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THE PREPARATION AND CHARACTERIZATION

OF SOME

BROMOSELENATES(IV)

by

Pierre J. B. Lahaie

A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of M. Sc. in Chemistry

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ABSTRACT

The Raman spectra of five bromoselenate(IV) anions, \( \text{SeO}_2\text{Br}^- \), \( \text{SeOBr}_3^- \), \( \text{SeOBr}_4^{2-} \), \( \text{SeBr}_5^- \) and \( \text{SeBr}_6^{2-} \) as solids and in solution are discussed. Except for \( \text{SeBr}_6^{2-} \), none of these anions have been characterized before. Raman spectra of these compounds are consistent with models predicted by the valence shell electron pair repulsion (VSEPR) theory, except in the case of the \( \text{SeBr}_6^{2-} \) anion. Compounds of the pentabromoselenate(IV) ion, \( \text{SeBr}_5^- \), are shown to be polymeric as solids and in concentrated solutions. The isolated \( \text{SeBr}_5^- \) anion is seen only in dilute solutions in acetonitrile. Evidence is given for the decomposition of the \( \text{SeBr}_5^- \) ion to \( \text{SeBr}_2 \) and \( \text{Br}_3^- \) in acetonitrile solution.

The Raman spectra of solutions of selenium dioxide in hydrobromic acid indicate the presence of \( \text{H}_2\text{SeO}_3 \), \( \text{SeOBr}_2 \), \( \text{SeBr}_5^- \) and \( \text{SeBr}_6^{2-} \). The equilibrium constant for the equilibrium:

\[
\text{H}_2\text{SeO}_3 + 2\text{HBr} = \text{SeOBr}_2 + 2\text{H}_2\text{O}
\]

has been evaluated.
ACKNOWLEDGEMENTS

The author is particularly indebted to Dr. J. B. Milne for his encouragement, interest and unfailingly assistance throughout the course of the M. Sc. program. A special word of thanks goes to all the people who were directly or indirectly involved with the completion of this thesis.
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INTRODUCTION

Since the early days when selenium was reacted with elemental halogen, the reactivity and stereochemistry of the halo-complexes formed has become an area of much interest. In most of these complexes, selenium is found to be in its penultimate valence state, having a non-bonding lone pair of electrons. Their structures can be predicted by use of the Valence Shell Electron Pair Repulsion (VSEPR) theory of Gillespie with a good degree of certainty, although vibrational and crystallographic techniques have produced a somewhat clearer picture as to the positions of the ligands, including the $4s^2$ lone pair, around selenium.

This introductory chapter reviews the halo and oxyhalo species of selenium in its penultimate valence state. These complexes will be discussed in the order of the extent of halogenation. Therefore, halo complexes of selenium dioxide will be dealt with first and hexahaloseeleniumates(IV) will be seen near the end. The complexes formed when SeO$_2$ is dissolved in various hydrohalic acids will also be discussed at the conclusion of this short review. The complexes studied in the present work will appear in the same order.
Monohalo- and Dihaloeselenate(IV) complexes:

Paetzold and Aurich$^3$ reported the synthesis of $K^+\text{SeO}_2\text{F}^-$ and recorded its infra-red and Raman spectra. Later studies of the monofluoroselenenate(IV) anion$^4,5$, $\text{SeO}_2\text{F}^-$, with different counter cations ranging from potassium through to quaternary ammonium cations, show that the ion is isolated and has $C_\infty$ symmetry; conforming with a pyramidal structure. The further fluorination of $\text{SeO}_2\text{F}^-$ to $\text{SeO}_2\text{F}_2^2-$ was also studied$^4$ and although a mixture of $K\text{SeO}_2\text{F}$ and $K_2\text{SeO}_2\text{F}_2$ was identified rather than the pure salt, the Raman spectrum of the mixture was consistent with $\text{SeO}_2\text{F}_2^2-$ having a $C_{2v}$ structure similar to the isoelectronic species $\text{ClO}_2\text{F}_2^-$ $^6$, $\text{IO}_2\text{F}_2^-$ $^7$ and $\text{TeO}_2\text{F}_2^2-$ $^8$, with the lone pair and the oxygen atoms occupying equatorial positions of a trigonal bipyramid.

Complex formation between selenium dioxide and halide in dimethylsulfoxide (DMSO) has been studied by UV and visible spectroscopy$^9$ and indicates that in the equilibrium,

$$\text{SeO}_2 + X^- = \text{SeO}_2X^- \quad (X = \text{Cl, Br, I})$$

$\text{SeO}_2$ acts as a hard Lewis acid. For $\text{SeO}_2X^-$ the chloride species is reported to be the most stable and the iodide the least. The $\text{SeO}_2\text{Cl}^-$ ion has been studied in detail$^{10}$ and
found, via Raman spectroscopy, to be monomeric and have $C_5$ symmetry. Further addition of $Cl^-$ to a solution of $SeO_2Cl^-$ ion in acetonitrile (MeCN) up to 2:1 $Cl^-/SeO_2$ gives no change in the Raman spectrum and shows that no complex ion other than $SeO_2Cl^-$ is formed in MeCN solution.

**Seleninyl halides**

Seleninyl fluoride, $SeOF_2$, is known to be monomeric in the gas phase, however Raman spectra of $SeOF_2^{12-14}$ show that there are frequency shifts and some major relative intensity effects between the spectra of the gas and the liquid. These are not sufficiently great to assume the presence of discrete polymeric species in the liquid. The spectra of both the liquid and the gas suggest a pyramidal structure, as would be predicted from VSEPR theory, since these agree with a species of $C_5$ symmetry. The solid spectrum is somewhat more complex due to a large degree of intermolecular interaction. The crystal structure of $SeOF_2$ at $-35^\circ C^{15}$ displays a structure consisting of pyramidal $SeOF_2$ units linked together by oxygen and fluoride bridges.

The Raman spectra of the gaseous, liquid and solid oxychloride of selenium, $SeOCl_2$, as well as of a $CCl_4$ solution have been studied$^{13,16-18}$. The spectra indicate associated molecules in the liquid and strong intermolecular
interactions in the solid. Monomeric molecules have been found in the vapor and in dilute solutions. Again, the molecule can be approximated as having $C_s$ symmetry both in the gas and liquid phase as well as in dilute solutions.

The Raman spectra of solid and molten SeOBr$_2$ as well as of a CCl$_4$ solution have been recorded and indicate associated molecules in the molten state and relatively strong intermolecular interactions in the solid. Monomeric pyramidal molecules are present in a CCl$_4$ solution.

As in the case of gaseous and liquid SeOF$_2$, gaseous and liquid SeOCl$_2$ and molten SeOBr$_2$, the Raman spectra indicate pyramidal molecules having $C_s$ symmetry. In liquid SeOCl$_2$ and molten SeOBr$_2$ the associated molecules can be thought of as SeOX$_2$ ($X = \text{Cl, Br}$) units having the central atom acting as an electron acceptor and the neighbouring SeOX$_2$ unit as being an electron donor, as shown below.
Oxotri- and Oxotetrahaloselenate(IV) complexes:

Paetzold and Aurich\textsuperscript{20} have prepared and characterized KSeOF\textsubscript{3} and they have shown that the SeOF\textsubscript{3}\textsuperscript{-} ion has a trigonal bipyramidal structure, which is consistent with the vibrational spectrum and the VSEPR model. Two of the fluorines are axial while the remaining three positions are occupied by the oxygen atom, the lone pair and the third fluorine atom.

The chloro anions derived from SeOCl\textsubscript{2} show an intriguing range of stereochemistries. The 1:1 complex of KCl and SeOCl\textsubscript{2}, which was first prepared by Wise\textsuperscript{21} and later formulated as K[SeOCl\textsubscript{3}] by Jackson and Smith\textsuperscript{22} has been studied by Raman spectroscopy\textsuperscript{20}. The spectrum was assigned for KSeOCl\textsubscript{3} assuming monomeric trigonal bipyramidal SeOCl\textsubscript{3}\textsuperscript{-} units. However, a more recent spectroscopic study of the oxotrichloroselenate(IV) anion\textsuperscript{10} indicates that for KSeOCl\textsubscript{3}, the greater complexity of the Raman spectrum and the large shifts in some of the vibrational modes compared to spectra of the same anion with larger counter cations, anion bridging occurs. This bridging probably occurs over chloride but also over oxygen, as in the case of the adducts SeOCl\textsubscript{2}, SbCl\textsubscript{5}\textsuperscript{28} and 2SeOCl\textsubscript{2}, SnCl\textsubscript{4}\textsuperscript{29} where the oxygen atoms complete the octahedra around Sb and Sn.
Cordeș\textsuperscript{23} has shown that there are essentially infinite chains of SeOCl\textsubscript{2} molecules linked by Cl\textsuperscript{-} bridges in 8-hydroxyquinolinium oxotrichloroselenate(IV). In this case, the anion consists of a distorted square pyramid about selenium. Each selenium is surrounded by one oxygen and five chlorine atoms. The selenium oxygen bond distance of 1.89\AA{} is equal to that found in the 1:2 addition compound of seleninyl chloride and pyridine\textsuperscript{24} and is comparable to the selenium-oxygen distance in SeOCl\textsubscript{2}, determined via electron diffraction\textsuperscript{25} to be 1.61\AA{}. The five selenium-chlorine distances vary considerably; two of these, 2.23 and 2.27\AA{}, are similar to values found by McCullough\textsuperscript{26,27} for a number of selenium-chlorine compounds. Two other chlorine atoms, at 2.96 and 2.99\AA{}, are almost exactly equidistant between two selenium atoms. The fifth chlorine neighbor of each selenium is at a distance of 3.3\AA{}, slightly shorter than the sums of the non-bonding radii, 3.8\AA{}. If the distances of 2.96\AA{} and 2.99\AA{} are considered too long to be covalent bonds, they can be interpreted as some type of ion-dipole association where the compound would be best described by the formula RH\textsuperscript{+-} Cl\textsuperscript{-}·SeOCl\textsubscript{2}.

The recent study on the SeOCl\textsubscript{3}\textsuperscript{-} ion\textsuperscript{10} also shows that in the case of the tetraethylammonium and tetraphenylarsonium compounds, Et\textsubscript{4}NSeOCl\textsubscript{3} and Ph\textsubscript{4}AsSeOCl\textsubscript{3} respectively,
the spectra are very similar to each other and to \( \text{SeOCl}_3^- \) in acetonitrile. The presence here of an isolated \( \text{SeOCl}_3^- \) ion is confirmed and this anion has \( C_3 \) symmetry, as previously suggested by Paetzold and Aurich\(^{20} \) for \( \text{KSeOCl}_3 \), with the trigonal bipyramidal coordination around selenium. 8-Hydroxyquinolinium oxotrichloroselenenate(IV), \( \text{C}_9\text{H}_8\text{NO}^+\text{SeOCl}_3^- \), exhibits weak chloride bridging and its spectrum is that of \( \text{SeOCl}_2 \) units moderately perturbed by the chloride bridges.

The polymeric nature of some of these compounds suggests that the \( \text{SeOCl}_3^- \) ion should readily accept a chloride ion to give the \( \text{SeOCl}_4^{2-} \) ion. Cordes and Bi-Cheng Wang\(^{30} \) prepared the dipyridinium salt of this ion and studied its crystal structure. \( \text{C}_{10}\text{H}_8\text{N}_2\text{H}_4^{2+} \text{SeOCl}_4^{2-} \), dipyridinium(II) oxotetrachloroselenenate(IV), also contains five co-ordinate selenium. Selenium-chlorine distances vary from 2.244 to 2.99\text{\AA}. The four Se-Cl bonds in each \( \text{SeOCl}_4^{2-} \) unit can be grouped into three categories; bonds of 3.0\text{\AA} which can be characterized as some type of ion dipole association, those of 2.24\text{\AA}, normal single bonds, and bonds of intermediate distance, 2.5\text{\AA}. Thus the anion is best approximated as trigonal bipyramidal \( \text{SeOCl}_3^- \) ions, each with a distant weakly bonded chloride anion.
The oxotetrafluorotellurate(IV) anion, TeOF₄²⁻, which is isoelectronic in valence electrons with the SeOCl₄²⁻ ion, has a discrete square-pyramidal structure with the oxygen occupying the axial position. The Raman spectra of (Et₄N)₂ SeOCl₄ and (Ph₄As)₂ SeOCl₄ and (Et₄N)₂ SeOCl₄ in acetonitrile are very similar to each other and very different from that of the SeOCl₃⁻ ion. These complexes display discrete SeOCl₄²⁻ ions having C₄ᵥ symmetry, where the square-pyramid around selenium has the oxygen occupying the axial position trans to the lone electron pair.

There is no report of the analogous SeOF₄²⁻ ion in the literature.

Penta- and hexahaloselenate(IV) complexes:

The reaction of liquid SeF₄ with an alkali metal fluoride gives salts of the SeF₅⁻ ion. Christe has observed the vibrational spectra of CsSeF₅, finding the results consistent with the anion having C₄ᵥ symmetry. Raman spectra of pentachloroselenate(IV) complexes indicate that the SeCl₅⁻ ion also has C₄ᵥ symmetry.

Seel and Massat have reported the isolation of the nitrosonium salt of the hexafluoroselenate(IV) ion, (NO)₂SeF₆. However, in the reaction of NO₂F with SeF₄, Aynsley et al. succeeded only in preparing the pentafluoro species (NO₂)SeF₅. Salts of the hexachloro and hexabromose-
lenate(IV) ions, $\text{SeCl}_6^{2-}$ and $\text{SeBr}_6^{2-}$, have been isolated by a number of authors. Hendra and Jovic\textsuperscript{35} have studied the vibrational spectra of some of these compounds and have found them to have octahedral symmetry. A later study on the $\text{SeCl}_6^{2-}$ ion via Raman spectroscopy\textsuperscript{10} supports this conclusion. A crystal structure determination on $\text{K}_2\text{SeCl}_6$\textsuperscript{36} has also shown the anion to be a regular octahedron. Greenwood and Straughan\textsuperscript{37} came to this same conclusion in studying metal-halogen vibrations of simple octahedral ions containing selenium and tellurium. Interligand repulsions are sufficiently strong to overcome the stereochemical effect of the lone electron pair in the case of $\text{SeCl}_6^{2-}$ and $\text{SeBr}_6^{2-}$.

K. J. Wynne\textsuperscript{38} has studied the factors involved in the stereochemistry of AX$_6$E systems (A=Sb, Bi; Se, Te; X=Cl$^-$, Br$^-$; E=lone pair) and explains the stereochemically inactive lone pair using the theory of hard and soft acids and bases (HSAB) proposed by Pearson\textsuperscript{39}. Wynne considers two empirical rules concerning the stereochemistry of AX$_6$E systems:

1. Only the hardest donors (O,F) generally lead to the stereochemical activity of the lone pair.

2. Soft donors generally lead to a stereochemically inert lone pair.
Complexes of Se(IV) in Hydrohalic acid:

The behaviour of Se(IV) in aqueous HF\(^{40}\) and HCl\(^{35,41,42}\) has been studied by Raman spectroscopy. In aqueous HF, the major components at high HF concentrations were found to be SeOF\(_2\) and HSeO\(_2\)F\(^{43}\). Similarly in aqueous HCl (up to 12.7 M) the following equilibrium occurs:

\[
H_2SeO_3 + 2HCl \rightarrow SeOCl_2 + 2H_2O
\]

A solution of SeO\(_2\) in HCl\(_{aq}\) saturated with HCl\(_g\) at 0°C (15M) indicates largely the presence of SeCl\(_5^-\) due to the principal reaction occurring in this solution:

\[
3HCl + SeOCl_2 \rightarrow H_3O^+ + SeCl_5^-\]

In this solution, the presence of some hexachloroselenate(IV) ion, SeCl\(_6^{2-}\), cannot be ruled out completely.

By the use of Raman spectroscopy Futekov and Specker\(^{44}\) have reported that when selenious acid reacts with concentrated hydrobromic acid (7-8M), SeOBr\(_2\), possibly as a dihydrate, is present as a reaction product. At higher concentrations, however, the equilibrium shifts towards H\(_2\)SeBr\(_6\). Hendra and Jovic\(^{35}\) have done a similar study and discuss the results in terms of an equilibrium between SeBr\(_5^-\) and SeBr\(_6^{2-}\) at high HBr concentrations:

\[
SeBr_5^- + Br^- \rightarrow SeBr_6^{2-}\]
The chemistry of Selenium-Bromine systems has not been studied extensively. Therefore, as part of the continuation of the research involving Se(IV) and its halo complexes, a number of bromoselenenate(IV) complexes were prepared and their spectra in MeCN were used to identify anions present in the Se(IV)/HBraq system.
1. **Materials**

Selenium dioxide (Alfa), tetramethylammonium bromide (Aldrich), tetraethylammonium bromide (Aldrich) and tetraphenylstibonium bromide (Alfa) were dried overnight on a vacuum line before use. Tetra-n-butylammonium bromide (Aldrich) was recrystallized from a 3:1 mixture of ethyl acetate: ethyl ether and stored in a vacuum desiccator over P₂O₅.

Acetonitrile (Fisher) was dried by refluxing over P₂O₅ followed by distillation (B.Pt. 81-82°C).

Seleninyl chloride (J.T. Baker, analyzed) was used after a single vacuum distillation.

Seleninyl bromide was prepared according to Lenher and was purified by subliming onto a cold finger at 0°C under vacuo. Bright yellow crystals of SeOBr₂ were obtained.

**Analysis.** Calculated for SeOBr₂: Br, 62.73% Found: 62.43%.

Selenium tetrabromide was prepared according to Brauer.

**Analysis.** Calculated for SeBr₄: Br, 80.19% Found: 80.3%.

All materials were stored in a dry box.

Both hydrobromic and perchloric acids were standardized before use.
2. **Chemical Analyses**

Bromide analyses were done by the Volhard method. Selenium was determined iodometrically while carbon, hydrogen and nitrogen analyses were obtained from Canadian Micro-analytical Service Limited.

3. **Raman Spectra**

Raman Spectra were recorded using a Jobin-Yvon grating monochromator in conjunction with PAR photon counting. Most spectra were excited with a Control Laser argon ion laser, using the 514.5nm line for both solids and solutions. Slit widths gave resolutions of 6-9 cm\(^{-1}\) for solid samples and 11 cm\(^{-1}\) for solutions at 500 cm\(^{-1}\). Spectra were calibrated by means of the argon lines present when the spike filter was not used. Low wattages were used for the solids (100-350mw) to avoid decomposition of the sample. The spectra of Me\(_4\)NSeOBr\(_3\), n-Bu\(_4\)NSeOBr\(_3\), (n-Bu\(_4\)N)\(_2\) SeOBr\(_4\), (Me\(_4\)N)\(_2\) SeOBr\(_4\), the pentabromoselenates(IV) and the hexabromoselenates(IV) were taken using a Spectra Physics 125A He/Ne laser. The 632.8nm line was used and the spectra were calibrated by means of the Ne lines present when the spike filter was not used. Slit widths gave resolutions of 3-4 cm\(^{-1}\) for solid samples and 5 cm\(^{-1}\) for solutions at 500 cm\(^{-1}\). All samples were contained in pyrex melting point tubes. In the case of solution spectra, saturated solutions in MeCN were used.
For the solutions of SeO₂ in HBr aq the Raman spectra were taken using the He/Ne laser at 632.8 nm. The resolution for these spectra was the same as for the MeCN solutions. The spectra were taken in 1 cm path length cells designed for fluorescence spectroscopy which were held in a water-jacketed aluminium holder maintained at 25°C. All spectral intensities were normalized by comparison to perchloric acid solutions which were run after each selenium dioxide - hydrobromic acid solution. The normalization assumption was that the 925 cm⁻¹ band of perchloric acid for a 1M solution (ν₁) had an area intensity of 1 in² (6.45 cm²). A plot of the intensity of the 925 cm⁻¹ band against concentration was shown to be linear up to 5.76M HClO₄ (Fig.14). Peak intensities were measured with a Hruden planimeter. Slit width, time constant, laser power, photon counting rate, scan rate, and sample position were held constant for each series of runs.

4. Preparation of the Compounds

All preparations were carried out in a dry box except for those crystallized from aqueous solution.

**Ph₄SbSeO₂Br:** Tetr phenylstibonium monobromoselenate(IV) was prepared by dissolving stoichiometric amounts of Ph₄SbBr and SeO₂ in a minimum amount of MeCN according to

\[ \text{MBr} + \text{SeO}_2 = \text{MSeO}_2\text{Br} \]
The solution was cooled over dry ice, filtered and the light yellow crystals of Ph₄SbSeO₂Br were pumped dry.

**Analysis.** Calculated for Ph₄SbSeO₂Br: C, 46.45%. H, 3.25%. Se, 12.72%. Br, 12.87%. Found: C, 46.25%. H, 3.25%. Se, 13.33%. Br, 13.25%.

**n-Bu₄NSEO₂Br:** Tetra-n-butylammonium monobromoselenate(IV) was considerably more soluble in MeCN than Ph₄SbSeO₂Br. It was prepared by dissolving stoichiometric amounts of n-Bu₄NBr and SeO₂ in a minimum amount of MeCN and pumping to dryness. A bright yellow compound, n-Bu₄NSEO₂Br, was obtained.

**MSeOBr₃:** Tetramethylammonium, tetraethylammonium and tetraphenylethynylammonium oxotribromoselenates(IV) were all prepared by dissolving 1:1 mixtures of the bromide and SeOBr₂ in a minimum amount of MeCN, crystallizing over dry ice, filtering and pumping dry.

\[ \text{MBr} + \text{SeOBr}_2 = \text{MSeOBr}_3 \]

**Analysis.** Calculated for Me₄NSEOBr₃: C, 11.75%. H, 2.96%. N, 3.42%. Br, 58.63%. Found: C, 11.60%. H, 2.60%. N, 3.46%. Br, 59.06%. Calculated for Et₄NSEOBr₃: C, 20.66%. H, 4.33%. N, 3.01%. Se, 16.98%. Br, 51.56%. Found: C, 20.42%. H, 4.01%. N, 2.90%. Se, 16.77%. Br, 51.47%. Calculated for Ph₄SbSeOBr₃: C, 37.71%. H, 2.64%. Br, 31.36%. Found: C, 35.87%. H, 2.25%. Br, 30.95%. 
Tetra-n-butyrammonium oxotribromoselenate(IV) was very soluble in MeCN. It was prepared by dissolving a 1:1 mixture of n-Bu₄NBr and SeOBr₂ in MeCN and pumping to dryness.

Tetraethylammonium oxotribromoselenate(IV) was also prepared from an aqueous hydrobromic acid solution. In the attempted preparation of Et₄NSeBr₅ from aqueous solution, HBraq (4 moles) was added to a 1:1 mixture of Et₄NBr: SeO₂. An orange precipitate formed which was immediately dissolved in a minimum amount of H₂O, heated slightly, and placed over ice for crystallization. The yellow product obtained was filtered and pumped to dryness. The product was Et₄NSeOBr₃, according to

\[ \text{MBr} + \text{SeO}_2 + 2\text{HBr} = \text{MSeOBr}_3 + \text{H}_2\text{O} \]

M₂SeOBr₄: Tetra-n-butyrammonium oxotetrabromoselenate(IV) was prepared by dissolving a 2:1 mixture of n-Bu₄NBr and SeOBr₂ in MeCN. A yellow compound was obtained upon pumping to dryness.

Tetramethylammonium oxotetrabromoselenate(IV) was prepared by mixing stoichiometric amounts of Me₄NBr, SeO₂ and concentrated HBraq. Evaporating over P₂O₅ yielded the yellow-orange (Me₄N)₂SeOBr₄.

\[ 2\text{MBr} + \text{SeO}_2 + 2\text{HBr} = \text{M}_2\text{SeOBr}_4 + \text{H}_2\text{O} \]
Analysis. Calculated for \((\text{Me}_4\text{N})_2\text{SeOBr}_4\): C, 17.05%. H, 4.29%. N, 4.97%. Br, 56.78%. Found: C, 16.82%. H, 4.17%. N, 4.17%. Br, 56.87%.

\(\text{MSeBr}_5\): Tetra-n-butylammonium and tetramethylammonium pentabromoselenates(IV) were prepared by dissolving 1:1 mole ratios of the bromide and SeBr\(_4\) in a minimum amount of MeCN. The solutions were placed over dry ice and the products which crystallized were filtered and pumped to dryness in the dry box.

Analysis. Calculated for \(\text{n-Bu}_4\text{NSeBr}_5\): C, 26.25%. H, 5.03%. N, 1.94%. Se, 10.95%. Br, 55.41%. Found: C, 27.09%. H, 5.27%. N, 1.92%. Se, 10.94%. Br, 55.67%.

Calculated for \(\text{Me}_4\text{NSeBr}_5\): Br, 72.3%. Found: 71.98%.

\(\text{M}_2\text{SeBr}_6\): Caesium hexabromoselenenate(IV) was prepared by adding a stoichiometric amount of \(\text{Cs}_2\text{CO}_3\) (in excess \(\text{HBr}_{aq}\)) to a saturated solution of SeO\(_2\) in HBr\(_{aq}\). The orange product which precipitated was filtered and pumped to dryness in a vacuum desiccator over P\(_2\)O\(_5\).

Tetraethylammonium hexabromoselenenate(IV) was prepared by dissolving a 2:1 mixture of \(\text{Et}_4\text{NBr}\) and SeBr\(_4\) in MeCN. The dark orange product was crystallized over dry ice and let to dry in the dry box.

Analysis. Calculated for \(\text{Cs}_2\text{SeBr}_6\): Br, 57.48%. Found: 58.17%.

Calculated for \((\text{Et}_4\text{N})_2\text{SeBr}_6\): Br, 58.54%. Found: 58.02%. 
RESULTS AND DISCUSSION

OXOBROMO COMPLEXES OF SELENIUM(IV)

The monobromoselenate(IV) anion, $\text{SeO}_2\text{Br}^-$

Selenium dioxide is known to be polymeric and insoluble in MeCN. However, it dissolves in this solvent in the presence of some soluble ionic bromide, according to:

$$\text{SeO}_2 + \text{Br}^- = \text{SeO}_2\text{Br}^- \quad \text{MeCN}$$

In this way, it behaves much like the corresponding fluorides and chlorides.

The Raman spectra of $\text{Ph}_4\text{SbSeO}_2\text{Br}$, $n\text{-Bu}_4\text{NSeO}_2\text{Br}$ and $\text{SeO}_2\text{Br}^-$ in solution are listed along with the assignment, in Table I. The spectra of $n\text{-Bu}_4\text{NSeO}_2\text{Br}$ and $\text{SeO}_2\text{Br}^-$ in solution are shown in Figure 1. The $\text{SeO}_2\text{Br}^-$ ion is expected to have $C_s$ symmetry and six normal modes ($\Gamma = 4A' + 2A''$).

\[
\begin{array}{c}
\text{O} \\
\text{Se} \\
\text{Br}
\end{array}
\]

Of these, the four $A'$ modes will be polarized. The Raman spectrum of $\text{SeO}_2\text{Br}^-$ in MeCN indicates three polarized modes at 139, 249 and 888 cm$^{-1}$. The highest frequency band is readily assigned to the symmetric $\text{SeO}_2$ stretching vibration $\nu_1(A')$. The lowest frequency and highest intensity band at
139 cm$^{-1}$ is assigned to the SeBr stretching mode, $\nu_2(A')$. There are two remaining polarized bands but only one is seen in solution. Both of these bands are symmetric deformations. Of these deformations, the symmetric SeO$_2$ deformation, $\nu_3(A')$, is expected to have the highest frequency. Therefore, the lower frequency band at 249 cm$^{-1}$ is assigned to $\nu_4(A')$, the symmetric SeOBr deformation. The symmetric SeO$_2$ deformation is seen in both solids at 396 cm$^{-1}$ for Ph$_4$SbSeO$_2$Br and 379 cm$^{-1}$ for n-Bu$_4$NSeO$_2$Br. Of the two remaining modes, the highest frequency one, 814 cm$^{-1}$ in Ph$_4$SeO$_2$Br, is assigned to the antisymmetric SeO$_2$ stretching vibration, $\nu_5(A'')$. The last vibrational mode, 169 cm$^{-1}$ in n-Bu$_4$NSeO$_2$Br and 172 cm$^{-1}$ in Ph$_4$SbSeO$_2$Br, is assigned to the antisymmetric SeOBr deformation, $\nu_6(A'')$. All lower frequency bands in the solid spectra are due to lattice vibrations. This assignment is supported by the great similarity in the vibrational spectrum of SeO$_2$Br$^-$ to those of SeO$_2$Cl$^-$ 10 and SeO$_2$F$^-$ 5.

The shift to lower frequency of the symmetric and antisymmetric SeO$_2$ stretching modes in Ph$_4$SbSeO$_2$Br and the difference in the intensities of these modes compared to what is observed in solution is an indication that there is probably some oxygen bridging present.
Table I. Raman spectra of the SeO$_2$Br$^-$ anion.

<table>
<thead>
<tr>
<th>Ph$_4$SbSeO$_2$Br</th>
<th>n-Bu$_4$NSEo$_2$Br</th>
<th>SeO$_2$Br$^-$ in MeCN$^a$</th>
<th>Mode No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>66(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>83(10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Lattice Modes</td>
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<tr>
<td></td>
<td>144(10)</td>
<td>139(10, p)</td>
<td>$\nu_2$(A$'$)</td>
<td>$\nu_s$(SeBr)</td>
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<tr>
<td>172(9, br)</td>
<td>169(1, sh)</td>
<td>-</td>
<td>$\nu_6$(A$''$)</td>
<td>$\delta_{as}$(SeOBr)</td>
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<tr>
<td>214(6)</td>
<td>253(1)</td>
<td>249(1, p)</td>
<td>$\nu_4$(A$'$)</td>
<td>$\delta_s$(SeOBr)</td>
</tr>
<tr>
<td>396(0)</td>
<td>379(0)</td>
<td>-</td>
<td>$\nu_3$(A$'$)</td>
<td>$\delta_s$(SeO$_2$)</td>
</tr>
<tr>
<td>814(1)</td>
<td>-</td>
<td>-</td>
<td>$\nu_5$(A$''$)</td>
<td>$\nu_{as}$(SeO$_2$)</td>
</tr>
<tr>
<td>864(3)</td>
<td>882(2)</td>
<td>888(6, p)</td>
<td>$\nu_1$(A$'$)</td>
<td>$\nu_s$(SeO$_2$)</td>
</tr>
</tbody>
</table>

a. n-Bu$_4$NSEo$_2$Br
Figure 1

Raman Spectra of $n$-Bu$_4$NSeO$_2$Br

A in acetonitrile

B in solid
S = SOLVENT
α = ANION
C = CATION
Solutions of Br\textsuperscript{-}: SeO\textsubscript{2} up to 4:1 mole ratio in MeCN showed no change in the Raman spectrum of the anion compared to a solution which is 1:1 bromide to SeO\textsubscript{2}. Apparently, the formation constant of the dibromoselenenate(IV) anion is very small compared to the monobromoselenenate(IV) anion\textsuperscript{10}. Wasif and Salama\textsuperscript{9} have shown, via UV spectroscopy, that SeO\textsubscript{2}, which is soluble in dimethyl sulfoxide (DMSO), forms a 1:1 complex with halide ion in DMSO. According to their stability constant, a 1M SeO\textsubscript{2}Br\textsuperscript{-} solution in DMSO is approximately 25\% dissociated. No evidence of dissociation of the SeO\textsubscript{2}Br\textsuperscript{-} ion in MeCN has been found. This can be seen by the Raman spectrum and the absence of SeO\textsubscript{2}, which is insoluble in MeCN.

Wasif and Salama\textsuperscript{9} have concluded that SeO\textsubscript{2} acts as a hard Lewis acid and the stability of the SeO\textsubscript{2}X\textsuperscript{-} species is as follows:

$$\text{SeO}_2\text{F}^- \rightarrow \text{SeO}_2\text{Cl}^- \rightarrow \text{SeO}_2\text{Br}^-$$

which is also the order of decreasing halide base hardness\textsuperscript{38, 39}. This behaviour is reflected in the ease of preparation of the monofluoroselenenate(IV) anion\textsuperscript{5} with small cations such as K\textsuperscript{+} and Cs\textsuperscript{+} and the preparation of the monochloroselenenate(IV) anion\textsuperscript{10} with Me\textsubscript{4}N\textsuperscript{+} as cation compared to the limited capability of preparing the monobromoselenenate(IV) complexes with such small cations. The attempted preparation of the monobromoselenenate(IV) complexes with Cs\textsuperscript{+}, Et\textsubscript{4}N\textsuperscript{+} and Me\textsubscript{4}N\textsuperscript{+} yielded SeO\textsubscript{2} and the simple bromide upon cooling.
Seleninyl Bromide, SeOBr₂

The Raman spectrum of SeOBr₂ has been reported by two groups. The spectrum of Futek and Specker⁴⁴ which has been partially assigned, has two bands, at 172 cm⁻¹ and 310 cm⁻¹ which do not appear in the spectrum of SeOBr₂ in the present work nor in that of Brockner and Demiray¹⁹. The present results, shown in Table II and Fig. 2, agree well with those of Brockner and Demiray although there are significant differences in the solid spectra. The spectrum they reported was taken at -196°C compared to 25°C for the present study. The differences are due, no doubt, to some phase change occurring between these two temperatures.

Only 5 of the 6 expected bands (I₃₅ = 4A′ + 2A″) appear in the liquid¹⁹ and solution spectra (Fig. 2). Since two strongly polarized bands appear between 200 and 300 cm⁻¹ and it is somewhat uncertain which is due to the symmetric SeBr stretch, ν₂(A′) and which is the symmetric SeOBr deformation ν₃(A′), a complete assignment of the SeOBr₂ spectrum is difficult. The highest and lowest frequency bands in the solution spectrum, 955 and 90 cm⁻¹, both of which are polarized, are readily assigned to ν₁(A′), the SeO stretch and ν₄(A′) the SeBr₂ deformation. The two remaining polarized modes belong to ν₂(A′) and ν₃(A′). Consideration of the SeOX symmetric deformations (ν₃) in the spectra of
Table II. Solid and solution Raman spectra of seleninyl bromide.

<table>
<thead>
<tr>
<th>SeOBr$_2$ at 25°C</th>
<th>SeOBr$_2$ in MeCN</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>97(10)</td>
<td>90(7,p)</td>
<td>$\nu_4$(A') $\delta_s$(SeBr$_2$)</td>
</tr>
<tr>
<td>200(7)</td>
<td>194(2,dp)</td>
<td>$\nu_6$(A'') $\delta_{as}$(SeOBr)</td>
</tr>
<tr>
<td>222(10)</td>
<td>218(10,p)</td>
<td>$\nu_3$(A') $\delta_s$(SeOBr)</td>
</tr>
<tr>
<td>265(5)</td>
<td></td>
<td>$\nu_5$(A'') $\nu_{as}$(SeBr$_2$)</td>
</tr>
<tr>
<td>282(5,sh)</td>
<td>279(9,p)</td>
<td>$\nu_2$(A') $\nu_s$(SeBr$_2$)</td>
</tr>
<tr>
<td>292(7)</td>
<td></td>
<td>$\nu_1$(A') $\nu$(SeO)</td>
</tr>
<tr>
<td>883(3)</td>
<td>955(2,p)</td>
<td>$\nu_1$(A') $\nu$(SeO)</td>
</tr>
</tbody>
</table>
Figure 2

Raman spectra of SeOBr$_2$

A in acetonitrile

B solid
SeOF$_2$\textsuperscript{12,14} and SeOCl$_2$\textsuperscript{13,16-18} shows that there is little change in frequency with change in mass of X (Fig. 3) and a frequency for SeOBr$_2$ can be quite reliably estimated to be 200 cm$^{-1}$. The SeOBr symmetric deformation is thus assigned to the mode at 218 cm$^{-1}$. The SeBr symmetric stretch, $\nu_2(A')$, is expected to be at higher frequency than $\nu_3(A')$, from comparison of SeOF$_2$ and SeOCl$_2$ liquid spectra, therefore the band at 279 cm$^{-1}$ is assigned to $\nu_2(A')$. This is supported by the fact that in the spectrum of SeOBr$_2$ in MeCN, the degree of polarization of the lower of the two bands is greater which is the expected situation judging from the spectrum of SeOCl$_2$ \textsuperscript{41}. The two remaining bands to be assigned are $A''$ modes, an SeBr antisymmetric stretch, $\nu_5(A'')$, and an SeOBr antisymmetric deformation, $\nu_6(A'')$. Only one depolarized band, at 194 cm$^{-1}$, is observed in the solution spectrum of SeOBr$_2$ but the sixth vibrational mode is observed in the solid spectrum at 265 cm$^{-1}$. This band is evidently masked in the solution spectrum by the stronger $\nu_2(A')$ band at 279 cm$^{-1}$. The two SeX stretching modes, $A'$ and $A''$, and the two SeOX deformations, also $A'$ and $A''$, make up two closely spaced pairs of bands in the case of liquid SeOCl$_2$ and SeOF$_2$. The two $A''$ modes for SeOBr$_2$ are assigned consistent with this. Thus the band at 194 cm$^{-1}$ is assigned to $\nu_6(A'')$, the antisymmetric SeOBr deformation mode, and the hidden band lying under the envelope at 279 cm$^{-1}$ is assigned
Figure 3

Plot of stretching frequencies

$\nu_2$ and $\nu_3$ in SeOX$_2$ species
to $\nu_5(A''$), the antisymmetric SeBr stretching vibration. It should be noted that this assignment resembles that of Futekov and Specker\textsuperscript{44}, which has the SeBr stretching modes at higher frequency than the SeOBr\textsubscript{2} deformations. The complete assignment is given in Table II.

Comparison of the solid and solution spectra of SeOBr\textsubscript{2} leads to conclusions concerning the structure similar to those for SeOF\textsubscript{2} and SeOCl\textsubscript{2}. The solid shows evidence of oxygen bridging by the drop in frequency of the SeO stretching mode, going from solution to solid, and also by the fact that this mode is split, as it is in solid SeOCl\textsubscript{2}\textsuperscript{19} and solid SeOF\textsubscript{2}\textsuperscript{12}. However, contrary to SeOCl\textsubscript{2} and SeOF\textsubscript{2}, we can only speculate that there may be some bromide bridging.

The oxotribromoselenate(IV) anion, SeOBr\textsubscript{3}⁻

The Raman spectra of Et\textsubscript{4}NSeOBr\textsubscript{3} as a solid and n-Bu\textsubscript{4}NSeOBr\textsubscript{3} in solution are shown in Fig. 4 and listed along with the spectra of Me\textsubscript{4}NSeOBr\textsubscript{3}, Et\textsubscript{4}NSeOBr\textsubscript{3} and Ph\textsubscript{4}SbSeOBr\textsubscript{3} in Table III. The Raman spectra of solid Et\textsubscript{4}NSeOBr\textsubscript{3}, n-Bu\textsubscript{4}NSeOBr\textsubscript{3} and Ph\textsubscript{4}SbSeOBr\textsubscript{3} are very similar to each other and to the spectrum of the SeOBr\textsubscript{3}⁻ ion in MeCN solution and are consistent with an isolated SeOBr\textsubscript{3}⁻ ion with Cs symmetry ($\Gamma = 6A' + 3A''$).
This ion is expected to have nine bands in its Raman spectrum of which six will be polarized. Because of the greater bond strength of equatorial ligands compared to axial ligands in a trigonal bipyramidal structure, two sets of SeBr stretching vibrations are expected, a single mode at higher frequencies for the equatorial bromine and two bands, symmetric and antisymmetric, for the axial bromines. This situation exists in SeOCl$_3^-$ where the SeCl equatorial stretch occurs at 336 cm$^{-1}$ while the SeCl axial symmetric and antisymmetric stretches occur at 248 and 228 cm$^{-1}$, respectively. In the spectrum of the SeOBr$_3^-$ anion the band at 936 cm$^{-1}$ is readily assigned to the symmetric SeO stretch, $\nu_1$(A$'$). In the spectrum of the SeOCl$_3^-$ anion the equatorial SeCl stretch, $\nu_2$(A$'$), occurs at 336 cm$^{-1}$ and is close to the mean of the SeCl stretching frequencies in the corresponding seleninyl halide, SeOCl$_2$, which is 353 cm$^{-1}$. On a similar basis, the polarized band at 265 cm$^{-1}$ for the SeOBr$_3^-$ anion is
Table III. Raman spectra of the oxotribromoselenenate(IV) anion.

<table>
<thead>
<tr>
<th>Me₄NSeOB₃</th>
<th>(Me₄N)₂SeOBr₄</th>
<th>Et₄NSeOB₃</th>
<th>n-Bu₄NSeOB₃</th>
<th>Ph₄SbSeOB₃</th>
<th>SeOBr₃⁻</th>
<th>Assignment</th>
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<td>74(1,sh)</td>
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<td>101(1)</td>
<td>82(0)</td>
<td>86(2)</td>
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<td>253(2,p?)</td>
<td>262(2)</td>
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<td>939(1)</td>
<td>928(1)</td>
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</tr>
</tbody>
</table>

a. n = Bu₄NSeOB₃

- ν₅(A')  δₛ(SeOBr₃)
- ν₇(A'')  νₐₛ(SeBr₃)
- ν₃(A')  νₛ(SeBr₃)
- ν₄(A')  δ(SeO, in plane)
- ν₂(A')  ν(SeBrₑq)
- ν₁(A')  ν(SeO)
Figure 4

Raman Spectra of the SeOBr$_3^-$ ion

A  in acetonitrile (n-Bu$_4$NSeOBr$_3$)

B  solid Et$_4$NSeOBr$_3$
assigned to $\nu_2(A')$, close to the mean of the SeBr stretching frequencies in SeOBr$_2$, which is 284 cm$^{-1}$. The SeBr equatorial stretch in the T-shaped SeBr$_3$-ion$^{49}$, which is structurally closely related to the SeBr$_3$ unit in the trigonal bipyramidal SeOBr$_3$-ion, occurs at 264 cm$^{-1}$. The band at 155 cm$^{-1}$, which is depolarized, is assigned to the antisymmetric SeBr stretching mode, $\nu_7(A'^\prime)$. The symmetric SeBr stretching mode is expected to lie at higher frequency than the corresponding antisymmetric mode$^{10}$. Just as in the case of the SeBr$_3$-ion a similar and very close parallel exists between SeCl$_3$- $^{49}$ and SeOCl$_3$-. The three SeCl stretching modes and the analogous modes in SeOCl$_3$- are alike in their relative positions and their polarizations. The peak at 253 cm$^{-1}$, which appears to be polarized, is assigned to the symmetric SeO deformation, $\nu_4(A')$. The analogous deformation occurs at 268 cm$^{-1}$ in SeOCl$_2$ $^{50}$ and 287 cm$^{-1}$ in SeOCl$_3$- $^{10}$. The remaining polarized band at 138 cm$^{-1}$ is assigned to the last A' mode, the symmetric SeOBr deformation, $\tilde{\nu}_5(A')$. The other deformations, $\nu_6(A')$, $\nu_8(A'^\prime)$ and $\nu_9(A'^\prime)$, are not observed in solution and cannot justifiably be distinguished from lattice modes in the solids. They are expected to occur at frequencies lower than the SeBr stretching vibrations.
The Raman spectrum of Me₄NSeOBr₃ consists of 13 anion lines in the spectral region studied (50 - 1000 cm⁻¹), and the structure is apparently more complex than that of the isolated SeOBr₃⁻ anion. As in the case of KSeOCl₃¹⁰, which is polymeric, the shifts in some of the bands, particularly the SeO stretching vibration to lower frequency, and the increase in the number of bands in the SeO deformation region, seem to indicate that oxygen bridging is likely. Both halogen and oxygen bridging are observed in oxotrichloroselenates(IV)¹⁰,²³ and the smaller cation size favours anion bridging. Attempts to prepare CsSeOBr₃ from CsBr and SeOBr₂ in acetonitrile lead to the formation of SeO₂ and Cs₂SeBr₆.

The oxotetrabromoselenenate(IV) anion, SeOBr₄²⁻

The spectra of (n-Bu₄N)₂SeOBr₄ solid and in solution are shown in Fig. 5 and listed in Table IV. The addition of n-Bu₄NBr to a 1M solution of n-Bu₄NSeOBr₃ in MeCN causes the strong peaks of the SeOBr₃⁻ ion (138, 155 and 194 cm⁻¹) to be replaced by a single strong feature with a weak shoulder at 158 cm⁻¹. As in the case of the oxotetra-chloroselenates(IV)³¹, the oxotetrabromoselenenate(IV) is formed,

\[
\text{SeOBr}_3^- + \text{Br}^- \rightarrow \text{SeOBr}_4^{2-} \text{MeCN}
\]
Evaporation of a 2:1 solution of n-Bu₄NBr: SeOBr₂ gave an orange product with a Raman spectrum quite similar to the solution spectrum. When a bromide with a smaller cation than n-Bu₄N⁺, such as Me₄N⁺ or Et₄N⁺, was used in attempts to make the oxotetrabromoselenenate(IV), oxotribromoselenates(IV) were formed. Apparently, the oxotribromoselenates(IV) of these smaller cations are less soluble than the oxotetrabromoselenates(IV) and the SeOBr₄²⁻-ion is sufficiently dissociated to SeOBr₃⁻ that the oxotetrabromoselenenate(IV) cannot be prepared in this way. The Raman spectra of solutions where the bromide to SeOBr₂ molar ratio exceeds 2:1 show no changes compared to the 2:1 solution except for increases in cation bands. A series of solutions of 2:1 n-Bu₄NBr:SeOBr₂ in MeCN had Raman spectra that did not change in the range 1.0 to 0.1 molal. Only below 0.1 molal was the detection of some oxotribromoselenenate(IV) possible indicating that the dissociation is completely repressed above 0.1 molal.

Since the Raman spectra of (n-Bu₄N)₂SeOBr₄ and SeOBr₄²⁻ in MeCN are very similar to each other and much different from the SeOBr₃⁻-ion indicates the presence of a new ion. The expected stereochemistry for this anion is that of a square pyramid with the oxygen axial and trans to the lone electron pair.
Table IV. Raman spectra of the oxotetraphosphoselenate(IV) anion

<table>
<thead>
<tr>
<th>(n-Bu₄N)₂SeOBr₄</th>
<th>SeOBr₄²⁻ in MeCN²</th>
<th>Mode No.</th>
<th>Description</th>
</tr>
</thead>
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<tr>
<td>89(2)</td>
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<td></td>
<td>deformations, Lattice Modes</td>
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<td>110(2)</td>
<td>-</td>
<td></td>
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<tr>
<td>128(3)</td>
<td>141 (5,p?)</td>
<td>\nu₇(E₁)</td>
<td>\nu_{as}(SeBr₄)</td>
</tr>
<tr>
<td>156(10)</td>
<td>158 (10,p)</td>
<td>\nu₂(A₁)</td>
<td>\nu_{s}(SeBr₄, in phase)</td>
</tr>
<tr>
<td>178(2)</td>
<td>193(3,dp)</td>
<td>\nu₄(B₁)</td>
<td>\nu_{s}(SeBr₄, out of phase)</td>
</tr>
<tr>
<td>256(3)</td>
<td>265(2,dp)</td>
<td>\nu₈(E)</td>
<td>\delta(SeO, wag)</td>
</tr>
<tr>
<td>941(1)</td>
<td>932(1,p)</td>
<td>\nu₁(A₁)</td>
<td>\nu(SeO)</td>
</tr>
</tbody>
</table>

a. (n-Bu₄N)₂SeOBr₄
Figure 5

Raman Spectra of \((n-\text{Bu}_4\text{N})_2\text{SeOBr}_4\)

A in acetonitrile

B solid
For this $C_{4v}$ structure, nine normal modes are expected. ($\Gamma = 3A_1 + 2B_1 + B_2 + 3E$). The spectra in Fig. 5 show seven definite bands, of which two are clearly polarized. The spectra are more consistent with the $C_{4v}$ structure than with other possible structures such as a square pyramid with the oxygen in the energetically less favourable cis position (to the lone pair), giving this model $C_s$ symmetry with irreducible representation $\Gamma = 8A' + 4A''$.

If the electron pair is stereochemically inactive we could expect a trigonal bipyramidal structure with the oxygen equatorial.
In this case, the symmetry is $C_{2v}$ and 5 polarized bands are expected, $\Gamma = 5A_1 + A_2 + 3B_1 + 3B_2$. In both these latter cases, more polarized bands would be expected than are actually observed in the spectrum of SeOBr$_4^{2-}$ in MeCN.

A partial assignment under $C_{4v}$ symmetry is given in Table IV. On the basis of their intensity and polarization the bands at 932 and 158 cm$^{-1}$ are readily assigned to $\nu_1(A_1)$, the SeO stretching mode, and $\nu_2(A_1)$, the SeBr$_4$ symmetric in phase stretching mode, respectively. The broad peak near 260 cm$^{-1}$ consists of two peaks as shown by the spectrum with the polarization of the incident laser beam rotated 90°. The lower frequency band at 248 cm$^{-1}$ is polarized and belongs to the tetrabutylammonium cation while the band at higher frequency, 265 cm$^{-1}$, is assigned to the SeO deformation, $\nu_8(E)$. The position of this mode is comparable with that of the SeO deformations in SeOBr$_3^{2-}$ (Table III), SeOCl$_3^{2-}$ 10 and SeOCl$_4^{2-}$ 31. It is difficult to decide whether the shoulder on the low frequency side of $\nu_2(A_1)$ at 141 cm$^{-1}$ is polarized or not but it is unlikely
that it is, since the only remaining $A_1$ mode is the SeBr$_4$ umbrella vibration, $\nu_3(A_1)$, which lies at 142 cm$^{-1}$ in the spectrum of SeOCl$_4^{2-}$, and is expected to lie far below 141 cm$^{-1}$ in the SeOBr$_4^{2-}$ spectrum. The shoulders at 141 and 193 cm$^{-1}$ are assigned instead to the two remaining SeBr vibrations, $\nu_4(B_1)$ and $\nu_7(E)$. Since, in the spectra of the related species SeCl$_5^{-}$, TeOF$_4^{2-}$, and TeCl$_5^{-}$, $\nu_4(B_1)$ lies at higher frequency than $\nu_7(E)$, the band at 141 cm$^{-1}$ is assigned to $\nu_7(E)$, the antisymmetric SeBr$_4$ stretching mode and the band at 193 cm$^{-1}$ is assigned to $\nu_4(B_1)$, the symmetric SeBr$_4$ out of phase stretch. The remaining bands at 89 and 110 cm$^{-1}$ may be due to anion deformations but due to their position no clear distinction can be made between these and lattice modes.

Attempts were made to prepare oxotetram bromoselenates(IV) from aqueous solution but only in the case of the tetramethylammonium bromide was a compound of the correct stoichiometry formed. The Raman spectrum of this compound resembles closely the spectrum of the oxotribromoselenate(IV) anion and is therefore listed in Table III. The compound is best formulated as Me$_4$NSeOBr$_3$.Me$_4$NBr. Similarly, dipyridinium oxotetrachloroselenate(IV) has been found to be made up of SeOCl$_3^{-}$ anions with secondary bonding to chloride ions which leaves the trigonal bipyramidal structure of the SeOCl$_3^{-}$ ion essentially unaltered.
The pentabromoselenenate(IV) anion, SeBr$_5^-$

The spectra of the SeBr$_5^-$ anion show considerable variation in solids, melt and concentrated and dilute solutions in MeCN. The spectra of solid n-Bu$_4$NSeBr$_5$ and solid Me$_4$NSeBr$_5$ are shown in Fig. 6. The spectra of a melt of n-Bu$_4$NSeBr$_5$ and a saturated solution of n-Bu$_4$NSeBr$_5$ in MeCN are shown in Fig. 7. Fig. 8 shows the spectrum of SeBr$_5^-$ in MeCN. All spectra are listed in Table V. Over the concentration range 0.21 molal to 0.036 molal n-Bu$_4$NSeBr$_5$ in MeCN the normalized intensities (with respect to the 912 cm$^{-1}$ band of MeCN having an intensity of 1 cm) of the peaks at 150 and 250 cm$^{-1}$ show a linear dependence on concentration (Fig. 9), suggesting a single species in solution. The profile of the spectrum also remains the same. As the concentration of the solute is increased above 0.21 molal the peak at 250 cm$^{-1}$ grows in intensity relative to that at 150 cm$^{-1}$ and shifts to lower energy. In addition, a band grows in at 183 cm$^{-1}$. The spectrum of molten n-Bu$_4$NSeBr$_5$, which melts in the range 58–60°C, is similar to that of the saturated solution although the band at 150 cm$^{-1}$ is much less intense. These changes are attributed to the condensation of the anion to form polymeric species like those formed in the case of TeCl$_5^-$ 53, TeBr$_5^-$ 54 and BiBr$_5^{2-}$ 55, which are all isoelectronic with SeBr$_5^-$ in valence electrons.

$n$SeBr$_5^-$ $= (SeBr_5)_n$
Some indication of the formation of bridged species has been found for the pentachloroselenenate(IV) anion\textsuperscript{10} as well.

Selenium tetrabromide is known to be fully dissociated\textsuperscript{56} in a wide range of solvents to give an equilibrium mixture of selenium mono- and dibromides and elementary bromine. In the gas phase, SeBr\textsubscript{4} decomposes completely to SeBr\textsubscript{2} and Br\textsubscript{2}. In MeCN, the same holds true according to the reaction,

\[
\text{SeBr}_4^- = \text{SeBr}_2^- + \text{Br}_2(\text{g})
\]

Further decomposition to Se\textsubscript{2}Br\textsubscript{2} is a minor reaction, if it occurs at all in MeCN. The pentabromoselenenate (IV) anion may undergo related reactions,

\[
\text{SeBr}_5^- = \text{SeBr}_3^- + \text{Br}_2 \quad (2)
\]
\[
\text{SeBr}_5^- = \text{SeBr}_2^- + \text{Br}_3^- \quad (3)
\]

Another possible decomposition reaction, which does not involve a change of valence of selenium is

\[
2\text{SeBr}_5^- = \text{SeBr}_4^- + \text{SeBr}_6^{2-} \quad (4)
\]
followed by a subsequent decomposition according to (1). Solutions of Br$_2$ in MeCN where [Br$_2$] = 2.43 molal indicate that the band due to bromine at 304 cm$^{-1}$ is approximately 8 times more intense than the 375 cm$^{-1}$ band of the solvent MeCN. If reactions (2) or (4) proceed to completion, the expected bromine concentrations for the 0.206 molal SeBr$_5^-$ solution, the spectrum of which is shown in Fig. 8, would be respectively 0.206 molal and 0.103 molal in bromine. At these concentrations any band due to bromine would be readily noticed. Since no band is observed at 304 cm$^{-1}$, bromine cannot be an important component. Equilibrium (3) could, however, be occuring in solutions of n-Bu$_4$NSeBr$_5$, since a peak at 280 cm$^{-1}$ is observed in Fig. 8, which is the frequency of the strongest band characteristic for SeBr$_2$ $^{57}$. The concentration of SeBr$_2$ in this solution is estimated to be 0.05m on the basis of quantitative measurements of the Raman spectrum of SeBr$_2$ in MeCN$^{57}$. The spectrum in Fig. 8 is, however, due for the most part to the SeBr$_5^-$ anion. Any bands due to Br$_3^-$ in this solution would be masked since they are not intense and occur at 160 and 190 cm$^{-1}$ $^{58}$.

The isolated SeBr$_5^-$ anion is expected to have C$_{4v}$ symmetry ($\Gamma = 3A_1 + 2B_1 + B_2 + 3E$) just as is the case with SeCl$_5^-$ $^{10}$. 
Figure 6

Raman Spectra of solid $\text{SeBr}_5^-$ compounds

A $\text{n-Bu}_4\text{NSeBr}_5$

B $\text{Me}_4\text{NSeBr}_5$
Figure 7

Raman Spectra of n-Bu₄NSeBr₅

A as a melt

B saturated in acetonitrile
Figure 8

Raman Spectrum of SeBr$_5^-$ in acetonitrile
Figure 9

Plot of normalized intensities of the bands at 150 and 250 cm$^{-1}$ in SeBr$_5^-$ versus concentration
All nine vibrational modes will be active in the Raman spectrum and of these, three will be polarized. In the spectrum of SeBr$_5^-$ in MeCN, we find that there are 3 polarized bands and one single depolarized band. This observation is not consistent with a trigonal bipyramidal geometry ($D_{3h}$: $\Gamma = 2A_1 + 2A_2'' + 3E' + E''$) which would arise if the lone electron pair were stereochemically inactive.

In this model, there are three stretching modes active in the Raman effect, two of which are polarized, and all of the deformations are depolarized.

Thus, the spectra are more consistent with the $C_{4v}$ structure. In the spectrum of a square pyramidal species, the axial ligand stretching vibration, $\nu_1(A_1)$, has the highest frequency. In SeBr$_5^-$ this mode is assigned to the band at 247 cm$^{-1}$. The most intense band, at 151 cm$^{-1}$, which is also polarized, is readily assigned to the symmetric in
Table V. Raman spectra of the pentabromoselenenate(IV) anion

<table>
<thead>
<tr>
<th>Me₄NSeBr₅</th>
<th>n-Bu₄NSeBr₅</th>
<th>n-Bu₄NSeBr₅</th>
<th>n-Bu₄NSeBr₅</th>
<th>SeBr₅⁻</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(solid)</td>
<td>(molten, 60°C)</td>
<td>(Sat'd in MeCN)</td>
<td>in MeCN³</td>
<td>Mode No.</td>
<td>Description</td>
</tr>
<tr>
<td>95(0)</td>
<td>98(0)</td>
<td>98(1)</td>
<td>95(0, br)</td>
<td>112(1, p?)</td>
<td>ν₃(A₁) $\delta_s$(SeBr₄, umbrella)</td>
</tr>
<tr>
<td>147(3)</td>
<td>132(1)</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>163(1)</td>
<td>145(1)</td>
<td>152(10, p)</td>
<td>151(10, p)</td>
<td>151(10, p)</td>
<td>ν₂(A₁) ν(SeBr₄, in phase)</td>
</tr>
<tr>
<td>-</td>
<td>196(10)</td>
<td>190(2)</td>
<td>190(2)</td>
<td>180(2, sh)</td>
<td>ν₄(B₁) ν(SeBr₄, out of phase)</td>
</tr>
<tr>
<td>220(0)</td>
<td>228(3)</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>261(10)</td>
<td>257(2)</td>
<td>248(10, p, br)</td>
<td>243(7, p, br)</td>
<td>247(2, p)</td>
<td>ν₁(A₁) ν(SeBr₄x)</td>
</tr>
<tr>
<td>295(0)</td>
<td>-</td>
<td>280(1, sh)</td>
<td>-</td>
<td>280(1, sh)</td>
<td>ν(SeBr in SeBr₂)</td>
</tr>
</tbody>
</table>

a. 0.21 m n-Bu₄NSeBr₅
phase SeBr₄ stretching vibration, \( \nu_2(A_1) \). The third polarized mode at 112 cm\(^{-1}\) is assigned to the last \( A_1 \) mode, the umbrella deformation, \( \nu_3(A_1) \). The only depolarized band, that at 180 cm\(^{-1}\), is assigned to the symmetric out of phase SeBr₄ stretching vibration, \( \nu_4(B_1) \). Since this is the only depolarized band seen and is expected to be more intense than the antisymmetric SeBr₄ stretching mode, \( \nu_7(E) \), as in the case of SeCl₅\(^-\) \textsuperscript{10}, this assignment is preferred over \( \nu_7(E) \). In SeCl₅\(^-\), the antisymmetric SeCl₄ stretching vibration, \( \nu_7(E) \), lies very close to the symmetric out of phase stretch, \( \nu_4(B_1) \), and in SeOCl₄\(^2-\) \textsuperscript{31} these two modes are coincident. However, in SeOBr₄\(^2-\) the corresponding \( \nu_7(E) \) mode is expected to lie at much lower frequency than \( \nu_4(B_1) \) and hence \( \nu_7(E) \) is not seen in the spectrum of SeBr₅\(^-\). The \( \nu_7(E) \) mode, since it lies at low frequency, may be lost in the Rayleigh scattered background (Fig. 8).

The spectra of solid Me₄NSeBr₅ and n-Bu₄NSeBr₅, listed in Table V and shown in Fig. 6, exhibit little parallel with each other or with the dilute solution spectra although the strongest peaks in the spectra of both solids are observed in the spectra of the saturated solution in MeCN and the melt of n-Bu₄NSeBr₅ (Fig. 7). Several structures may be adopted by the SeBr₅\(^-\) anion in condensed form. The polymer may be cis or trans bridged.
The crystal structure of $\text{PCl}_4^+\text{TeCl}_5^-$ shows $[\text{TeCl}_5^-]_n$ chains with cis bridging and overall pseudo-octahedral coordination of Te$^{53}$. The chloride bridges in the structure are symmetric and have relatively long Te-Cl bonds while the Te-Cl bonds trans to the bridging chlorides and the Te-Cl bonds above and below the bridging plane are short. The cubane like $\text{Te}_4\text{Br}_{16}$ $^{54}$, which is isomorphous with $\text{SeBr}_4$, can be reacted with bromide to form monomeric and oligomeric halogenotellurates. The dimeric $\text{Te}_2\text{Br}_{10}^{2-}$ anion$^{54}$ consists of two distorted TeBr$_6$ octahedra sharing an edge. It is not possible to determine unequivocally between the two
structures proposed for \((\text{SeBr}_5)_n^+\). The isoelectronic species, \(\text{BiBr}_5^2^-\) 59, has been studied by vibrational spectroscopy and found to have overall \(C_{2v}\) site symmetry although it has pseudo-octahedral coordination around bismuth and has two bridging bromines.

When dilute solutions of \(\text{Me}_4\text{NSeBr}_5\) are made up in aqueous medium, some elemental bromine is expelled, as is indicated by the oxidation of iodide ion giving the \(\text{CCl}_4\) layer a light reddish color upon vigorous shaking. This does not occur with \(\text{n-Br}_4\text{NSeBr}_5\). At first, it was thought that there may be some molecular bromine bridging as is the case in \(\text{Sb}_2\text{Br}_9^{3-}\) 60. However, when \(\text{Me}_4\text{NSeBr}_5\) is dissolved in MeCN, a solvent which it is not very soluble in, no band due to elemental bromine is seen in the Raman spectrum. An attempt to form the isoelectronic analogue to \(\text{Sb}_2\text{Br}_9^{3-}\), \(\text{Se}_2\text{Br}_9^-\) in MeCN solution, leads only to an increase in the intensity of the bands at 280 cm\(^{-1}\) and 304 cm\(^{-1}\) relative to the bands due to \(\text{SeBr}_5^-\), indicating the presence of \(\text{SeBr}_4\) in equilibrium with \(\text{SeBr}_2\) and \(\text{Br}_2\) (equation 1). However, when concentrated solutions of \(\text{Me}_4\text{NSeBr}_5\) in aqueous solution are made up, the presence of bromine is more obvious in the \(\text{CCl}_4\) layer. Concentrated solutions yield low bromide analyses.

Possibly, in the case of \(\text{Me}_4\text{NSeBr}_5\), an adduct exists as it does in Quinuclidinium Dodecabromantimon(III) antimon(V)ate-2-Dibromine, \((\text{C}_7\text{H}_{13}\text{NH})_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12.2}\text{Br}_2\) 61.
The crystals of this compound consist of cations, SbBr$_6^{3-}$ and SbBr$_6^{-}$ anions and molecular bromine which bridges adjacent anions. We can only speculate that the larger cation stabilizes the SeBr$_5^{-}$ anion to a greater extent and that in Me$_4$NSeBr$_5$ some of the Se-Br bonds are more labile than in n-Bu$_4$NSeBr$_5$ leading to the evolution of elemental bromine when a large amount of Me$_4$NSeBr$_5$ is dissolved in aqueous medium.

The hexabromoselenate(IV) anion, SeBr$_6^{2-}$

A non-octahedral structure is predicted for AX$_6$E molecules by the valence shell electron pair repulsion (VSEPR) theory$^2$. The theory states that they should be based on a seven coordinate structure with a lone pair of electrons in one of the positions. Despite the prediction by VSEPR theory, many AX$_6$E molecules exhibit octahedral symmetry. In fact, more examples are currently known where the lone pair is stereochemically inactive$^{38}$ than where it is active. However, one example, XeF$_6$ $^{38}$, is known to have a distorted structure. Gillespie explains the failure of VSEPR theory as due to ligand-ligand repulsions dominating the stereochemistry.

The Raman spectra of solid Cs$_2$SeBr$_6$ and (Et$_4$N)$_2$SeBr$_6$ are shown in Fig. 10. The spectrum of (Et$_4$N)$_2$SeBr$_6$ in MeCN is shown in Fig. 11 and all spectra are listed in Table VI. There is no evidence in the solution
Table VI. Raman spectra of the hexabromoselenate(IV) anion

<table>
<thead>
<tr>
<th></th>
<th>(\text{Cs}_2\text{SeBr}_6^a)</th>
<th>((\text{Et}_4\text{N})_2\text{SeBr}_6^a)</th>
<th>(\text{SeBr}_6^{2-}) in (\text{MeCN}^b,c)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>98(7)</td>
<td>90(3)</td>
<td>-</td>
<td>(\nu_5(T_{2g}))</td>
<td></td>
</tr>
<tr>
<td>145(5)</td>
<td>143(10)</td>
<td>153(10,p)</td>
<td>(\nu_1(A_{1g}))</td>
<td></td>
</tr>
<tr>
<td>162(10)</td>
<td>160(7)</td>
<td>165(2,sh)</td>
<td>(\nu_2(E_g))</td>
<td></td>
</tr>
</tbody>
</table>

a. Exciting line 632.8nm
b. Exciting line 514.5nm
c. \((\text{Et}_4\text{N})_2\text{SeBr}_6\)
Figure 10

Raman Spectra of solid SeBr$_6^{2-}$ compounds

A  Cs$_2$SeBr$_6$

B  (Et$_4$N)$_2$SeBr$_6$
Figure 11

Raman spectrum of $(\text{Et}_4\text{N})_2\text{SeBr}_6$

in acetonitrile
spectrum for decomposition to Se(II) as observed for SeBr₄ and, to a lesser extent, SeBr₅⁻ in MeCN. It seems that the most highly coordinated and symmetric a central atom is, the more stable the species is. The Raman spectrum of the SeBr₆²⁻ anion has been reported by Hendra and Jovic³⁵, who assigned the stronger band in the spectrum of Cs₂SeBr₆ at 162 cm⁻¹ to $\nu_1(A_{1g})$ following the order of frequency $\nu_1(A_{1g}) > \nu_2(E_g)$ for all of the hexahalometallates which have been studied. In the high resolution spectrum of (Et₄N)₂SeBr₆ in MeCN there is a shoulder to high frequency of the strongest peak at 153 cm⁻¹. It is the band at 153 cm⁻¹ which is polarized and therefore belongs to $\nu_1(A_{1g})$ while the shoulder at 165 cm⁻¹ is $\nu_2(E_g)$. The relative intensities of these two bands remain the same in the spectrum of solid (Et₄N)₂SeBr₆ but the relative intensities are reversed in the spectrum of Cs₂SeBr₆. This cannot be due to intensity borrowing since the two modes are of different class. The observation of the $E_g$ mode a higher frequency than the $A_{1g}$ mode is truly an exception compared to previous assignments of hexahalometallates with octahedral symmetry³⁵,³⁸.
BROMOSELENATE(IV) EQUILIBRIA IN AQUEOUS HYDROBROMIC ACID

Seleninyl halides have been shown by Raman spectroscopy to be formed in solutions of selenium dioxide in hydrofluoric\textsuperscript{40}, hydrochloric\textsuperscript{35,41,42} and hydrobromic\textsuperscript{44} acids. In the case of seleninyl chloride\textsuperscript{42}, an equilibrium constant of $3.2 \times 10^{-6}\text{mol}^{-2}\text{L}^{2}$ has been determined for the equilibrium.

$$\text{H}_2\text{SeO}_3 + 2\text{HCl} = \text{SeOCl}_2 + 2\text{H}_2\text{O}$$

The Raman spectra of selenium dioxide in hydrobromic acid have been studied\textsuperscript{35,44} and these solutions have shown to consist chiefly of SeOBr\textsubscript{2}, SeBr\textsubscript{5}\textsuperscript{-} and SeBr\textsubscript{6}\textsuperscript{2-}. However, no quantitative measurements have been made on these solutions. Moreover, the spectra of the actual SeO\textsubscript{2}Br\textsuperscript{-}, SeOBr\textsubscript{3}\textsuperscript{-}, SeOBr\textsubscript{4}\textsuperscript{2-} and SeBr\textsubscript{5}\textsuperscript{-} anions were not considered in the earlier work, nor were polarization measurements made, which strengthen the interpretation. In view of this, the present study was undertaken to determine what species are present in these solutions on the basis of the information obtained on various bromoselenate(IV) anions in solids and aprotic media and also to determine quantitatively if equilibrium constants can be evaluated.

The Raman spectra of 1.0M solutions of selenium dioxide in hydrobromic acid over an HBr concentration range 0-8.9M, namely those at 8.9, 7.0, 5.0, 3.0 and 0M HBr, are shown in Fig. 12 and the bands of the 8.9M hydrobromic acid
solution are listed in Table VII along with the bands belonging to SeO$_2$Br$^-$, SeOBr$_2$, SeOBr$_3^-$, SeOBr$_4^{2-}$, SeBr$_5^-$ and SeBr$_6^{2-}$ in acetonitrile and their relative intensities. The 1.0M SeO$_2$ in 8.9M HBr solution spectrum is listed in Table VII since this spectrum displays bands corresponding to all the different species which occur in these hydrobromic acid solutions and does not contain any selenious acid. This will become evident later in the chapter.

The spectrum of the 1.0M SeO$_2$ in 0M HBr solution, shown in Fig. 12, is that of selenious acid. As the concentration of hydrobromic acid is increased, starting at 3.0M HBr, there is an increase in the intensity of the peaks in the region 100-300 cm$^{-1}$, the region of SeBr stretching modes. At concentrations of hydrobromic acid greater than 3.0M the intensity of the SeO single bond peak, at 695 cm$^{-1}$, falls as the SeBr bond intensity increases. The new bromo species present here has an SeO double bond, as can be seen by the increase of the SeO double bond stretch intensity, at 900 cm$^{-1}$, relative to the SeO single bond stretch intensity with increase in hydrobromic acid concentration, and is the major component in these solutions up to a hydrobromic acid concentration of 5.0M. Comparison of the spectrum of SeOBr$_2$ in MeCN, listed in Table VII, with that of the 1.0M SeO$_2$ in 5.0M HBr solution shows that SeOBr$_2$ is the principal species in the HBr solution. The possibility of having any
Raman Spectra of 1.0M SeO$_2$ solutions in aqueous HBr

A  1.0M SeO$_2$ in 8.9M HBr
B  1.0M SeO$_2$ in 7.0M HBr
C  1.0M SeO$_2$ in 5.0M HBr
D  1.0M SeO$_2$ in 3.0M HBr
E  1.0M SeO$_2$ in 0M HBr (1.0M H$_2$SeO$_3$)
### Table VII. Raman spectra of bromoselenium (IV) species\(^a\).

<table>
<thead>
<tr>
<th>Species</th>
<th>1 Molar SeO(_2) in 8.9M HBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeO(_2)Br(^-)</td>
<td>90(7, p)</td>
</tr>
<tr>
<td>SeBr(_3)(^-)</td>
<td>112(1, p?)</td>
</tr>
<tr>
<td>SeBr(_4)(^2-)</td>
<td>141(5, p?)</td>
</tr>
<tr>
<td>SeBr(_5)(^-)</td>
<td>151(10, p)</td>
</tr>
<tr>
<td>SeBr(_6)(^2-)</td>
<td>153(10, p)</td>
</tr>
<tr>
<td>SeOBr(_2)(^g)</td>
<td>145(9, p)</td>
</tr>
<tr>
<td>139(10, p)</td>
<td>155(8, dp)</td>
</tr>
<tr>
<td>138(10, p)</td>
<td>158(10, p)</td>
</tr>
<tr>
<td>155(8, dp)</td>
<td>165(2, sh)</td>
</tr>
<tr>
<td>180(2, sh)</td>
<td></td>
</tr>
<tr>
<td>194(8, p)</td>
<td>194(2, dp)</td>
</tr>
<tr>
<td>193(3, dp)</td>
<td>190(5, p?)</td>
</tr>
<tr>
<td>249(1, p)</td>
<td>247(2, p)</td>
</tr>
<tr>
<td>253(2, p?)</td>
<td>218(10, p)</td>
</tr>
<tr>
<td>265(3, p)</td>
<td>205(6, p)</td>
</tr>
<tr>
<td>265(2, dp)</td>
<td>280(1, sh)</td>
</tr>
<tr>
<td>279(9, p)</td>
<td>265(2, p)</td>
</tr>
<tr>
<td>888(6, p)</td>
<td>955(2, p)</td>
</tr>
<tr>
<td>936(1, p)</td>
<td>900(0, p)</td>
</tr>
<tr>
<td>932(1, p)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Solution spectra in MeCN

b. Table I
c. Table III
d. Table IV
e. Table V
f. Table VI
g. Table II
SeO₂Br⁻ ion in the 1.0M SeO₂ in 5.0M HBr solution can be ruled out as an important species on the basis of the absence of a very prominent band at 139 cm⁻¹, due to the $\nu_2(A')$ (Table I) mode of this ion. We would also expect to see an antisymmetric SeO stretch at approximately 814 cm⁻¹. The Raman spectrum of the SeOBr₃⁻ ion in acetonitrile is quite different from that of the 1.0M selenium dioxide in 5.0M hydrobromic acid solution, especially with respect to peak intensities and polarizations. If the highest frequency SeBr vibrational band in the 1.0M SeO₂ in 5.0M HBr solution, at 265 cm⁻¹, were due in part to the SeOBr₃⁻ ion in this solution, a very intense polarized band at 138 cm⁻¹, $\nu_5(A')$ (Table III) would be expected. Since this band is not clearly distinguished in this spectrum, the presence of relatively large concentrations of the SeOBr₃⁻ ion can be ruled out. Another strong band due to the SeOBr₃⁻ anion at 194 cm⁻¹, $\nu_3(A')$ (Table III), which is polarized, would also be expected. Similarly, the band at 265 cm⁻¹ in the SeO₂ in HBr solution corresponds well in frequency with the band at 265 cm⁻¹ in the solution spectrum of the SeOBr₄²⁻ ion (Fig. 5). However, in the spectrum of SeOBr₄²⁻ in MeCN, the peak at 265 cm⁻¹ is due to the $\nu_8(E)$ (Table IV) mode and is depolarized, whereas in the HBr solution the band at 265 cm⁻¹ is polarized. In addition, if this band were due to the SeOBr₄²⁻ ion in solution then,
along with a strong polarized band at 158 cm\(^{-1}\), \(\nu_2(A_1)\) (Table IV), we would expect a strongly depolarized band at 141 cm\(^{-1}\) due to the \(\nu_7(E)\) mode of SeOBr\(_4\)\(^{2-}\) in MeCN. On this basis, the SeOBr\(_4\)\(^{2-}\) ion cannot be present in significant quantities in this solution. The most intense peaks in the spectrum of the 1.0M SeO\(_2\) in 8.9M HBr solution, at 145 and 155 cm\(^{-1}\), can be shown to be due, respectively, to the \(\nu_2(A_1)\) (Table V) mode of the SeBr\(_5\)\(^-\) ion in MeCN and to the \(\nu_1(A_{1g})\) (Table VI) mode of the SeBr\(_6\)\(^{2-}\) ion in MeCN at 153 cm\(^{-1}\). By comparison, these bands can be seen to be virtually non-existent in the 1.0M SeO\(_2\) in 5.0M HBr solution. Therefore, the 1.0M SeO\(_2\) in 5.0M HBr solution consists almost entirely of SeOBr\(_2\) and H\(_2\)SeO\(_3\). The equilibrium occurring in the 1.0M SeO\(_2\) in 0 to 5.0M HBr solutions is

\[ H_2SeO_3 + 2HBr = SeOBr_2 + 2H_2O. (1) \]

For purposes of determining the concentrations of the various Se(IV) species in hydrobromic acid solutions, it was necessary to measure the molar intensities of the SeO double and combined single bond stretching mode peaks (896 and 695 cm\(^{-1}\), respectively) and the combined deformation modes (100 - 400 cm\(^{-1}\)) of selenious acid. In spite of the complex condensation equilibrium known to occur in these solutions\(^{62}\), the dependence of intensity on concentration
for these peaks is known to be linear over the range 0 - 2.0 molar selenious acid in H₂O (Fig. 13). It should be noted, as it was in the experimental section, that all spectral intensities were normalized by comparison to perchloric acid solutions which were run after each selenium dioxide-hydrobromic acid solution. The normalization assumption was that the 925 cm⁻¹ band of a 1.0M perchloric acid solution had an area intensity of 1 ln² (6.45cm²). A plot of the intensity of the 925 cm⁻¹ band of perchloric acid against concentration is shown to be linear up to 5.76M perchloric acid (Fig. 14). The measured normalized peak intensities for the SeBr stretching region (100 - 300 cm⁻¹), the SeO double bond and the SeO single bond frequencies for all SeO₂ in HBr solutions studied, are listed in Table VIII.

From the measurement of normalized peak intensities and a knowledge of molar peak intensities, the concentrations of the species present may be determined and the equilibrium constant calculated. The equilibrium constant for equation 1 is given by

\[ K = \frac{[\text{SeOBr}_2] a^2_w}{[\text{H}_2\text{SeO}_3] a^2_{\text{HBr}}} \]  (2)
Figure 13

Plot of integrated peak intensities of the 896 and 695 cm⁻¹ bands in H₂SeO₃ versus concentration
Figure 14

Plot of Integrated Peak Intensities of the 925 cm\(^{-1}\) band in HClO\(_4\) versus concentration
Table VIII  Values of Normalized Intensities for Solutions of Selenium Dioxide in Hydrobromic Acid

<table>
<thead>
<tr>
<th>Solution</th>
<th>ISeBr(cm²)</th>
<th>ISe=O(cm²)</th>
<th>ISe-O(cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0M SeO₂ in 8.9M HBr</td>
<td>194.78</td>
<td>2.99</td>
<td>-</td>
</tr>
<tr>
<td>1.0M SeO₂ in 8.0M HBr</td>
<td>217.46</td>
<td>6.94</td>
<td>-</td>
</tr>
<tr>
<td>1.0M SeO₂ in 7.0M HBr</td>
<td>181.43</td>
<td>8.95</td>
<td>3.05</td>
</tr>
<tr>
<td>1.0M SeO₂ in 6.0M HBr</td>
<td>96.90</td>
<td>7.15</td>
<td>2.43</td>
</tr>
<tr>
<td>0.776M SeO₂ in 6.0M HBr</td>
<td>92.71</td>
<td>6.67</td>
<td>3.41</td>
</tr>
<tr>
<td>0.513M SeO₂ in 6.0M HBr</td>
<td>68.04</td>
<td>4.07</td>
<td>2.02</td>
</tr>
<tr>
<td>0.260M SeO₂ in 6.0M HBr</td>
<td>49.33</td>
<td>2.96</td>
<td>-</td>
</tr>
<tr>
<td>1.0M SeO₂ in 5.0M HBr</td>
<td>27.90</td>
<td>5.26</td>
<td>5.54</td>
</tr>
<tr>
<td>1.0M SeO₂ in 4.5M HBr</td>
<td>17.39</td>
<td>6.00</td>
<td>6.20</td>
</tr>
<tr>
<td>1.0M SeO₂ in 4.0M HBr</td>
<td>10.17</td>
<td>4.65</td>
<td>5.37</td>
</tr>
<tr>
<td>1.0M SeO₂ in 3.5M HBr</td>
<td>8.81</td>
<td>5.43</td>
<td>7.73</td>
</tr>
<tr>
<td>1.0M SeO₂ in 3.0M HBr</td>
<td>6.17</td>
<td>4.35</td>
<td>6.76</td>
</tr>
<tr>
<td>1.0M SeO₂ in 2.0M HBr</td>
<td>5.28</td>
<td>4.26</td>
<td>5.22</td>
</tr>
<tr>
<td>1.0M SeO₂ in 1.0M HBr</td>
<td>3.45</td>
<td>4.75</td>
<td>6.37</td>
</tr>
</tbody>
</table>
where \( a_w \) is the rational activity of water and \( a_{HBr} \) is the molar activity of hydrobromic acid. The activity coefficients of seleninyl bromide and selenious acid are assumed to be equal. From a knowledge of the concentration of seleninyl bromide or selenious acid and the solution stoichiometry, the concentration of all other species may be calculated. From the hydrobromic acid concentration both \( a_{HBr} \) and \( a_w \) may be obtained from data of Haase, Naas and Thumm\(^{64}\). The activities reported by these authors were given as molal activities of HBr and were converted to molar activities using density data\(^{65}\). The values of \( C_{HBr} \) and \( a_w \) are listed in Table IX. The concentration of selenious acid may be determined from the intensity of the band at 695 cm\(^{-1}\), assuming no other bromoselenate(IV) in solution exhibits an SeO single bond stretch. Because of the low relative intensity of this peak and the complication which results from the selenious acid dimerization\(^{62}\), this peak cannot be used to calculate values for \( K \), in the hydrobromic acid concentration range studied (1.0M - 5.0M). Because of the greater intensity of the SeBr stretching bands in the spectra, they are better suited for the calculation of \( K \). Allowance must, however, be made for the weak peaks due to \( H_2SeO_3 \) deformation modes, which lie in this region of the spectrum. The normalized molar intensities of the selenious acid vibrational modes are listed in Table X and the
Table IX. Values of Concentrations and Activities of HBr (Molar) and Activities of Water

<table>
<thead>
<tr>
<th>$c_{HBr}$</th>
<th>$a_W$</th>
<th>$a_{HBr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.997</td>
<td>0.0803</td>
</tr>
<tr>
<td>0.2</td>
<td>0.993</td>
<td>0.1560</td>
</tr>
<tr>
<td>0.3</td>
<td>0.990</td>
<td>0.2325</td>
</tr>
<tr>
<td>0.4</td>
<td>0.986</td>
<td>0.3116</td>
</tr>
<tr>
<td>0.5</td>
<td>0.982</td>
<td>0.3935</td>
</tr>
<tr>
<td>0.6</td>
<td>0.978</td>
<td>0.4794</td>
</tr>
<tr>
<td>0.7</td>
<td>0.974</td>
<td>0.5691</td>
</tr>
<tr>
<td>0.8</td>
<td>0.970</td>
<td>0.6640</td>
</tr>
<tr>
<td>0.9</td>
<td>0.967</td>
<td>0.7632</td>
</tr>
<tr>
<td>1.0</td>
<td>0.962</td>
<td>0.8690</td>
</tr>
<tr>
<td>1.20</td>
<td>0.953</td>
<td>1.0968</td>
</tr>
<tr>
<td>1.39</td>
<td>0.944</td>
<td>1.3525</td>
</tr>
<tr>
<td>1.58</td>
<td>0.934</td>
<td>1.6416</td>
</tr>
<tr>
<td>1.77</td>
<td>0.924</td>
<td>1.9346</td>
</tr>
<tr>
<td>1.96</td>
<td>0.913</td>
<td>2.3285</td>
</tr>
<tr>
<td>2.83</td>
<td>0.853</td>
<td>5.006</td>
</tr>
<tr>
<td>3.69</td>
<td>0.782</td>
<td>10.210</td>
</tr>
<tr>
<td>4.46</td>
<td>0.703</td>
<td>19.040</td>
</tr>
<tr>
<td>5.21</td>
<td>0.619</td>
<td>34.428</td>
</tr>
<tr>
<td>5.96</td>
<td>0.536</td>
<td>62.891</td>
</tr>
<tr>
<td>6.65</td>
<td>0.460</td>
<td>111.753</td>
</tr>
<tr>
<td>7.30</td>
<td>0.390</td>
<td>199.217</td>
</tr>
<tr>
<td>7.93</td>
<td>0.332</td>
<td>350.577</td>
</tr>
<tr>
<td>8.56</td>
<td>0.277</td>
<td>552.796</td>
</tr>
</tbody>
</table>
corrected and normalized intensities of the SeBr stretching region (100 - 300 cm\(^{-1}\)) are listed in Table XI. An estimate of the molar intensity of the SeBr peaks for SeOBr\(_2\) (100 - 300 cm\(^{-1}\)) may be calculated from the intensities in the spectrum for the 5.0M hydrobromic acid solution and a knowledge of the concentration of selenious acid and the total Se(IV) concentration.

\[
C_{\text{total Se(IV)}} = [\text{H}_2\text{SeO}_3] + [\text{SeOBr}_2] \tag{3}
\]

In order to make this initial estimate, the selenious acid concentration was calculated using the molar intensity for the SeO single bond peak given in Table X and the intensity of the peak at 695 cm\(^{-1}\). The molar intensity of the SeBr bands for SeOBr\(_2\) was found in this way to be 205 cm\(^2\).

For the calculation of \(K\), the following procedure was used. By use of the molar intensity of SeOBr\(_2\), a preliminary value for the concentration of selenenyl bromide was calculated, the selenious acid concentration was determined using equation 3 and a correction of the SeBr envelope could then be made to allow for selenious acid deformations lying under the SeBr peaks. The molar intensity of the selenious acid deformations is given in Table X. The concentration of hydrobromic acid was then calculated from
Figure 15

Raman Spectra of solutions used to calculate K

A  1.0M SeO₂ in 5.0M HBr
B  1.0M SeO₂ in 4.5M HBr
C  1.0M SeO₂ in 4.0M HBr
Table X. Molar Intensities of Selenious Acid Bands

<table>
<thead>
<tr>
<th>freq. (cm⁻¹)</th>
<th>mode description</th>
<th>molar intensity (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 - 400</td>
<td>deformations</td>
<td>2.50</td>
</tr>
<tr>
<td>695</td>
<td>SeO single bond stretch</td>
<td>6.34</td>
</tr>
<tr>
<td>896</td>
<td>SeO double bond stretch</td>
<td>5.12</td>
</tr>
</tbody>
</table>

Table XI. Normalized Intensities of SeBr Peaks, Concentrations and Equilibrium Constants for Seleninyl Bromide Formation

<table>
<thead>
<tr>
<th>C_HBr</th>
<th>I_{SeBr}(cm²)</th>
<th>[SeOBr₂]</th>
<th>[H₂SeO₃]</th>
<th>[HBr]</th>
<th>a_w</th>
<th>a_{HBr}</th>
<th>10^{-4}K(mol⁻²L²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.02</td>
<td>8.34</td>
<td>0.0407</td>
<td>0.9593</td>
<td>3.938</td>
<td>0.757</td>
<td>13.00</td>
<td>1.4</td>
</tr>
<tr>
<td>4.505</td>
<td>15.03</td>
<td>0.0734</td>
<td>0.9266</td>
<td>4.358</td>
<td>0.677</td>
<td>23.50</td>
<td>1:3</td>
</tr>
<tr>
<td>5.0</td>
<td>25.83</td>
<td>0.1262</td>
<td>0.8738</td>
<td>4.747</td>
<td>0.640</td>
<td>30.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

NOTE: All concentrations are in molar terms. I_{SeBr} values are corrected for H₂SeO₃ deformations. Kavg = 1.3 × 10⁻⁴ mol⁻²L²
\[ [\text{HBr}] = C_{\text{HBr}} - 2 [\text{SeOBr}_2] \]  

From this information, \( a_{\text{HBr}} \) and \( a_w \) could be obtained (Table IX), and the equilibrium constant, \( K \), could be calculated using equation 2. Peak intensities, concentrations, activities and equilibrium constants are listed in Table XI. The spectra of the solutions used are shown in Fig. 15. The estimated molar intensity of the SeBr bands for \( \text{SeOBr}_2 \), 205 cm\(^{-2}\), gave the best constancy of \( K \) over the range of concentrations studied without need of adjusting it as was done in the case of the equilibrium constant calculation for the Se (IV)/HCl system\(^ {41} \). The average value for \( K \) was found to be 1.3 \( \times 10^{-4} \)mol\(^{-2}\)L\(^2\). The solutions of selenium dioxide in hydrobromic acid where the hydrobromic acid concentration was less than 4.0M gave values of \( K \) which were 2 to 5 times larger. This can only be attributed to the difficulty in measuring the SeBr stretching region intensity to a good degree of certainty, since this region was not much more intense than the selenious acid deformation region. The solutions which were used for the final determination of \( K \) where those of 1.0M \( \text{SeO}_2 \) in 4.0, 4.5 and 5.0M HBr.
Solutions of Selenium Dioxide in Hydrobromic Acid
at Concentrations of HBr greater than 5.0 Molar

Comparison of the Raman spectrum of selenium
dioxide in 5.0M hydrobromic acid to that in 6.0M HBr
(Fig. 16) reveals bands at 145 cm\(^{-1}\) and 155 cm\(^{-1}\), which are
due to the presence of the SeBr\(_5^-\) and SeBr\(_6^{2-}\) ions. These
bands are due to the \(v_2(A_1)\) (Table V) mode of the SeBr\(_5^-\) ion
on MeCN and to the \(v_1(A_{1g})\) (Table VI) mode of the SeBr\(_6^{2-}\)
ion on MeCN, 151 and 153 cm\(^{-1}\) respectively (Table VII).
This is particularly clear in the spectrum with 90\(^{\circ}\) rotation
of the plane of polarization. Assuming that these SeBr
stretching modes, in the 6.0M HBr solution, are due to the
presence of the SeBr\(_5^-\) ion alone, an attempt can be made to
calculate the concentration of SeBr\(_5^-\) in this solution.
Assuming that the molar intensity of the SeO double bond is
due only to SeOBr\(_2\) and H\(_2\)SeO\(_3\) and assuming that the
selenious acid concentration can be calculated from the SeO
single bond intensity, it was thought possible to calculate
the SeBr\(_5^-\) concentration. However, the molar intensity of
the SeO double bond, corrected for the H\(_2\)SeO\(_3\) contribution
yielded values of [SeOBr\(_2\)], which resulted in

\[
[H_2SeO_3] + [SeOBr_2] > C_{total\ Se(IV)}
\]

and thus the SeBr\(_5^-\) concentration could not be calculated.
A list of values for SeO double bond intensities (from
Table VIII), corrected SeO double bond intensities, H\(_2\)SeO\(_3\)
and SeOBr\(_2\) concentrations are given in Table XII. The high
concentrations of SeOBr₂ can be accounted for by the possible presence of other bromoselenate(IV) species which contribute to the SeO double bond intensity. For this reason, the presence of the SeOBr₃⁻ ion appears likely. Also the SeOBr₄²⁻ anion may be present in small proportions. It should be noted that oxotribromoselenenate(IV) compounds could be prepared from aqueous solution but oxotetram bromoselenenate(IV) compounds could not. The values for total concentration of Se(IV) given in Table XII show that, as the hydrobromic acid concentration increases (from 6.0 to 7.0 molar), the excess concentration of Se(IV) gets larger. For the 1.0M SeO₂ in 7.0M HBr the total Se(IV) concentration is calculated to be 53% higher than it actually is. Since SeOBr₃⁻ is the only species which could contribute to the SeO double bond molar intensity, it would have to be present in appreciable amounts. However, as was discussed earlier, the presence of SeOBr₃⁻ in low concentrations is possible but substantial amounts cannot be accounted for reasonably in the solution spectra (Fig. 12 and Table VII) of 1.0M SeO₂ in HBr. Furthermore, at concentrations of HBr greater than 5.0 molar, the SeO single bond intensities are quite small and large errors could be involved in the measurement of their intensities. This would cause large variations in the selenious acid concentrations which in turn would change the values of seleninyl bromide.
Figure 16

Raman Spectra of 1.0M SeO₂ in concentrated aqueous HBr solutions

A 1.0M SeO₂ in 8.9M HBr
B 1.0M SeO₂ in 8.0M HBr
C 1.0M SeO₂ in 7.0M HBr
D 1.0M SeO₂ in 6.0M HBr
E 1.0M SeO₂ in 5.0M HBr
Table XII. SeO double bond Corrected and Uncorrected Intensities, and Concentrations of $H_2SeO_3$ and $SeOBr_2$

<table>
<thead>
<tr>
<th>Solution</th>
<th>a ISe=0</th>
<th>ISe=0</th>
<th>$[H_2SeO_3]$</th>
<th>b ISe=0</th>
<th>ISe=0</th>
<th>$[SeOBr_2]$</th>
<th>Total Se(IV) conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.513M SeO$_2$ in 6M HBr</td>
<td>4.07</td>
<td>2.02</td>
<td>0.3186</td>
<td>2.44</td>
<td></td>
<td>0.3948</td>
<td>0.7134</td>
</tr>
<tr>
<td>0.776M SeO$_2$ in 6M HBr</td>
<td>6.67</td>
<td>3.41</td>
<td>0.5378</td>
<td>3.92</td>
<td></td>
<td>0.6343</td>
<td>1.1721</td>
</tr>
<tr>
<td>1.0M SeO$_2$ in 6M HBr</td>
<td>7.15</td>
<td>2.43</td>
<td>0.3833</td>
<td>5.19</td>
<td></td>
<td>0.8398</td>
<td>1.2231</td>
</tr>
<tr>
<td>1.0M SeO$_2$ in 7M HBr</td>
<td>8.95</td>
<td>3.05</td>
<td>0.4810</td>
<td>6.49</td>
<td></td>
<td>1.0502</td>
<td>1.5312</td>
</tr>
</tbody>
</table>

a. Intensities are in cm$^2$

b. Concentrations in molar terms

c. Corrected for $H_2SeO_3$ double bond
concentrations. Therefore, we can say that the errors on the values of the SeO single bond intensities are more likely to be the reason for the excess calculated value of total Se(IV) concentration.

The Raman spectra of the 1.0M selenium dioxide in 5.0, 6.0, 7.0, 8.0 and 8.9 molar hydrobromic acid solutions are shown in Fig. 16. These spectra show that, as the hydrobromic acid concentration is increased, the intensities of the bands due to the SeBr$_5^-$ and SeBr$_6^{2-}$ ions, 145 and 155 cm$^{-1}$ respectively, increase relative to those for SeOBr$_2$. At a concentration of 5.0M HBr, SeOBr$_2$ is seen as being the only bromo species present in this solution and at a concentration of hydrobromic acid of 6.0M, the contribution due to SeOBr$_2$ is greater than that of the other bromo species. In the 1.0M SeO$_2$ in 7.0M HBr solution the highest intensity band for SeOBr$_2$ at 205 cm$^{-1}$, is almost equal in intensity to the bands in the 150 cm$^{-1}$ region due to the SeBr$_5^-$ and SeBr$_6^{2-}$ ions and finally at a concentration of hydrobromic acid of 8.9M the bands due to the SeBr$_5^-$ and SeBr$_6^{2-}$ are seen to be approximately twice as intense as the band at 205 cm$^{-1}$ due to SeOBr$_2$.

A study was also done where the hydrobromic acid concentration was kept constant, at 6.0 molar, but the selenium dioxide concentration varied from 1.0M to 0.26M. These spectra are shown in Fig. 17. As the concentration of
Figure 17

Raman Spectra of SeO₂ solutions in 6.0M HBr

A  1.0M SeO₂
B  0.776M SeO₂
C  0.513M SeO₂
D  0.26M SeO₂
SeO$_2$ falls from 1.0M to 0.26M, the opposite effect to what was seen in the solutions shown in Fig. 12 (1.0M SeO$_2$ in 0 - 8.9M HBr) and Fig. 16 occurs. There is not much change in the solution spectra of 1.0M SeO$_2$ in 6.0M HBr compared to that of the 0.776M SeO$_2$ in 6.0M HBr solution. However, at a selenium dioxide concentration of 0.513M the spectrum can be seen to display intensities of the SeBr$_5^-$ and SeBr$_6^{2-}$ ions, 145 and 155 cm$^{-1}$ respectively, which are almost identical in intensity to the 205 cm$^{-1}$ band of SeOBr$_2$. The SeO single bond intensity, at 695 cm$^{-1}$, also falls relative to the SeBr envelope and to the SeO double bond intensity, at 900 cm$^{-1}$, until it disappears completely at a concentration of 0.26M SeO$_2$. This effect can be accounted for reasonably by the fact that as more SeO$_2$ is added to the hydrobromic acid solution more HBr is consumed, to form the bromoselenenate(IV) species observed. Thus more H$_2$O is formed and oxobromo species, mainly SeOBr$_2$, are favoured. These observations are further justified by the changes in the spectra with 90° rotation of the plane of polarization. In the 0.26M SeO$_2$ in 6.0M HBr solution, no H$_2$SeO$_3$ is present and we could expect, as was explained before, that at lower SeO$_2$ concentrations the spectra would indicate largely the presence of the SeBr$_5^-$ and SeBr$_6^{2-}$ ions and smaller contributions due to SeOBr$_2$. 
Selenium Dioxide in Hydrobromic Acid
Saturated with Hydrogen Bromide at 0°C

The Raman spectrum of a 1.0M selenium dioxide solution in hydrobromic acid saturated with hydrogen bromide is shown in Fig. 18. The hydrogen bromide concentration of an aqueous solution saturated at 0°C is 15.74M, calculated using density data taken at 4°C. The densities of aqueous HBr solutions at 0°C were not available, hence those measured at 4°C were used. It was estimated that this introduced an error in the molarity of approximately 1%, which is far within the experimental error of the measurement of peak intensities (±5%). On comparing the spectrum of the saturated HBr solution with that of the 1.0M selenium dioxide in 8.9M hydrobromic acid solution (Fig. 12 and Fig. 16) it can be seen that the two spectra are quite similar. However, the saturated solution spectrum shows a larger contribution at 145 and 155 cm⁻¹, due to the SeBr₅⁻ and SeBr₆²⁻ ions respectively, compared to the band at 212 cm⁻¹. The spectrum in Fig. 18 provides no evidence for the presence of SeOBr₂ or SeOBr₃⁻ since there is no SeO double bond stretch observable. Although the band at 212 cm⁻¹ is close in frequency to what we would expect for the most intense band of SeOBr₂, 205 cm⁻¹, it cannot be due to SeOBr₂. Therefore, the band at 212 cm⁻¹ is most likely due to condensation of the SeBr₅⁻ ion to a dimeric or
Figure 18.

Raman Spectrum of 1.0M SeO₂ in

15.74M HBr
polymeric anion as was observed in the case of \( n\)-Bu\(_4\)NSeBr\(_5\) in acetonitrile at high concentration. The band at 212 cm\(^{-1}\) could be interpreted in terms of the shifts of the bands at 180 cm\(^{-1}\) to higher frequency, and 247 cm\(^{-1}\) to lower frequency as was observed in the saturated solution of SeBr\(_5^-\) in MeCN (Table V). Therefore, the spectrum of 1.0M SeO\(_2\) in 15.47M HBr can be interpreted as being due to the SeBr\(_6^{2-}\) ion and to a high concentration of SeBr\(_5^-\) ion.

When the 1.0M selenium dioxide in 8.9M hydrobromic acid solution was saturated with hydrogen bromide at 0°C, a reddish-brown precipitate would form depending on how long the hydrogen bromide gas was allowed to pass through the solution once saturation was complete. For the solution used in Raman spectral study, the hydrogen bromide gas was passed through the solution at a slow rate and careful observation made it possible to cease the saturation before the point of precipitation. However, when the HBr gas was allowed to flow rapidly through the 1.0M SeO\(_2\) solution at 0°C, a dark red-brown precipitate would form after a short period of time. Krebs and Hein\(^{67}\) have identified this compound as being the hydrate of hexabromoselenic(IV) acid, \( \text{H}_2\text{SeBr}_6\cdot8\text{H}_2\text{O} \). This further justifies the presence of SeBr\(_6^{2-}\) in solutions of SeO\(_2\) in HBr.
CONCLUSION

The Raman spectral study of the compounds prepared in this thesis indicated structures of the isolated anions SeO₂Br⁻, SeOBr₃⁻, SeOBr₄²⁻ and SeBr₅⁻ (in low concentration solutions in MeCN) to obey the predictions of VSEPR theory. The SeBr₅²⁻ anion is known to possess octahedral symmetry, contrary to the expected geometry from VSEPR theory and is therefore exceptional in this series. Seleninyl bromide, SeOBr₂, showed evidence of oxygen bridging in the solid but bromide bridging was not as evident as the chloride bridging is in solid seleninyl chloride. In solution, SeOBr₂ was best approximated as having C₅ symmetry, as is predicted by VSEPR theory.

Although SeBr₄ decomposes to SeBr₂ and Br₂ in MeCN, it was shown that addition of bromide ion stabilizes Se(IV) in acetonitrile. The SeBr₅⁻ compounds indicated bridging in their solid Raman spectra and in the Raman spectra of concentrated solutions. However, we could only speculate, from what is known about isoelectronic species, as to the type of bridging occurring. The Raman spectra of dilute solutions of SeBr₅⁻ in MeCN indicated the decomposition of this anion to SeBr₂ and Br₃⁻, however, these spectra were due, for the most part, to the SeBr₅⁻ ion.

The spectra of the new bromoselenate(IV) anions SeO₂Br⁻, SeOBr₃⁻, SeOBr₄²⁻ and SeBr₅⁻ were considered in interpreting the spectra of Se(IV) in aqueous HBr. The spectra of these solutions taken when the plane of
polarization was rotated 90° also helped in clarifying the presence of the different bromo species. The species \( \text{H}_2\text{SeO}_3, \text{SeOBr}_2, \text{SeBr}_5^- \) and \( \text{SeBr}_6^{2-} \) were definitely identified in these solutions. Se\(^{77}\) N.M.R. could help in confirming the conclusions of the Raman work as well as identifying species which may be present in small amounts, such as \( \text{SeOBr}_3^- \), \( \text{SeOBr}_4^{2-} \) and \( \text{SeBr}_2 \). By varying the Se(IV) concentration in solutions of SeO\(_2\) in hydrobromic acid saturated with hydrogen bromide, the condensation of SeBr\(_5^-\) to polymeric species would become more evident by the increase of the intensity of the band at 212 cm\(^{-1}\) relative to that at 145 cm\(^{-1}\) with increasing Se(IV) concentration.

The equilibrium constant determined for the equilibrium:

\[
\text{H}_2\text{SeO}_3 + 2\text{HBr} = \text{SeOBr}_2 + 2\text{H}_2\text{O}
\]

is of the order of 100 times larger than the corresponding equilibrium constant for the chloride system which demonstrates that, in aqueous solution, seleninyl bromide is more stable than seleninyl chloride. This is further supported by the fact that SeOBr\(_3^-\) compounds could be prepared from aqueous solution.
REFERENCES


50. J. B. Milne, Submitted for Publication in Spectrochimica Acta A.


57. L. Frost and J. B. Milne, Unpublished Results.


