602m	638m	444m
$\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$	1604m	630w	
WCl_4py_2	1605m	638w	
$\text{W}(\text{CO})_3\text{py}_2\text{Cl}_2$	1605m	1640w	
$\text{W}(\text{CO})_3\text{py}_2\text{Br}_2$	1604m	1638w	
$\text{W}(\text{CO})_3\text{py}_2\text{I}_2$	1605m	640w	

Peaks of complexed pyridine below 600 cm^{-1} were recorded on CsI disks. Those above 600 cm^{-1} were obtained on nujol mulls.

FIGURE 33

Infrared spectra of (a) $\text{MoCl}_3(\text{NCPh})_3$
(b) $\text{cis-W(CO)}_3(\text{NCCH}_3)_3$.

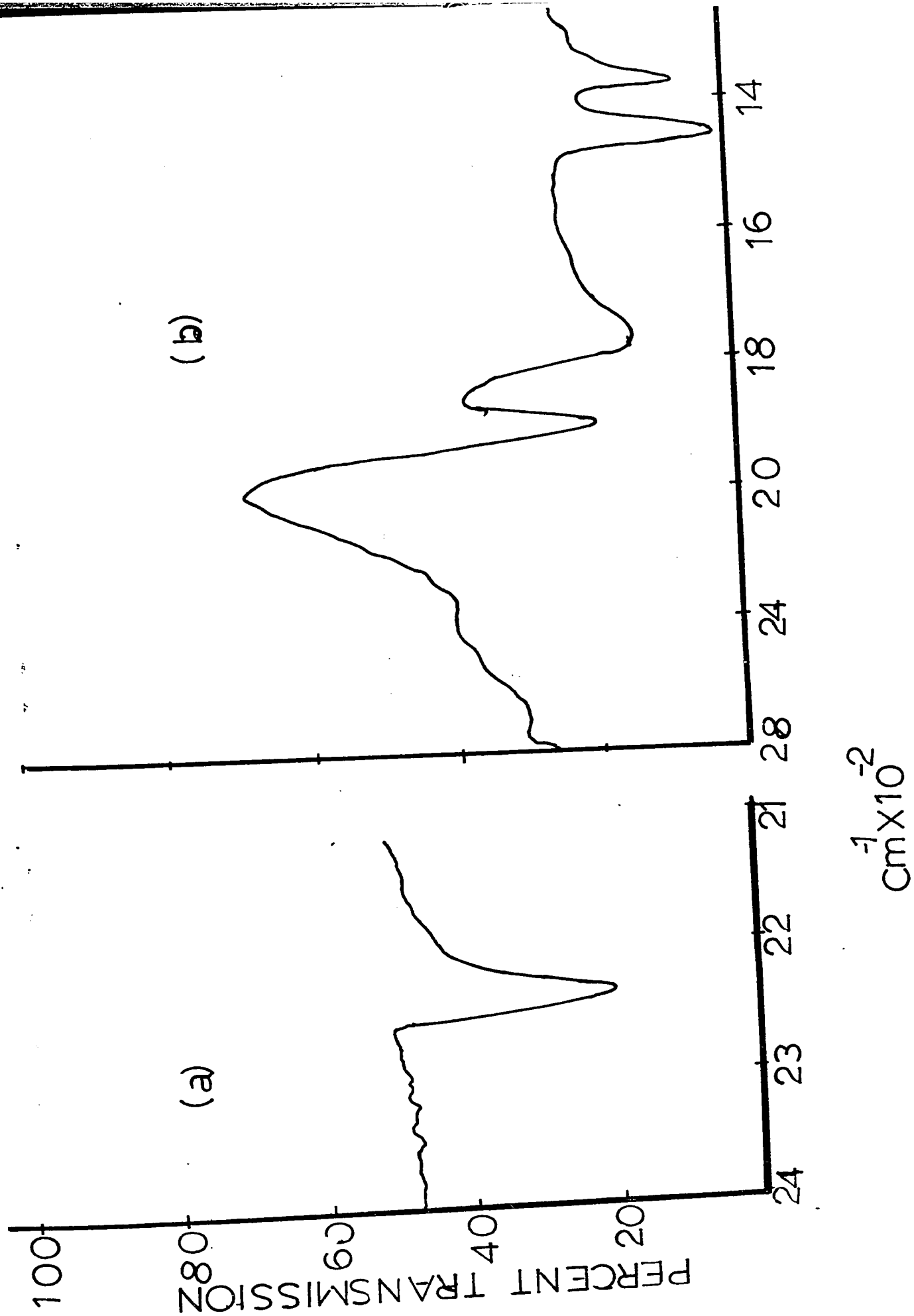


FIGURE 34

Infrared spectra of (a) $\text{MoCl}_3(\text{NCCH}_3)_4$
(b) $\text{MoCl}_3(\text{NCPh})_3$
(c) $\text{MoCl}_3(\text{NCCH}_2\text{CH}_2\text{CH}_3)_3$
(d) $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$.

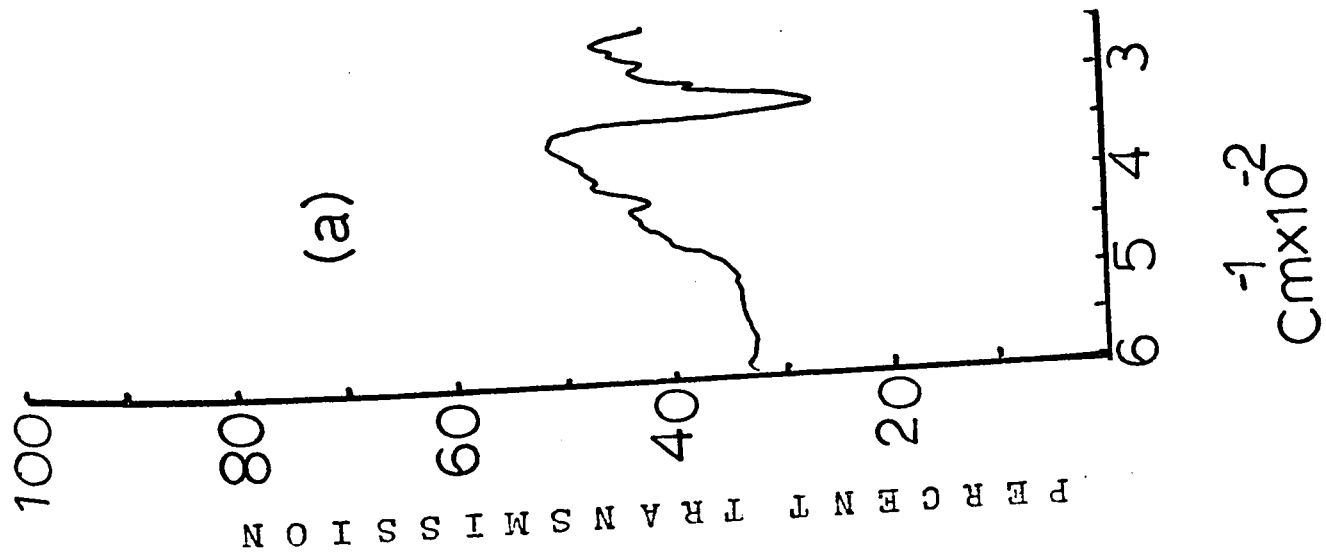


FIGURE 35

Infrared spectra of (a) $\text{MoCl}_3(\text{C}_4\text{H}_8\text{O})_3$
(b) MoCl_3py_3
(c) and (d) MoBr_3py_3

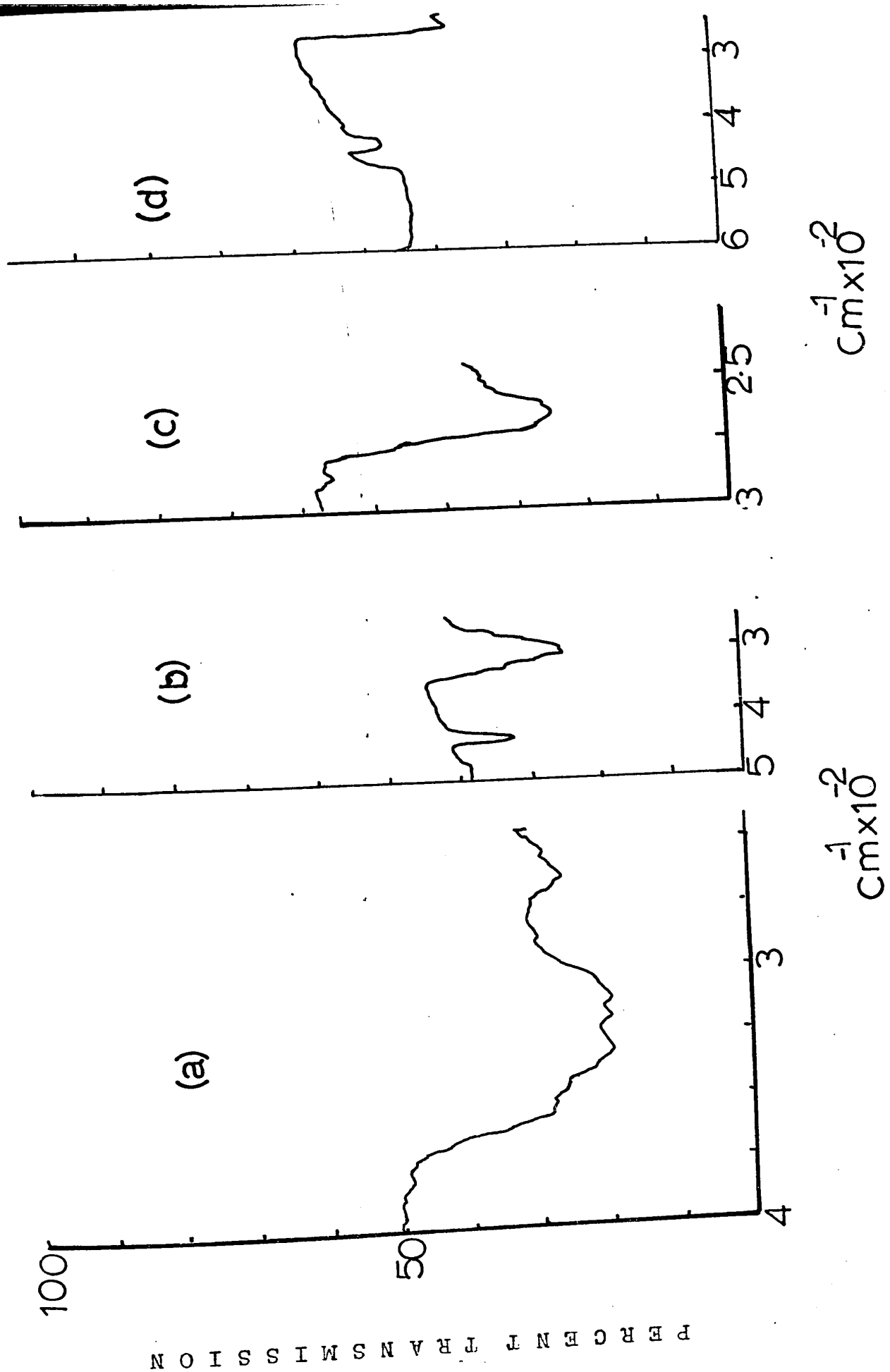


FIGURE 36

Infrared spectra of (a) $\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3$
(b) $\text{MoBr}_3(\text{C}_4\text{H}_8\text{S})_3$
(c) $\text{MoBr}_3(\text{C}_4\text{H}_8\text{O})_3$

100

PERCENT TRANSMISSION

50

(a)

$\text{cm}^{-1} \times 10^{-2}$

3

4

(b)

$\text{cm}^{-1} \times 10^{-2}$

3

4

(c)

$\text{cm}^{-1} \times 10^{-2}$

5

3

4

6

FIGURE 37

Far infrared spectra of (a) $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$
(b) $[\text{Mo}(\text{phen})_2\text{I}_2]\text{I}$

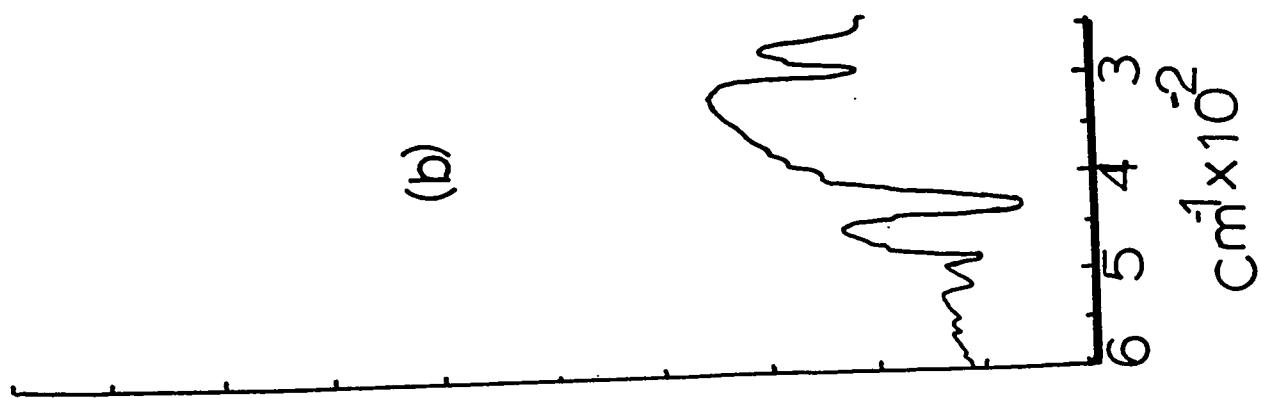
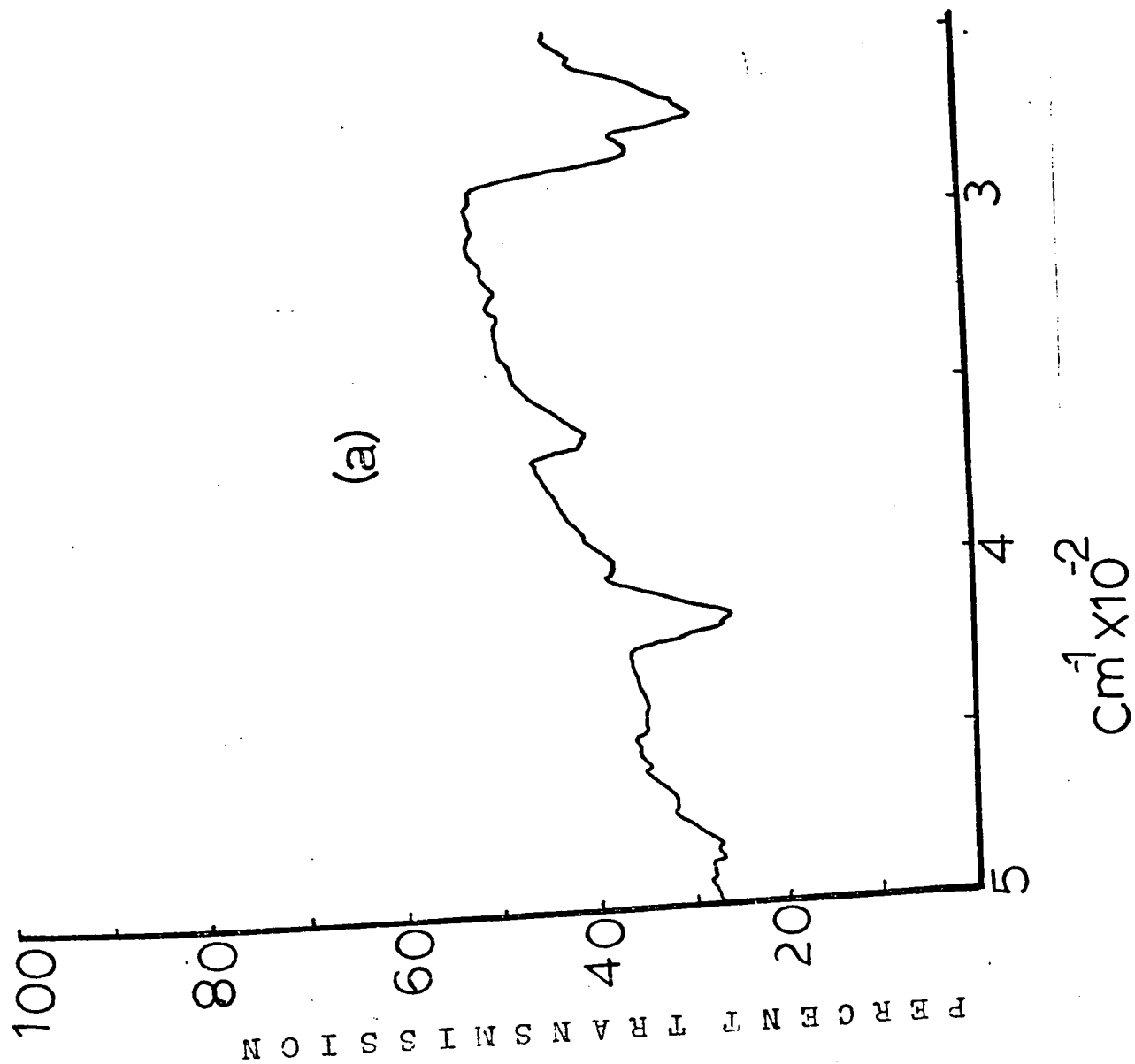


FIGURE 38

Far infrared spectrum of WCl_3py_3

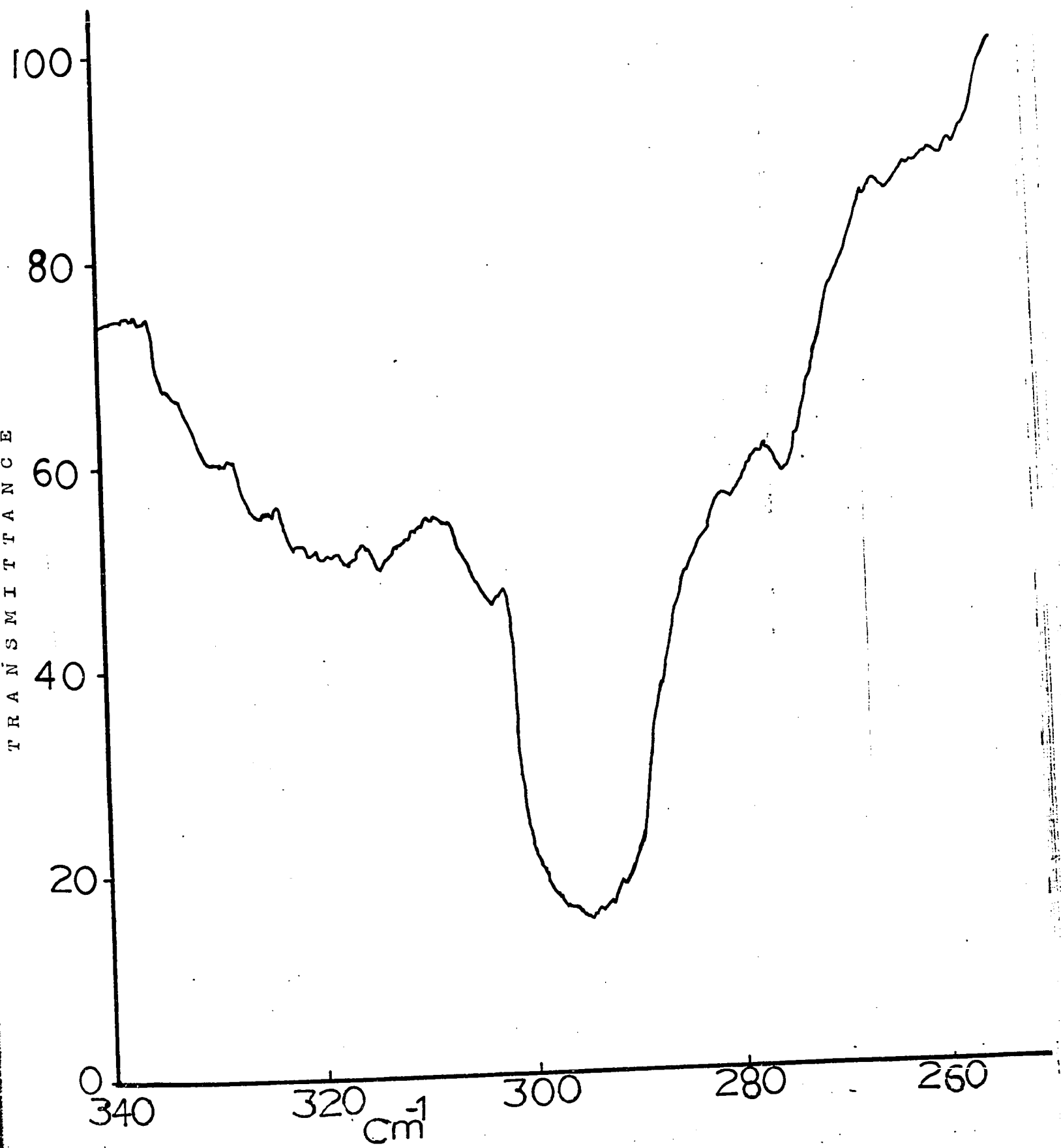


FIGURE 39

Far infrared spectrum of WCl_3py_3 ($260\text{-}200\text{ cm.}^{-1}$).

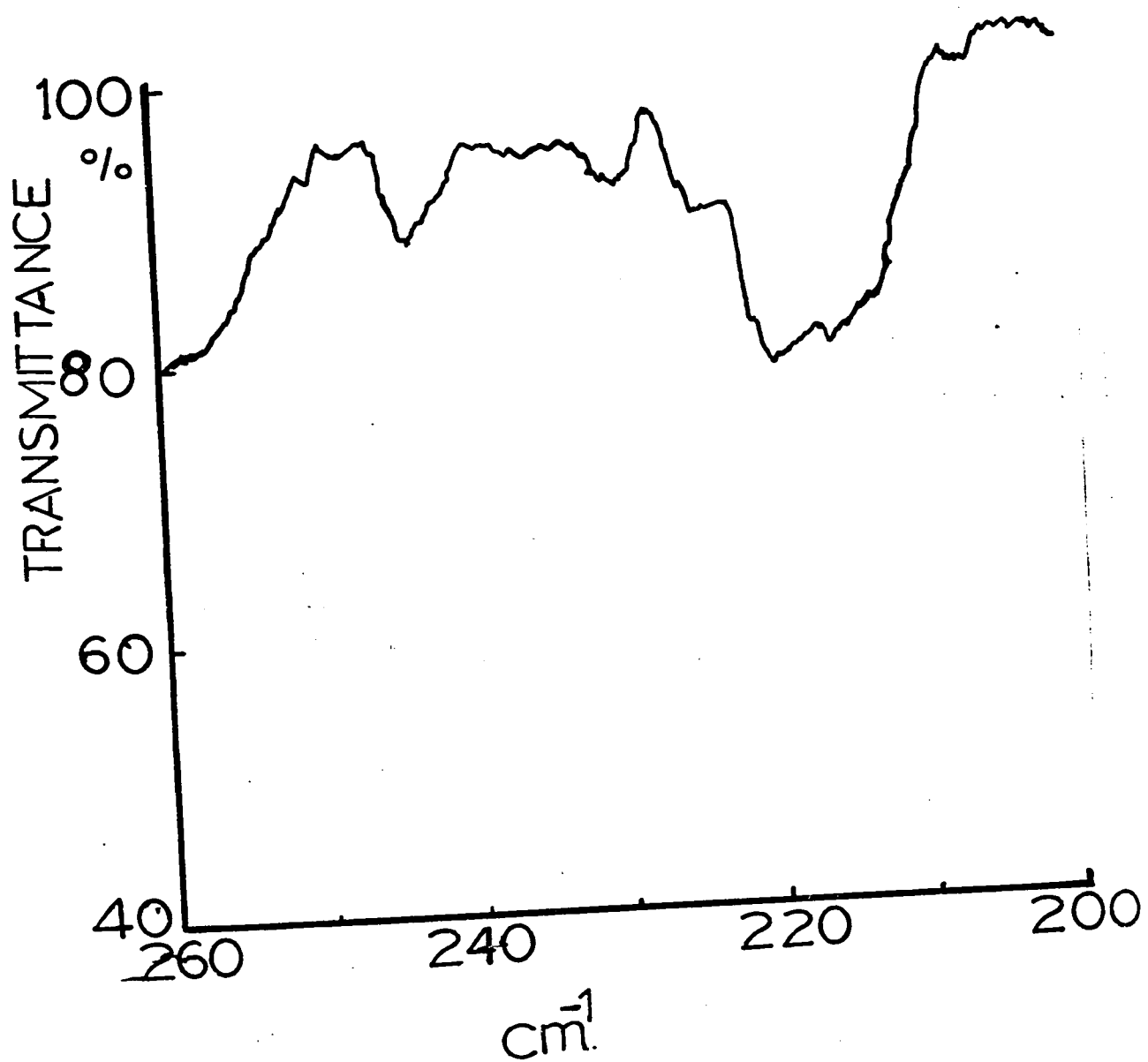


FIGURE 40

Far infrared spectrum of WBr_3py_3 (260-200 cm^{-1}).

(261, 262, 264) spectra of pyridine have been thoroughly studied by various workers. Gill et.al. (265) and Clark and Williams (266) have made systematic studies of pyridine complexes and have shown that the most useful peaks for identification purposes are those which occur at 1578 cm^{-1} , 605 cm^{-1} and 405 cm^{-1} in free pyridine. When pyridine is co-ordinated, these peaks are shifted to 1600 , 630 and 440 cm^{-1} , respectively. The absorption frequencies for these peaks in some complexes of molybdenum and tungsten are given in Table 24. In the complex $[\text{MoCl}_3\text{py}_3]\text{py}$, the shift in the peaks for the fourth pyridine is only slight (5 cm^{-1}).

4. Far infrared spectra.

The main absorption peaks in the region below 600 cm^{-1} are summarized in Table 25. For some of the bands, assignments have also been included.

(i) Band assignments in pyridine, nitrile and tetrahydrofuran complexes.

The far infrared spectra of the type MoCl_3L_3 (L = nitrile, pyridine or tetrahydrofuran) have a strong band centered around 300 cm^{-1} . Nitriles are either transparent in this region or absorb very weakly (267, 268). Pyridine has no absorption peaks in this region (263). Furthermore, in the bromo complexes of the type MoBr_3L_3 , the strongest band between 350 and 250 cm^{-1} is observed around $260\text{--}270\text{ cm}^{-1}$.

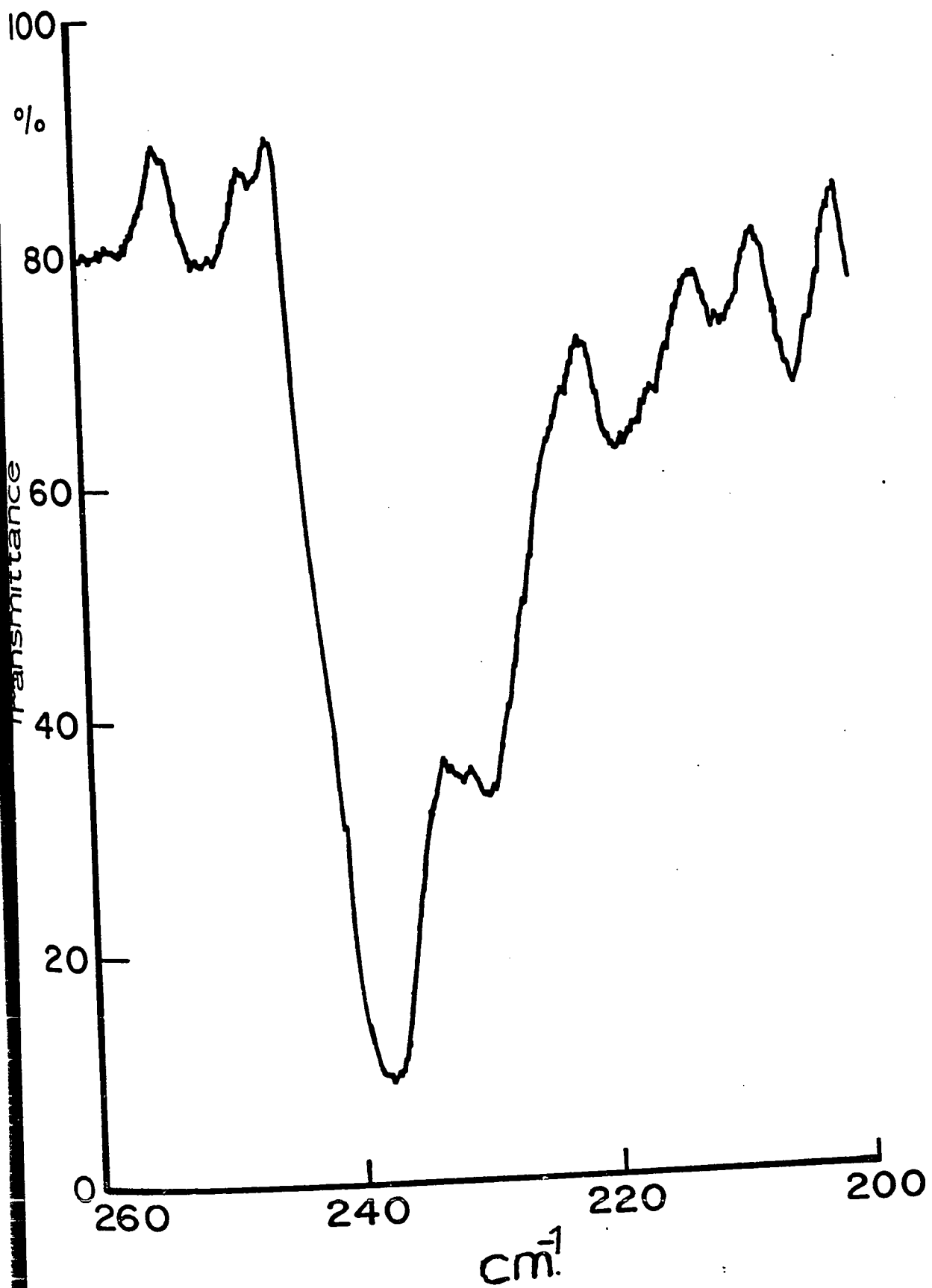


TABLE 25

INFRARED ABSORPTION BANDS FOR SOME MOLYBDENUM(III)
COMPLEXES (600-250 cm^{-1}) AND FOR WCl_3py_3 AND
 WBr_3py_3 (600-200 cm^{-1}).

<u>Compound</u>	<u>Absorption band (cm^{-1})</u>	
	<u>Mo-Cl or W-Cl</u>	<u>Others</u>
1 $\text{MoCl}_3(\text{NCPh})_3$	320s, 305m	548s, 460sh, 395w, 340m, 295sh, 282w, 270sh.
2 $\text{MoCl}_3(\text{NCCH}_3)_3$	319s, 299m	560w, 480sh, 415w, 287w, 275w, 263w.
3 $\text{MoCl}_3(\text{NCCH}_2\text{Ph})_3$	320s, 305m	570sh, 540s, 460m, 444m 395w, 295m, 287w, 270w.
4 $\text{MoCl}_3(\text{NCCH}_2\text{CH}_3)_3$	320s, 305m	565w, 460m, 445s, 395w, 355sh, 295sh, 285w, 270w.
5 $\text{MoCl}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$	320s, 305s	565w, 480sh, 420m, 295sh, 280w, 270sh.
6 $\text{MoCl}_3[\text{NCCH}(\text{CH}_3)_2]_3$	320s, 303s	560w, 480w, 450w, 370w, 335s, 295w, 280w, 270w.
7 $\text{MoCl}_3[\text{NC}(\text{CH}_2)_3\text{CH}_3]_3$	(320 305)br	540w, 450w, 410m, 340sh, 280w, 270sh, 262.
8 $\text{MoBr}_3(\text{NCPh})_3$	(310-285)br	548s, 450sh, 390w, 335w, 270m.
9 $\text{MoBr}_3(\text{NCCH}_3)_3$		560m, 412m, 305w, 290br, 270br.
10 $\text{MoBr}_3(\text{NCCH}_2\text{Ph})_3$		447s, 395w, 365w, 265m

TABLE 25 (cont.)

<u>Compound</u>	<u>Absorption band (cm.⁻¹)</u>	
	<u>Mo-Cl or</u> <u>W-Cl</u>	<u>Others</u>
11 $\text{MoBr}_3(\text{NCCH}_2\text{CH}_3)_3$		556m, 480w, 455w, 410w, 373w, 335sh, 310sh, 290w, 270s.
12 $\text{MoBr}_3[\text{NC}(\text{CH}_2)_2\text{CH}_3]_3$		570w, 450w, 410w, 375m, 309sh, 287sh, 268s.
13 $\text{MoBr}_3[\text{NCCH}(\text{CH}_3)_2]_3$		580sh, 570w, 550m, 480m, 375w, 335br, 290br.
14 $\text{MoBr}_3[\text{NC}(\text{CH}_2)_3]_3$		410w, 270m, 255w.
15 $\text{MoCl}_3(\text{C}_5\text{H}_5)_3$	318vs	555w, 438m, 340sh, 290sh, 278m.
16 $\text{MoBr}_3(\text{C}_5\text{H}_5\text{N})_3$		438m, 264s, br.
17 $\text{MoCl}_3(\text{C}_4\text{H}_8\text{O})_3$	313s	360sh, 331s, 264w.
18 $\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3$	310s	516s, 474w, 334s, 289m, 270w.
19 $\text{MoBr}_3(\text{C}_4\text{H}_8\text{O})_3$		575, 380sh, 270br.
20 $\text{MoBr}_3(\text{C}_4\text{H}_8\text{S})_3$		510s, 470w, 306sh, 280sh, 256s.
21 $[\text{Mo}(\text{phen})_2\text{I}_2]\text{I}$		510w, 490m, 440s, 295m.
22 $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$		485v.w., 428m, 400 v.w., 365m, 283m, 273m.
23 WCl_3py_3	295v.s.	445s, (330-314) br, 276w, 244v.w., 219m.
24 WBr_3py_3		445s, 250w, 238v.s, 230m, 219, 210, 205w.

s = strong

v.s. = very strong

m = medium

w = weak

sh = shoulder

br = broad

The band at $300\text{--}320\text{ cm.}^{-1}$ in the spectra of complexes of the type MoCl_3L_3 has, therefore, been assigned to Mo-Cl stretching modes. Figures 34-36 show some spectra of complexes of the type MoX_3L_3 .

The chloro complexes also show weak bands between 300 and 250 cm.^{-1} . Some of these are probably due to Mo-Cl stretching modes but an unequivocal assignment is not possible due to the low intensity of the bands. More detailed investigations by other workers have shown that Metal-Nitrogen stretching modes in nitrile complexes are weak and occur at much lower energies (269). Hence, it is unlikely that any of the weak peaks in the spectral range $250\text{--}300\text{ cm.}^{-1}$ in nitrile complexes are due to Mo-N stretching modes.

(ii) Complexes of tungsten(III).

The spectrum of the tungsten complex, WCl_3py_3 , contains a strong band which has shoulders on either side centered around 295 cm.^{-1} region. The spectrum of the bromo complex is blank between 320 cm.^{-1} and 250 cm.^{-1} . The strong band in the spectrum of WCl_3py_3 (Fig. 38) is due to a W-Cl stretching mode. The complexity of the spectrum of this compound suggests that the latter may be a mixture of isomers. Between the 200 cm.^{-1} and 260 cm.^{-1} , the two complexes show other peaks, some of which are doubtless due to W-N stretching modes (Figs. 39, 40).

The spectrum of the bromo compound, WBr_3py_3 , exhibits

six bands between 200 cm.^{-1} and 260 cm.^{-1} . A comparison of this spectrum with that of the chloro analogue suggests that the most intense band in the spectrum of WBr_3py_3 , which occurs at 238 cm.^{-1} , is due to a W-Br stretching mode. The band at 219 cm.^{-1} in the spectra of WCl_3py_3 and WBr_3py_3 (Figs. 39, 40) is probably due to a W-N stretching mode.

(iii) 2,2'-bipyridyl and 1,10-phenanthroline complexes

The infrared spectra of bipyridyl and phenanthroline do not show any significant absorption bands in the spectral range $300\text{-}250\text{ cm.}^{-1}$ (270). On the other hand, some molybdenum(III) complexes containing these ligands show bands of weak to medium intensity between 270 and 295 cm.^{-1} . The iodo complex, $[\text{Mo}(\text{bipy})_2\text{I}_2]\text{I}$, for example, has absorption bands at 270 and 285 cm.^{-1} . The complex $[\text{Mo}(\text{phen})_2\text{I}_2]\text{I}$ has an absorption band at 295 cm.^{-1} . This band is attributed to a Mo-N stretching mode because Mo-I vibrations are expected to occur at much lower energies than these.

(iv) Miscellaneous vibrations:

1. Mo-S stretching modes: In niobium complexes of the type $\text{NbX}_4(\text{C}_4\text{H}_8\text{S})_2$ ($\text{X} = \text{Cl}, \text{I}$), the Metal-Sulphur stretching modes have been found around 300 cm.^{-1} (271). Mo-S in the complexes $\text{MoX}_3(\text{C}_4\text{H}_8\text{S})_3$ may, therefore, be expected in the same spectral range. In the chloro complex, Mo-S vibrations are difficult to assign because they occur in the same range as that for $\nu(\text{Mo-Cl})$. In $\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3$, there is a strong band at 334 cm.^{-1} . While this may be a Mo-S stretching mode,

it is almost certain that it is not "pure" and must be strongly coupled to the Mo-Cl stretching modes. No similar band is observed in the bromo complex (Fig. 36).

2. $\nu(\text{Mo-Cl})$ in K_3MoCl_6 : A strong absorption band observed at 285 cm^{-1} is attributed to a Mo-Cl stretching mode.

3. $\nu(\text{Y-O})$ ($\text{Y} = \text{P, As}$): In triphenylphosphine oxide, $\nu(\text{P-O})$ was found at 1195 cm^{-1} (nujol). In complexes of molybdenum(II) containing the ligand Ph_3PO , $\nu(\text{P-O})$ was at 1160 cm^{-1} . This lowering in frequency was the same ($\Delta\nu = 35 \text{ cm}^{-1}$) for all the compounds made, some of which were not isolated pure.

A strong band at 882 cm^{-1} (nujol) in the spectrum of Ph_3AsO but absent in that of Ph_3As was assigned to an As-O stretching mode. In all the complexes of molybdenum(II) which contained Ph_3AsO , e.g. $\text{Mo}(\text{CO})_3\text{AsO})_{1.5}\text{Cl}_2$, this band was found at 840 cm^{-1} (nujol).

4. $\nu(\text{C-N})$ in phenylisocyanide: The free ligand in pentane had a very strong peak at 2110 cm^{-1} which is believed to be due to $\nu(\text{C-N})$. In the complex, $\text{Mo}(\text{CO})(\text{CNPh})_4\text{Cl}_2$, a very strong band observed at 2085 cm^{-1} is probably due to a C-N stretching mode. Weaker bands were also observed at 2140 cm^{-1} and 2000 cm^{-1} . The lower energy band was probably due to a C-O stretching mode.

MOLECULAR WEIGHTS

G.

The molecular weights of some compounds were estimated (osmometric method) by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany. In most cases, the results were unsatisfactory because the compounds were not sufficiently soluble or they decomposed. The results obtained for various compounds are summarized in Table 26.

On the basis of molecular weight, the complex $\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Cl}_2$ is monomeric. The bromo analogue was, unfortunately, unstable. The acetonitrile complex, $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$, also appears to be monomeric in solution. Many complexes of molybdenum(II) are usually seven-coordinate. Such complexes are expected to be diamagnetic (12). The paramagnetism of the complex $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$ suggests that, in the solid state, it is also monomeric and hence hexa coordinated.

Although the tungsten complexes $\text{W}(\text{CO})_3\text{py}_2\text{Cl}_2$ and $\text{W}(\text{CO})_3\text{py}_2\text{Br}_2$ were not sufficiently soluble for molecular weight determination, they are probably seven coordinate complexes. The iodo complex was soluble but, as for most other compounds listed in Table 26, the molecular weight value is not reliable.

The complex of empirical formula $\text{Mo}(\text{CO})_2(\text{AsEt}_3)\text{Cl}_2$ is probably dimeric since the observed molecular weight (515) is higher than the calculated value (384).

Compounds for which molecular weights were much lower

TABLE 26

EXPERIMENTAL MOLECULAR WEIGHTS OF SOME
MOLYBDENUM AND TUNGSTEN COMPLEXES

<u>Compound</u>	<u>Found</u>	<u>Calculated</u>	<u>Solvent</u>
1 $W(CO)_3(NCCH_3)_3$	564	391.0	acetone
2 $Mo_3Br_8(NCPh)_6$	161	1545.9	acetone
3 $[Mo(CO)_2(AsEt_3)Cl_2]_x$	515	385	acetone
4 $Mo(CO)_2[P(OCH_3)_3]_3Cl_2$	559	595	benzene
5 $Mo(CO)_2[P(OCH_3)_3]_3Br_2$	422	684	acetone
6 $Mo(CO)_3(PEt_3)_2Cl_2$	330	487.2	acetone
7 $W(CO)_3py_2I_2$	429	679.9	acetone
8 $W(CO)_3py_2Br_2$	*	585.9	$CHCl_3$
9 $W(CO)_3py_2Cl_2$	*	497	$CHCl_3$
10 $Mo(phen)I_3$	140**	656.9	DMF
11 $Mo(bipy)_2I_3$	129**	945.2	DMF

* Compound not sufficiently soluble in the solvent used.

** Value said to be concentration dependent.

*** Compound said to decompose in solvent used.

TABLE 26 (cont.)

	<u>Compound</u>	<u>Found</u>	<u>Calculated</u>	<u>Solvent</u>
12	$\text{Mo}_2(\text{bipy})_3\text{Cl}_6$	60***	873.1	DMSO
13	$\text{Mo}_2(\text{bipy})_3\text{Br}_6$	73***	1139.9	DMSO
14	$\text{W}(\text{CO})_3\text{py}_3$	232***	502.2	py
15	WCl_4py_2	103***	483.9	DMF
16	WI_4py_4	242***	1007.9	py
17	$\text{Mo}_2(\text{CO})_6(\text{Ph}_3\text{AsO})_3\text{Cl}_4$	173	1646.3	CHCl_3
18	$\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$	298	292	acetone
19	$\text{WBr}_2(\text{NCPH})_2$	521	549.9	acetone

than the calculated ones were either ionized, e.g. the complexes $\text{Mo}_2(\text{bipy})_3\text{X}_6$ ($\text{X} = \text{Cl}, \text{Br}$) or decomposed on dissolution.

The triethylphosphine complex, $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$, had a low molecular weight, most probably because of decomposition. When this compound was left to stand, a strong odour of triethylphosphine could be detected. If the compound was dissolved in benzene, ether, methylene chloride or chloroform, the solution turned purple. In ethanol, the colour of the solution turned yellow. If the molecular weight obtained (330) is correct, it implies that the compound decomposes in solution losing one triethylphosphine ligand to give $\text{Mo}(\text{CO})_3(\text{PEt}_3)\text{Cl}_2$ (M. wt. 369). This is reasonable because, as we saw on page 10, complexes of the type $\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{X}_2$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) lose a molecule of CO in refluxing methylene chloride to give complexes of the type $\text{M}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2$.

It would have been interesting to obtain the correct molecular weight of compound 17 in Table 26 because, as noted earlier, it was one of the compounds which gave satisfactory analyses and yet no presence of CO groups could be detected.

It is almost certain that compound 19 is not monomeric as suggested by the molecular weight determination. Other abnormal values of molecular weights are obvious from the Table and hence, a meaningful interpretation of some of the data is difficult.

REFERENCES

1. Advanced Inorganic Chemistry by F. A. Cotton and G. Wilkinson; Interscience, Second Ed., 1966, Chapter 30.
2. J. Chatt; Proc. Roy. Soc., (London) B, 172, 327, (1969).
3. R. H. Burris; *ibid.* B, 172, 339, (1969).
4. L. A. Syrtsova, N. Levchenko, E. N. Frolov, G. I. Likhtenshtein, T. N. Pisarkaya, L. V. Vorobev and V. A. Gromoglasova; Mol. Biol., 1971, 5, (5), 726, (Russ.), Chem. Ab., 76, 3187m.
5. T. S. Piper and G. Wilkinson; J. Inorg. Nucl. Chem., 3, 104, (1956).
6. R. J. Haines, R. S. Nyholm and M. H. B. Stiddard; J. Chem. Soc. (A), (1967), 94.
7. P. M. Treichel, K. W. Barnett and R. L. Shubkin; J. Organometal. Chem., 7, 449, (1967).
8. R. B. King; Inorg. Chem., 7, 90, (1968).
9. M. Lustig and L. W. Houk; Inorg. Nucl. Chem. Letters; 5, 851, (1969).
10. R. B. King and A. Efraty; J. Chem. Soc. (D), 1970, 1370.
11. J. L. Thomas and H. H. Brintzinger; J. Amer. Chem. Soc., 94, 1386, (1972).
12. H. L. Nigam, R. S. Nyholm and M. H. B. Stiddard; J. Chem. Soc., (1960), 1806.
13. J. Lewis, R. S. Nyholm, C. S. Pande and M. H. B. Stiddard; J. Chem. Soc. (1963), 3600.

14. M. H. B. Stiddard; J. Chem. Soc., (1962), 4712.
15. J. Lewis, R. Whyman; J. Chem. Soc., (1965), 5486.
16. R. S. Nyholm, M. R. Snow and M. H. B. Stiddard; J. Chem. Soc., (1965), 6570.
17. H. C. E. Mannerskantz and G. Wilkinson; J. Chem. Soc., (1962), 4454.
18. J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sadhu and M. H. B. Stiddard; J. Chem. Soc., (1964), 3009.
19. J. R. Moss and B. L. Shaw; J. Chem. Soc.(A), (1970), 595.
20. J. Lewis and R. Whyman; J. Chem. Soc. (A), (1967), 77.
21. R. B. King; Inorg. Chem., 3, 1039, (1964).
22. M. C. Ganorkar and M. H. B. Stiddard; J. Chem. Soc., (1965), 3494.
23. E. W. Abel, I. S. Butler and J. G. Reid; J. Chem. Soc., (1963), 2068.
24. R. Colton and I. B. Tomkins; Aust. J. Chem., 19, 1143, (1966).
25. R. Colton and I. B. Tomkins; Aust. J. Chem., 19, 1519, (1966).
26. M. W. Anker, R. Colton and I. B. Tomkins; Aust. J. Chem., 20, 9, (1967).
27. R. Colton and C. J. Rix; Aust. J. Chem., 22, 305, (1969).
28. R. Colton and I. B. Tomkins; Aust. J. Chem., 20, 13, (1967).
29. R. Colton, G. R. Scollary and I. B. Tomkins; Aust. J. Chem., 21, 15, (1968).

30. M. W. Anker, R. Colton and I. B. Tomkins; Aust. J. Chem., 21, 1159, (1968).
31. R. Colton and C. J. Rix; Aust. J. Chem., 22, 2535, (1969).
32. R. Colton and G. R. Scollary; Aust. J. Chem., 21, 1435, (1968).
33. F. Bonati and G. Minghetti; Inorg. Chem., 9, 2642, (1970).
34. R. F. Broadbent and J. V. Kingston; J. Inorg. Nucl. Chem., 32, 2919, (1970).
35. J. A. Bowden and R. Colton; Aust. J. Chem., 21, 2657, (1968).
36. L. Brencze; J. Organometal. Chem., 37, C37-C38, (1972).
37. Present work.
38. G. Holste and H. Schäfer; J. Less-common Metals, 20, 164, (1970).
39. R. Colton and C. J. Rix; Aust. J. Chem., 21, 1155, (1968).
40. M. G. B. Drew, I. B. Tomkins and R. Colton; Aust. J. Chem., 23, 2517, (1970).
41. A. Mawby and G. E. Pringle; J. Inorg. Nucl. Chem., 34, 517, (1972).
42. M. G. B. Drew; J. Chem. Soc., Dalton Trans., 1972(5), 626.
43. M. G. B. Drew and A. P. Wolters; J. Chem. Soc. Chem. Commun., 1972(8), 457.
44. R. Colton; Coordination Chemistry Reviews 6, 269, (1971).
45. R. Colton and J. J. Howard; Aust. J. Chem., 22, 2543, (1969).
46. W. Hieber and E. Romberg; Z. anorg. allgem. Chem., 221, 321, (1935).

47. C. Djordjevic, R. S. Nyholm, C. S. Pande and M. H. B. Stiddard; J. Chem. Soc.(A), (1966), 16.
48. D. L. Kepert and K. Vrieze in Halogen Chemistry, V. Gutmann, Editor, Academic Press, Volume 3, (1967) page 1.
49. H. Schäfer, H. Plantz, H. Bauman, W. Beckmann, C. Brendel, U. Lange, H. G. Schultz and R. Siepmann; Z. anorg. allgem. Chem., 389, 57 (1972).
50. H. Schäfer and H. G. Schnering; Angew. Chem., 76, 833, (1964).
51. The Nature of the Chemical Bond by L. Pauling, Cornell University Press, Third Edition, (1960), page 440.
52. C. Brosset; Arkiv Kemi, Mineral. Geol., A20, No. 7, 16 pp. (1945).
53. C. Brosset; ibid., A22, No. 11, 10 pp., (1946), (see also Chem. Abstr. 41, 1168d, (1947)).
54. H. Schäfer, H. G. Schnering, J. Tillack, F. Kuhnen, H. Wöhrle and H. Baumann; Z. anorg. allgem. Chem., 353, 231, (1967).
55. L. J. Guggenberger and A. W. Sleight; Inorg. Chem., 8, 2041, (1969).
56. R. Siepmann and H. G. Schnering; Unpublished work, quoted in Ref. 49, R. Siepmann, Dissertation, Munster, (1967).
57. K. Lindner; Ber. dt. chem. Ges., 55, 1458 (1922).
58. K. Lindner, E. Haller and H. Helwig; Z. anorg. allgem. Chem., 130, 209, (1923).
59. R. S. Nyholm; Advancement Sci., 3, 421, (1967).
60. F. A. Cotton; Quart. Rev. (London), 20, 389, (1966).

61. R. B. King in Progress in Inorganic Chemistry; S. J. Lippard, Editor, Interscience, Volume 15, (1972), 287.
62. E. W. Abel and F. G. A. Stone; Quart. Rev. (London), 23, 325, (1969).
63. J. E. Fergusson; Ref. 48, p. 227.
64. J. C. Sheldon; J. Chem. Soc., (1960), 1007.
65. J. C. Sheldon; ibid., (1963), 4183.
66. J. C. Sheldon; ibid., (1964), 1287.
67. J. E. Fergusson, B. H. Robinson and C. J. Wilkins; J. Chem. Soc.(A), (1967), 486.
68. J. Lewis, R. S. Nyholm and P. W. Smith; J. Chem. Soc., (1962), 2592.
69. E. Bannister and G. Wilkinson; Chem. Ind., (1960), 319.
70. T. A. Stephenson, E. Bannister and G. Wilkinson; J. Chem. Soc., (1964), 2538.
71. E. W. Abel, A. Singh and G. Wilkinson; ibid., (1959), 3097.
72. D. Lawton and R. Mason; J. Amer. Chem. Soc., 87, 921, (1965).
73. F. A. Cotton and J. G. Norman, Jr.; J. Coord. Chem., 1, 161, (1972).
74. F. A. Cotton and M. Jeremic; Syn. Inorg. Metal-Org. Chem., 1, 265, (1971).
75. G. Wilkinson; Unpublished work, quoted in Ref. 71.
76. A. Mawby and G. E. Pringle; J. Inorg. Nucl. Chem., 34, 525, (1972).
77. R. B. King and M. B. Bisnette; Inorg. Chem., 4, 475, (1965).

78. M. L. H. Green, J. Knight, L. C. Michard, G. G. Roberts and W. E. Silverthorn; J. Chem. Soc.(D), (1971), 1619.
79. D. F. Lewis and S. J. Lippard; Inorg. Chem., 11, 621, (1972).
80. Halides of the Second and Third Row Transition Metals by J. H. Canterford and R. Colton, John-Wiley and Sons, Ltd., (1968), Chapter 6 and references therein.
81. K. Rinke and H. Schäfer; Angew. Chem., Inter. Ed. (English), 6, (7), 637, (1967).
82. R. Siepmann, H. G. Schnering and H. Schäfer; ibid., 6, 637, (1967).
83. O. Olson; Ber., 46, 566, (1913).
84. W. Klemm and H. Steinberg; Z. anorg. allgem. Chem., 227, 193, (1936).
85. J. Lewis, D. J. Machin, R. S. Nyholm, P. Pauling and P. W. Smith; Chem. Ind. (London), (1960), 259.
86. A. Chillesotti; Atti R. Accad. Lincei, (1903)(V), 12, 67.
87. F. Foerster and E. Fricke; Z. angew. Chem., 36, 458, (1923).
88. W. R. Bucknall, S. R. Carter and W. Wardlaw; J. Chem. Soc., (1927), 512.
89. K. H. Lohman and R. C. Young; Inorg. Syn., 4, 97, (1953).
90. J. V. Brencic and F. A. Cotton; Inorg. Syn., 13, 170, (1972).
91. H. B. Jonassen, S. Cantor and A. R. Tarsey; J. Amer. Chem. Soc., 78, 271 (1956).
92. R. Saillant, J. L. Hayden and R. A. D. Wentworth; Inorg.,

- Chem., 6, 1497, (1967).
93. W. H. Watson, Jr., and J. Waser; Acta Cryst., 11, 689, (1958).
94. C. Brosset; Arkiv Kemi, Mineral. Geol., 12A, No. 4, 8 pp. (1935); Nature, 135, 874, (1935).
95. W. Wardlaw and A. J. I. Harding; J. Chem. Soc., (1926), 1592.
96. C. Furlani and O. Piovesana; Mol. Phys., 9, 341, (1965).
97. E. A. Allen, K. Feenan and G. W. A. Fowles; J. Chem. Soc., (1965), 1636.
- 98a P. W. Smith and A. G. Wedd; J. Chem. Soc.(A), (1966), 231.
- 98b P. W. Smith and A. G. Wedd; ibid.(A), (1968), 1377.
99. K. Komorita, S. Miki and S. Yamada; Bull. Chem. Soc. Japan, 38, 123, (1965).
100. D. A. Edwards and G. W. A. Fowles; J. Less-Common Metals, 4, 512, (1962).
101. H. B. Jonassen and L. J. Bailin; Inorg. Syn., 7, 140, (1963).
102. R. C. Young; J. Amer. Chem. Soc., 54, 1402, (1932).
103. W. M. Carmichael, D. A. Edwards and R. A. Walton; J. Chem. Soc.(A), (1966), 97; (see also Mol. Phys., 10, 205, (1966)).
104. D. A. Edwards, G. W. A. Fowles and R. A. Walton; J. Inorg. Nucl. Chem., 27, 1999, (1965).
105. A. Rosenheim, G. Abel and R. Lewy; Z. anorg. allgem. Chem., 197, 189, (1931).

106. M. C. Steele; Aust. J. Chem., 10, 489, (1957).
107. F. Klanberg and H. W. Kohlschütter; Z. Naturforsch, 15b, 616, (1960).
108. P. A. Marzilli and D. A. Buckingham; Aust. J. Chem., 19, 2259, (1966).
109. Kh. U. Ikramov, A. Kushakbaev, N. A. Purpierv and M. M. Yunusova; Uzb. Khim. Zh., 15(5), 27, (1971); C.A. 75 1153 4Ob.
110. R. A. Laudise and R. C. Young; Inorg. Syn., VI, 149, (1960).
111. O. Olson; Ber., 46, 566 (1913); C. A. 7, 1848 (1913).
112. H. B. Jonassen, A. R. Tarsey, S. Cantor and G. F. Helfrich; Inorg. Syn., 5, 139, (1957).
113. O. Collenberg and J. Backer; Z. Elektrochem., 30, 230, (1924); Chem. Ab., 18, 3526 (1924).
114. O. Collenberg and K. Sandved; Z. anorg. allgem. Chem., 130, 1, (1923).
115. J. L. Hayden and R. A. D. Wentworth; J. Amer. Chem. Soc., 90, 5291, (1968).
116. P. W. Smith and A. G. Wedd; J. Chem. Soc.(A), (1970), 2447.
117. R. Saillant and R. A. D. Wentworth; Inorg. Chem., 7, 1606, (1968).
118. S. Aléonard; Compt. Rend., 260, 1977, (1965).
119. J. S. Yoo, E. Griswold and J. Kleinberg; Inorg. Chem., 4, 365, (1965).
120. H. Funke and W. Hanke; Angew. Chem., 71, 408, (1959); Z. anorg. chem., 307, 157, (1961).

121. B. Sarpy and M. Dettke; Angew. Chem., 75, 1022, (1963);
Angew. Chem., Inter., English Edition, 2, 690, (1963).
122. D. G. Blight and D. L. Kepert; J. Chem. Soc.(A), (1968),
534.
123. P. M. Boorman, N. N. Greenwood and M. A. Hildon; J.
Chem. Soc.(A), (1968), 2466.
124. D. G. Blight, D. L. Kepert, R. Mandyscaewsky and K. R.
Trigwell; J. Chem. Soc., Dalton Trans., (1972), 313.
125. B. N. Figgis; Introduction to Ligand Field Theory,
Interscience, (1966), Chapter 7.
126. B. N. Figgis, J. Lewis and F. E. Mabbs; J. Chem. Soc.,
(1961), 3138.
127. B. N. Figgis and J. Lewis in "Progress in Inorganic
Chemistry", F. A. Cotton, Editor, Interscience, Vol.
6, (1964), p. 37.
128. W. A. Runciman and K. A. Schroeder; Proc. Roy Soc.,
(London), A265, 489, (1962).
129. J. Maas and J. Sand; Ber., 41, 1500, (1908); Chem.
Abst., 2, 2053, (1908); Ber., 42, 2642, (1909).
130. J. Lewis, R. S. Nyholm and P. W. Smith; J. Chem. Soc.,
(1961), 4590.
131. L. Malatesta in "Progress in Inorganic Chemistry".
Edited by F. A. Cotton, Interscience, Vol. 1, (1959),
p. 283; Endeavour, 28, 30, (1969).
132. Th. Kruck; Z. Naturforsch.; 19b(2), 165, (1964).
133. Th. Kruck and A. Prasch; ibid., 19b(8), 669, (1964).
134. R. J. Clark and P. I. Hoberman; Inorg. Chem., 4(12),

1771, (1965).

135. Th. Kruck, W. Lang and A. Engelmann; Angew. Chem. Int., (English) Edition, 4, 148, (1965).
136. L. Malatesta and C. Cariello; J. Chem. Soc., (1958), 2323.
137. L. Malatesta and M. Angoletta; J. Chem. Soc., (1957), 1186.
138. H. Behrens and A. Muhler; Z. anorg. allgem. Chem., 341, 124 (1965).
139. J. R. Olechowski, C. G. McAlister and R. F. Clark; Inorg. Chem., 4, 246, (1965).
140. L. M. Venanzi; Chem. Britain, 4, 162, (1968).
141. K. A. Jensen; Acta Chem. Scand., 3, 474, (1949).
142. R. S. Nyholm; J. Chem. Soc., (1951), 2602.
143. E. W. Abel; Quart. Rev., 17, 133, (1963).
144. W. R. McWhinnie and J. D. Miller in "Advances in Inorganic Chemistry and Radiochemistry", edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Vol. 12, (1969), page 135 and ref. therein.
145. D. W. Dubois, R. T. Iwamoto and J. Kleinberg; Inorg. Chem., 8, 815, (1969).
146. E. U. Condon and G. H. Shortley; The Theory of Atomic Spectra, Cambridge University Press, (1957), Chapter 7.
147. C. J. Ballhausen; Introduction to Ligand Field Theory, McGraw-Hill Book Company, (1962), Chapter 4.
148. B. N. Figgis; Introduction to Ligand Field Theory, Interscience (1966), Chapter 4.

149. H. Bethe; Ann. Physik, 3, 135, (1929), English Translation, Consultants Bureau, Inc., (1957).
150. Reference 148, Chapter 7.
151. R. Finkelstein and J. H. Van Vleck; J. Chem. Phys., 8, 790, (1940).
152. J. S. Griffith; The Theory of Transition Metal Ions, Cambridge University Press, (1961), Chapter 9.
153. Y. Tanabe and S. Sugano; J. Phys. Soc. Japan, 9, 753-79, (1954).
154. G. Racah; Phys. Rev., 61, 186, (1942); Ibid., 62, 438, (1942).
155. A. B. P. Lever; Advances in Chemistry Series, Vol. 62, 29, (1966).
156. Reference 147; Chapter 6, page 116.
157. C. K. Jorgensen; Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press and Addison-Wesley (1962), Chapter 6.
158. Reference 147, Chapter 8, page 191.
159. L. F. Bates; Modern Magnetism, Cambridge University Press, Fourth Edition, (1961), Chapter 1.
160. J. H. Van Vleck; Electric and Magnetic Susceptibilities, Oxford, (1932).
161. P. W. Selwood; Magnetochemistry, Interscience, Second Edition, (1956).
162. B. N. Figgis and J. Lewis in "Technique in Inorganic Chemistry", edited by H. B. Jonassen and A. Weissberger, Interscience, Vol. IV, (1965), pp. 137 ff.

- 163. Reference 161, Chapter 6.
- 164. W. G. Penney and R. Schlapp; Phys. Rev., 41, 194, (1932).
- 165. Ref. 148, Chapter 10.
- 166. L. E. Orgel; Introduction to Transition Metal Chemistry-Ligand Field Theory; Methuen and Co., Ltd., Second Ed., (1966), Chapter II.
- 167. Ref. 160; Chapter 11.
- 168. A. Weissberger, E. Proskauer, J. Riddick and E. Toops eds.; Technique in Organic Chemistry, Interscience, Vol. VII, 2nd Ed., (1955).
- 169. J. F. O'Donnell, J. T. Ayes and C. K. Mann; Anal. Chem., 37, 1161, (1965).
- 170. Parr Peroxide Bomb Instruction Manual, Parr Instrument Company, Moline, Illinois.
- 171. S. W. Parr; Ind. Eng. Chem., Analytical Edition, 2, 10, (1930).
- 172. F. E. Beamish; ibid., 5, 348, (1933).
- 173. J. F. Lemp and H. J. Broderson; J. Amer. Chem. Soc., 39, 2069, (1917).
- 174. I. M. Kolthoff; ed. Treatise on Analytical Chemistry, Interscience, Vol. 14, (1971), p. 8.
- 175. A. Steyermark and M. B. Faulkner; J. Ass. Off. Agr. Chemists, 35, 291, (1952).
- 176. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman; Applied Inorganic Analysis, John Wiley and Sons, Inc., New York, 2nd Ed., (1953), Chapter 45.
- 177. T. M. Chatard; Amer. J. Sci., (3), 1, 416, (1871).

178. Ref. 176, Chapter 17.
179. Standard Methods of Chemical Analysis; D. Van Nostrand Company, Inc., New York, London, Vol. 1, 6th Ed., (1962), Chapter 30.
180. E. A. Burns and D. N. Hume; J. Amer. Chem. Soc., 78, 3958, (1956).
181. R. G. W. Hollingshead; Oxine and its Derivatives, Butterworths, (1954), Vol. II, p. 428 ff. and refs. therein.
182. H. R. Fleck and A. M. Ward; Analyst, 58, 388, (1933).
183. P. H. M. P. Brinton and A. F. Stoppel; J. Amer. Soc., 46, 2454, (1924).
184. A. I. Vogel; A Textbook of Quantitative Inorganic Analysis, Longmans, Third Edition, (1961), Pp. 507-509.
185. Ref. 179, Chapter 49.
186. Ref. 176, Chapter 44.
187. L. W. McCay; J. Amer. Chem. Soc., 56, 2548, (1934).
188. M. Mativak; Chem. Analyst, 32, 83, (1943).
189. V. A. Nazarenko and F. G. Spivak; Zavodskaya Lab., 15, 131, (1949); Chem. Abs., 43, 5338.
190. E. M. Roizenblat and T. I. Fomicheva, Kh. Z. Brainina, Tr. Vses., Nauch. Issled Inst. Khim. Reaktivov Osobo Christ Khim. Veshchestv. No. 28, 104-9, (1966), Chem. Abst., 67, 39906h (1967).
191. W. G. Palmer; Experimental Inorganic Chemistry, Cambridge University Press, (1954), pp. 421-425.
192. Z. Z. Termendzhyan and D. S. Gaibakyan; Arm. Kim. Zh.,

- 24(7), 577, (1971); Chem. Ab., 75, 1473185 (1971).
193. D. S. Gaibakyan and Z. Z. Termendzhyan; Izv. Vyssh. Ucheb. Zaved. Khim; Khim. Tekhnol, 14(8), 1284, (1971), Chem. Abst. 15544Or (1971).
194. J. W. Mellor; A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Vol. XI, (1956), p.734.
195. H. Yagonda and H. A. Fales; J. Amer. Soc., 58, 1494, (1936).
196. Ref. 181, Chapter 27, p. 481.
197. J. T. Woods and M. G. Mellon; Ind. Eng. Chem., Analytical Ed., 13, 760, (1941).
198. H. Wu; J. Biol. Chem., 43, 189, (1920).
199. Handbook of Physics and Chemistry, Chemical Rubber Company, Cleveland, Ohio.
200. Ref. 191, p. 421.
201. Ref. 184, p. 462.
202. G. Fritz, D. Habel, D. Kummer and G. Teichmann; Z. anorg. allgem. Chem., 302, 60, (1959).
203. B. N. Figgis and R. S. Nyholm; J. Chem. Soc., (1958), 4190.
204. Othman Nor; Thesis, University of Ottawa, 1966.
205. W. Strohmeyer and G. Schöner; Chem. Ber., 94, 1346, (1961).
206. G. R. Dobson, M. A. El Sayed, I. W. Soltz and R. K. Sheline; Inorg. Chem., 1, 526, (1962).
207. W. Hieber and E. Romberg; Z. anorg. allgem. Chem., 221, 349, (1935).

208. R. Poilblanc and M. Bigorgne; Compt. Rend, 252, 3054, (1961).
209. R. Poilblanc and M. Bigorgne; Bull.Chim. Soc., France,
(1962), 1301.
210. J. Chatt, G.J. Leigh and N. Thankarajan, J. Organometal
Chem., 29, 105, (1971).
211. L. Malatesta, A. Sacco and S. Ghielmi; Gazz. chim. ital.,
82, 516, (1952); Chem. Ab., 48, 5130c (1954).
212. D.R. Rosseinsky; J. Chem. Soc., (1963), 1181.
213. H. Diebler and N. Sutin; J. Phys. Chem., 68, 174, (1964).
214. W. Hieber, W. Beck and G. Braun; Angew. Chem., 72, 795,
(1960).
215. W. Behrens and H. Wakamatsu, Z. anorg. allgem. Chem.,
320, 30, (1963).
216. H. Behrens and H. Wakamatsu, Chem. Ber., 99, 2753, (1966).
217. W. Hieber, J. Sedlmeir and W. Abeck; Chem. Ber., 86,
700, (1953).
218. I. Wender, H.W. Sternberg and M. Orchin; J. Amer.Chem. Soc.,
74, 1216, (1952).
219. R. Ercoli, F. Calderazzo and A. Alberola; ibid, 82, 2966, (1960).
220. N. A. Beach and H. Gray; ibid., 90, 5713 (1968).
221. J. S. Griffith; J. Inorg. Nucl. Chem., 2, 1, (1956).
222. R. E. McCarley; B. G. Hughes, J. C. Boatman; B. A. Torp;
Adv. Chem. Series, 37, 243 (1963).
223. R. A. Walton; Quart. Reviews (London), 19, 126, (1965).
224. B. J. Hathway and A. E. Underhill; J. Chem. Soc. (1960), 3705.
225. D. F. Evans, C. Zawoyski and R. L. Kay; J. Phys. Chem.,
69, 3878 (1965).

- 225b D. L. Kepert and R. S. Nyholm; J. Chem. Soc.(1965) 2871.
226. G. W. A. Fowles and R. A. Hoodless; *ibid.*, (1963), 33.
227. W. F. Luder and C. A. Kraus; J. Amer. Chem. Soc., 69, 2481 (1947).
228. D. S. Burgess, C. A. Kraus; *ibid.*, 70, 706 (1948).
229. C. R. Witschonke and C. A. Kraus, *ibid.*, 69, 2472 (1947).
230. C. D. Kennedy and R. D. Peacock; J. Chem. Soc. (1963) 3392.
- 230a Ref. 157, p. 291.
231. S. Sugano and Y. Tanabe; J. Phys. Soc. Japan, 13, 880, (1958).
232. Ref. 157, p. 109.
233. H. L. Schlafer and G. Glieman; Basic Principles of Ligand Field Theory, Wiley Interscience, New York, (1966), p. 112.
234. J. N. Murrell; Quart. Reviews (London), 15, 191 (1961).
235. E. Rabinowitch; Rev. Modern Phys, 14, 112, (1942).
236. L. E. Orgel; Quart. Reviews (London), 8, 422, (1954).
237. Ref. 1, p. 910.
238. E. König; Naturwis., 50, 641 (1963).
239. Ref. 152, p. 312.
240. M. W. Duckworth, G. W. Fowles and R. A. Hoodless; J. Chem. Soc., (1963), 5665.
241. R. J. H. Clark, J. Lewis, D. J. Machin and R. S. Nyholm; *ibid.*, (1963) 379.

242. M.Kotani; J. Phys. Soc. Japan, 4, 293, (1949).
243. A. Misono, Y. Uchida, M. Hidai and T. Kuse; J. Chem. Soc.(D), (1969), 208.
244. P.C. Ford and R.E. Clarke; Chem. Comm., (1968), 1109.
245. R.E. Clarke and P.C. Ford; Inorg. Chem., 9, 227, (1970).
246. M.F. Fàrona and K.F. Kraus; *ibid.*, 9, 1700 (1970).
247. G.W.A. Fowles and K.F. Gadd; J. Chem. Soc.(A), (1970), 2232.
248. D.F. Shriver and B. Swanson; Inorg. Chem., 10, 1354, (1971).
249. K.F. Purcell and R.S. Drago; J. Amer. Chem. Soc., 88, 919, (1966).
250. W. Gerrard, M.F. Lappert, H. Pyszora and J.W. Wallis; J. Chem. Soc., (1960), 2182.
251. I.R. Beattie and T. Gibson; J. Chem. Soc., (1964), 2292.
252. S. Califano, R. Moccia, R. Scarpati and G. Speroni; J. Chem. Phys., 26, 1777, (1957).
253. I.W. Soltz, G.R. Dobson and R.K. Sheline; Inorg. Chem., 2, 323, (1963).
254. H. Werner, K. Deckelmann and U. Schonenberger; *Helv. Chim. Acta*, 53, 2002, (1970).
255. D.L. Kepert and R.S. Nyholm; J. Chem. Soc., (1965), 2871.
256. P. Venkateswarlu; J. Chem. Phys., 19, 293, (1951).
257. H.W. Thompson and G. Steel; *Trans. Faraday Soc.*, 52, 1451, (1956).
258. H.J. Coever and C. Curran; J. Amer. Chem. Soc., 80, 3522, (1958).
259. A. Zecchina, E. Guglielminotti, S. Colluccia and E. Borello; J. Chem. Soc.(A), (1969), 2196.

260. C.P. Poole Jr. and D.S. MacIver; Adv. Catalysis, 17, 223, (1967).
261. F.A. Andersen, B. Bak, S. Brodersen and J.R. Andersen; J. Chem. Phys., 23, 1047, (1955).
262. C.H. Kline and J. Turkevich; ibid., 12, 300 (1944).
263. J.K. Wilmshurt and H.J. Bernstein; Can. J. Chem., 35, 1183, (1957).
264. E. Herz, L. Kahovec and K.W.F. Kohlraush; Z. physik. Chem., B53, 124 (1943); Chem. Ab., 37, 5314⁹ (1943).
265. N.S. Gill, R.H. Nuttall, D.E. Scaife and D. W. A. Sharp; J. Inorg. Nucl. Chem., 18, 79, (1961).
266. R.J.H. Clark and C.S. Williams; Inorg. Chem., 4, 350, (1965).
267. A. Hidalgo; Comp. Rend., 249, 395, (1959).
268. J.J. Lucier, E.C. Tuazon and F.F. Bentley; Spectrochim. Acta, 24A, 771, (1968).
269. G.A. Ozin and R.A. Walton; J. Chem. Soc. (A), 2236, (1970).
270. R.G. Inskeep; J. Inorg. Nucl. Chem., 24, 763, (1962).
271. J.B. Hamilton and R. E. McCarley; Inorg. Chem., 9, 1333 (1970).