

The Pursuit of High Blocking Temperature Single Molecule Magnets using 4f/5f Cyclooctatetraenyl Complexes

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Doctoral Thesis

Thesis submitted to the Faculty of Graduate & Postdoctoral Studies in partial fulfillment of the requirements for the PhD Degree in Chemistry

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Abstract

This dissertation describes the single molecule magnet (SMM) behaviour of f-block cyclooctatetraenyl sandwich complexes. Chapter one introduces the concepts that dictate SMM behavior particularly in f-elements. The emphasis is to understand the origin of magnetic behaviour and the properties that make lanthanide elements particularly interesting to explore. Current strategies used to predict such behaviour are discussed and a literature review on the subject is provided.

Chapter Two describes the magnetic properties of eight isostructural lanthanide sandwich complexes utilizing 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion as the ligand, $[\text{Li}(\text{DME})_3][\text{Ln}^{\text{III}}(\text{COT}'')_2]$ ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tb}$, $\text{COT}'' = 1,4$ -bis(trimethylsilyl)cyclooctatetraenyl dianion, $\text{DME} = \text{dimethoxyethane}$). The complexes display a wide range of magnetic behaviour. The best performing SMM was the erbium complex, which had a blocking temperature of 8 K. Investigating different lanthanide ions with the same ligand enabled us to evaluate our findings in relation to current models used to predict SMM behaviour in lanthanide complexes.

Chapter three extends the discussion of lanthanide sandwich complexes to include higher symmetry cyclooctatetraenyl complexes of Er^{III} and Dy^{III} , $[\text{K}(18\text{-C-6})][\text{Ln}^{\text{III}}(\text{COT})_2]$ ($18\text{-C-6} = 1,4,7,10,13,16$ -hexaoxacyclooctadecane, $\text{COT} = \text{cyclooctatetraene}$). The change in symmetry evoked by removing the trimethylsilyl- (TMS) groups on the ligand greatly influenced the magnetic properties of both complexes. *Ab initio* calculations revealed that the magnetic relaxation in the Er^{III} complex occurs via the second excited state which contributes to the very high blocking temperature of 10 K in this complex.

Chapter four presents an organometallic building block approach to create triple decker lanthanide COT'' complexes of Gd^{III} , Dy^{III} and Er^{III} with a molecular formula of $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$. Synthetically, we couple together the sandwich complexes discussed in Chapter 2 by oxidatively removing one ligand to produce linear complexes where the two metals are bridged by an aromatic COT'' ligand. The magnetic properties of all complexes are compared to their respective mononuclear analogs. Most interesting is the

unprecedented 4 K increase in blocking temperature of the triple decker Er^{III} analog compared to the Er^{III} mononuclear sandwich complex discussed in Chapter 2. This increase is due to a ferromagnetic dipole-dipole interaction between the Er^{III} ions through the COT'' ring. The aromatic bridging ligand provides a Gd^{III} - Gd^{III} interaction of $J = -0.448(1) \text{ cm}^{-1}$.

Chapter five extends the discussion of magnetic exchange coupling to include linear $\text{K}_2(\text{THF})_4[\text{Ln}^{\text{III}}_2(\text{COT})_4]$ ($\text{Ln} = \text{Gd}, \text{Dy}, \text{Er}$, COT = cyclooctatetraenyl dianion, THF = tetrahydrofuran) complexes of Gd^{III} , Dy^{III} and Er^{III} . Each complex is composed of two LnCOT_2 units bridged linearly by a potassium ion. The magnetic interaction between metal ions is much weaker than in the triple decker complexes discussed in Chapter 4, with a Gd^{III} - Gd^{III} interaction of $J = -0.007(4) \text{ cm}^{-1}$. The magnetic properties of the quadruple decker complexes were compared to their mononuclear equivalents (Chapter 3). Surprisingly, the Er^{III} complex showed an increase in magnetic blocking temperature over its mononuclear analog despite the large Er^{III} - Er^{III} separation of 8.819 Å. *Ab initio* calculations revealed that this increase is due to single ion effects, most likely an increase in symmetry.

Chapter six deviates from lanthanide magnetism to study the magnetic properties of uranium sandwich complexes with multiple ligand systems and oxidation states. Prior to this study the SMM behaviour of uranium sandwich complexes was unknown. We report the synthesis, structure and magnetic properties of both uranium-COT'' sandwich complexes and uranium-cycloheptatrienyl complexes with oxidation states spanning (III)-(V). None of the complexes showed zero-field SMM behaviour, indicating a sandwich-type ligand is not appropriate for harnessing the SMM character in uranium. We compared the slow magnetic relaxation of isostructural and valence isoelectronic uranium and neodymium complexes. The improved energy barrier in the uranium complex further motivates the use of uranium in SMM design due to its large spin-orbit coupling.

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Acknowledgments

First and foremost I would like to express my gratitude towards my supervisor Prof. Muralee Murugesu, not just because it is customary to do so, but because it is to him that I attribute most of my academic success at The University of Ottawa. I am appreciative for his continuous confidence in me, our countless office chats, and his willingness to let me explore my own project directions.

I would also like to sincerely acknowledge our fantastic collaborators that made this project a success. Computational collaborators include Dr. Liviu Ungur and Prof. Liviu Chibotaru from The Katholieke Universiteit Leuven, and Prof. Serge Gorelsky from the University of Ottawa. I would like to thank Prof. Eric Schelter from The University of Pennsylvania for his contributions to our cerium project. I would also like to thank Dr. Ilia Korobkov from The University of Ottawa for his crystallography work, and for his patience when I would jam his inbox full of crystal structure data on most weekends.

The Murugesu group has had so many fantastic members over my time. Prof. Po-Heng Lin, not only introduced me to magnetism, but he was also my side-kick for any and all crazy outdoor Canadian activities. I want to thank Dr. Matt Jeletic and Dr. Cyril Cook for our many chemistry discussions, but perhaps more importantly I hold you both responsible for my new found obsession with the NFL. To everyone else in the Murugesu group including, Becky, Katie, Amelie, Fatimah, Tomoko, Damir, Gabe, Yutang and Elaina, you made this experience unforgettable. Thank you for the comradery and for being my occasional drinking buddies. I have had the privilege to pass along my knowledge of chemistry to an amazingly talented undergrad student Katie, I'm so excited to see what you do with your career, and I know that you'll kick-ass at anything. Becky, you are the one lab mate in particular that I owe my personal sanity to over the past three years. Thanks for the pep talks, your amazing friendship, and your continued willingness to go to La Maison at a moment's notice.

Last but certainly not least, thank you to my wonderful family, including my parents John and Cathy Le Roy for your unconditional love and support during my unconventional (and what probably seemed at times as never ending) academic pursuit.

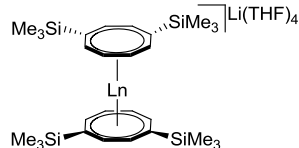
List of Abbreviations

SMM	Single molecule magnet
SIM	Single ion magnet
COT^{''}	1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion
DME	1,2-Dimethoxyethane
COT	Cyclooctatetraenyl dianion
THF	Tetrahydrofuran
Mn₁₂-OAc	[Mn ₁₂ O ₁₂ (O ₂ CMe) ₁₆ (H ₂ O) ₄]
T_B	Blocking temperature
TMS	Trimethylsilyl
ac	Alternating current
dc	Direct current
QTM	Quantum tunnelling of the magnetization
TA-QTM	Thermally assisted quantum tunnelling of the magnetization
SQUID	Superconducting quantum interference device
U_{eff}	Anisotropy (energy) barrier
H	Applied field
χ^{''}	Out-of phase magnetic susceptibility
M	Magnetisation
K	Kelvin
J	Coupling constant
g	Landé g factor
S	Spin
D	Axial anisotropy parameter
T	Temperature

ν	Frequency
τ	Relaxation time
KD	Kramers doublet
Pc	Phthalocyaninate
2.2.2.Cryptand	$K(C_{12}H_{24}O_6)$
18-C-6	1,4,7,10,13,16-hexaoxacyclooctadecane
z	Atomic mass
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
Cp	Cyclopentadienyl
Ln	Lanthanide
TM	Transition Metal
H_{dc}	Applied dc field
ZFS	Zero field splitting
k_B	Boltzmann constant
IR	Infrared spectroscopy
NMR	Nuclear magnetic resonance
CASSCF	Complete active space self-consistent field
Oe	Oersted

List of Complexes with Chemical Formulas and Abbreviated Names

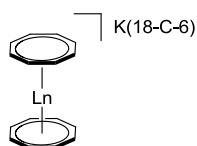
Chapter 2



$\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}'')_2]$, ($\text{M} = \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$, DME = dimethoxyethane and $\text{COT}'' = 1,4$ -bis(trimethylsilyl)cyclooctatetraenyl dianion).

Corresponding acronym: **CeCOT''₂**, **NdCOT''₂**, **GdCOT''₂**, **TbCOT''₂**, **DyCOT''₂**, **HoCOT''₂**, **ErCOT''₂** and **YbCOT''₂**

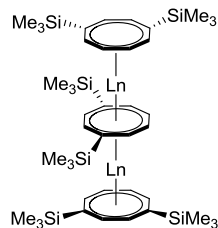
Chapter 3



$[\text{K}(18\text{-C-}6)][\text{Ln}^{\text{III}}(\text{COT})_2]$ ($\text{Ln} = \text{Dy}$ and Er , 18-C-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, COT = cyclooctatetraene dianion).

Corresponding acronym: **DyCOT₂**, and **ErCOT₂**

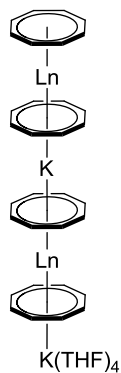
Chapter 4



$\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ ($\text{Ln} = \text{Gd}, \text{Dy}, \text{Er}$, $\text{COT}'' = 1,4$ -bis(trimethylsilyl)cyclooctatetraenyl dianion)

Corresponding acronym: **Gd₂COT''₃**, **Dy₂COT''₃** and **Er₂COT''₃**

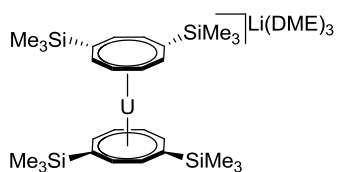
Chapter 5



$\text{K}_2(\text{THF})_4[\text{Ln}^{\text{III}}_2(\text{COT})_4]$ ($\text{Ln} = \text{Gd}, \text{Dy}, \text{Er}$, COT = cyclooctatetraenyl dianion, THF = tetrahydrofuran)

Corresponding acronym: **Gd₂K₂COT₂**, **Dy₂K₂COT₂** and **Er₂K₂COT₂**

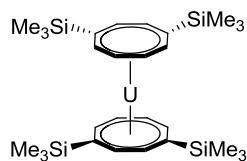
Chapter 6



$\text{Li}(\text{DME})_3[\text{U}^{\text{III}}(\text{COT}'')_2]$, (DME = dimethoxyethane and $\text{COT}'' = 1,4$ -bis(trimethylsilyl)cyclooctatetraenyl dianion).

Corresponding acronym: $\text{U}^{\text{III}}\text{COT}''_2$

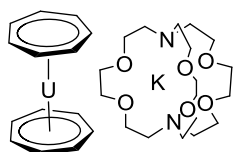
Chapter 6



$\text{Li}(\text{DME})_3[\text{U}^{\text{IV}}(\text{COT}'')_2]$, (DME = dimethoxyethane and $\text{COT}'' = 1,4$ -bis(trimethylsilyl)cyclooctatetraenyl dianion).

Corresponding acronym: $\text{U}^{\text{IV}}\text{COT}''_2$

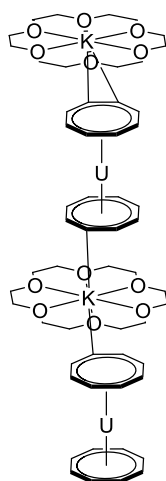
Chapter 6



$[2.2.2.\text{Cryptand}][\text{U}^{\text{V}}(\eta\text{-C}_7\text{H}_7)_2]$ (18-C-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane)

Corresponding acronym: $\text{U}^{\text{V}}\text{C7}_2'$

Chapter 6



$[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)][\text{U}^{\text{V}}(\eta\text{-C}_7\text{H}_7)_2]$ (2.2.2.Cryptand = $\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)$)

Corresponding acronym: $\text{U}^{\text{V}}\text{C7}_2'$

Contribution Statement

I performed all relevant experimental work in this thesis including synthesis, characterization and magnetic analysis. With that said, I was only one component of a fantastic team of collaborators, headed by Prof. Muralee Murugesu, to whom I owe the tremendous success of this ongoing project. Firstly, Dr. Liviu Ungur and Dr. Liviu Chibotaru contributed all *ab initio* calculations in Chapters 1-5, as well as DFT analysis presented in Chapters 3 and 5. Dr. Serge Gorelsky also contributed DFT analysis discussed in Chapters 2, 4, and 6. Dr. Eric Schelter contributed the electrochemistry for the cerium compound in Chapter 2 and Dr. Ilia Korobkov performed all single crystal X-ray diffraction analysis presented in this thesis.

Chapter 1

Introduction and Critical Review of Lanthanide and Actinide SMMs

1.1 Single Molecule Magnets

Remanent magnetization and coercivity are the basic characteristics of permanent magnets. These features also exist in molecular complexes, called accordingly, single-molecule magnets (SMMs). SMMs are discrete molecular complexes which exhibit superparamagnet-like behaviour and magnetic hysteresis at low temperatures. The interest in these molecular systems is not only due to their remarkable physical properties, but also their promise in future applications. Large anisotropy coupled with long relaxation times make SMMs potential candidates for applications ranging from high-density data storage to quantum computing.¹

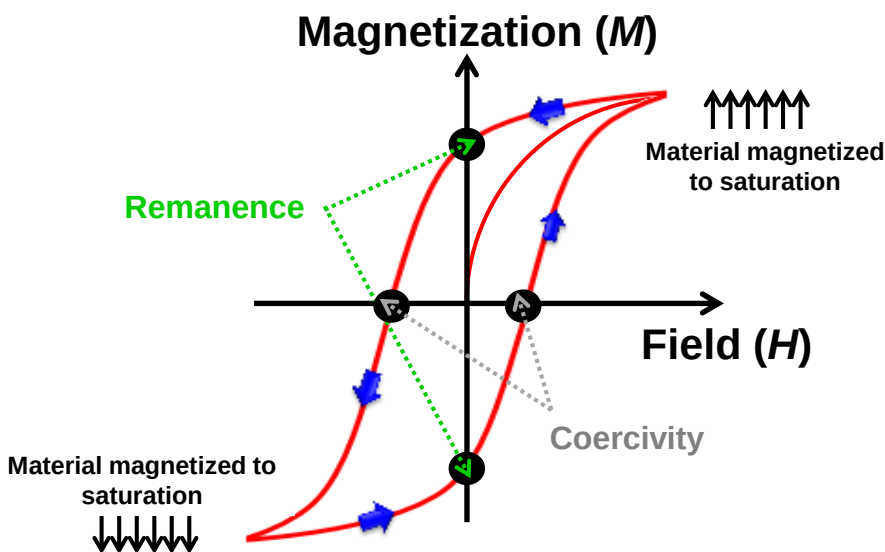


Figure 1.1. Basic hysteresis curve of a typical ferromagnet (including SMMs). Remanence is the magnetization left after the removal of an external magnetic field; this property is responsible for the magnetic memory effect used in typical magnetic data storage applications. Coercivity is the measure of magnetic field required to reverse magnetization.

1.1.1 General Physical Principles and Design Strategies

What distinguishes an SMM from a bulk magnet is the absence of long-range ordering in SMMs; thus the magnetic behaviour is directly molecular in origin. Therefore the success of an SMM is based on molecular features. There are two essential physical properties a discrete molecule must possess to exhibit SMM behaviour. These features include a doubly degenerate non-zero ground state ($S \neq 0$) and magnetic anisotropy (D). Since understanding the origin of magnetic relaxation is an ongoing theme discussed throughout this thesis, we begin by clearly demonstrating these key features in the first, and arguably the most well understood SMM. In 1993 Sessoli, Gatteschi, and Caneschi reported that the removal of an external magnetic field around a zero dimension molecule of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$, ($\text{Mn}_{12}\text{-OAc}$), resulted in the retention of magnetization.² This seminal report was the first observation of magnet-like behaviour being purely molecular in origin and appropriately launched the field known as single molecule magnetism.

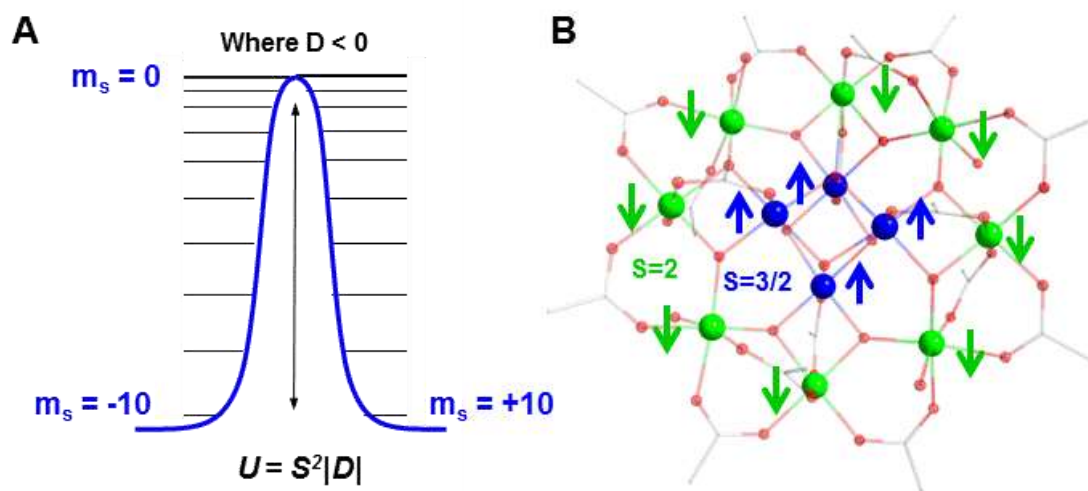


Figure 1.2. (A) Schematic representation of the low lying energy diagram of $\text{Mn}_{12}\text{-OAc}$. (B) X-ray structure of $\text{Mn}_{12}\text{-OAc}$ where the arrows illustrate the antiferromagnetic nature of the interaction between Mn^{3+} and Mn^{4+} ions in an external magnetic field at low temperature. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are drawn at 50% probability. Colour code: Blue (Mn^{4+}), green (Mn^{3+}), red (O) and grey (C). Crystal structure obtained from CCDC database number 916380.

The structure of $\text{Mn}_{12}\text{-OAc}$ consists of eight outer octahedral Mn^{III} ions ($S = 2$) and four inner tetrahedral Mn^{IV} ions ($S = 3/2$). Magnetically at low temperature, there is

antiferromagnetic coupling between Mn^{III} and Mn^{IV} ions resulting in a well isolated $S = 10$ doubly degenerate ground state (graphically represented in Figure 1.2A). Spin-orbit coupling in the high-spin Mn^{III} ions is the source of the anisotropy in this molecule.³ In addition, the negative sign of the axial zero-field splitting term (D) results in the bi-stable ground state with $m_s = \pm 10$ (Figure 1.2A). Like all other SMMs, it is this combination of properties (S and D) that result in an energy barrier against magnetization reversal (commonly called the anisotropic barrier) and magnetic hysteresis in this complex.

SMMs are not rare, as slow magnetic relaxation has been reported in hundreds of metal complexes, containing various metal ions spanning much of the periodic table. The greatest challenge currently facing this very active research field, and the central discussion of this thesis, is increasing the temperature at which this magnetic property is observed. The blocking temperature (T_B) of an SMM is the highest temperature a complex behaves as a magnet, where currently the highest T_B for an SMM is 14 K. This low temperature limit is gravely restricting the application of SMMs.

For the purpose of this thesis, when the low temperature magnetic “performance” of SMMs is discussed, we are referring to two different parameters, the anisotropy barrier (U_{eff}) and T_B , where in both cases larger values are desirable. For some applications large values are not necessary, however the focus of the present work is to increase T_B , and all other applications will not be discussed herein. Most of the time U_{eff} is experimentally obtained from alternating current (ac) magnetic susceptibility measurements, where a plot of the out-of phase (χ'') magnetic susceptibility versus frequency (ν) will yield shifting peak maxima towards lower frequency. The relaxation time (τ) is extracted from this plot where $\tau = 1/(2\pi\nu)$, (ν being the peak maxima) and U_{eff} is then determined from the linear section of the Arrhenius plot where $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$. T_B is determined from a simple hysteresis measurement (graphically illustrated in Figure 1.1) where for the purpose of this thesis, T_B is the highest temperature with a measurable coercive field. Both measurements are conducted using a helium-cooled super-conducting quantum interface device, commonly called a SQUID magnetometer.

1.1.2 The Metal Ion

Spin is an essential feature of any magnet. The spin ground states of reported SMMs range from $S = 1/2^4$ (single metal-ion) complexes, to an $S = 82/2^5$ metal cluster. Spin however, is not directly correlated to T_B , where higher spin complexes do not necessarily show higher T_B .⁵ Structurally, SMMs have been constructed from both d- and f- block metals where the unifying factor is that all SMMs contain at least one paramagnetic metal ion with an anisotropic electronic structure. In recent years, Kramer ions (metal ions with a 1/2 integer spin) are by far the most popular choice of metals as they guarantee a bi-stable low-lying electronic structure (Figure 1.2A); however, many of the highest T_B SMMs are constructed from non-Kramer ions. When choosing a metal ion, two facts are pertinent to understanding current SMM design. First, the role of the metal ion in an SMM is not exclusively about providing spin, and second, electronic anisotropy does not guarantee SMM behaviour even in complexes with large spin ground states.^{6,7}

1.1.3 Advances in Ligand Design

Structurally, SMMs are complexes consisting of one or more metal ions in a discrete ligand environment. SMM design has progressed a long way from only considering the total spin of the molecule. It is well understood that three molecular features dictate SMM behaviour; metal-metal interactions, geometry and ligand field effects. General design strategies for achieving high T_B SMMs in recent literature have focused on one or more of these three attributes.

The first strategy pertains to metal-metal interactions, where discrete multi-nuclear metal complexes containing strong ferromagnetic metal-metal interactions are desirable, as this leads to a large spin ground state. Controlling ferro- versus antiferromagnetic exchange is difficult. Moreover, synthesizing molecules with strong exchange coupling (J) is challenging, particularly in lanthanide (Ln) complexes due to the limited radial extension of 4f orbitals. A detailed discussion of how to overcome this characteristic in Ln-containing SMMs is provided in Section 1.2.2.

The second design principle is molecular symmetry, which has been an on-going discussion in the field of SMMs all the way back to the very first class of magnets

incorporating a Mn_{12} core.⁸ It is well established that high symmetry can suppress quantum tunneling of the magnetization (QTM) in both d- and f- block complexes which aids in the low temperature magnetic performance in such SMMs.⁹ QTM is a quantum mechanical phenomena that occurs when there is mixing of wavefunctions between two m_s states at the same energy (Figure 1.3A). QTM was first reported in 1996 by Barbara and independently by Ziolo where both groups observed quantum steps in magnetic hysteresis loops.¹⁰ Such steps (indicating QTM) signified quantum effects could be observed by simple measurements on bulk polycrystalline samples where the magnetic response was coming directly from inter- and intramolecular magnetic effects. Although this is one of the most interesting physical features of SMMs it also results in either completely suppressing SMM behaviour (where there is significant ground state tunneling), or decreasing U_{eff} (thermally-assisted QTM) through rapid magnetic relaxation (Figure 1.3A). Therefore strategies to prevent QTM in SMMs are sought after.

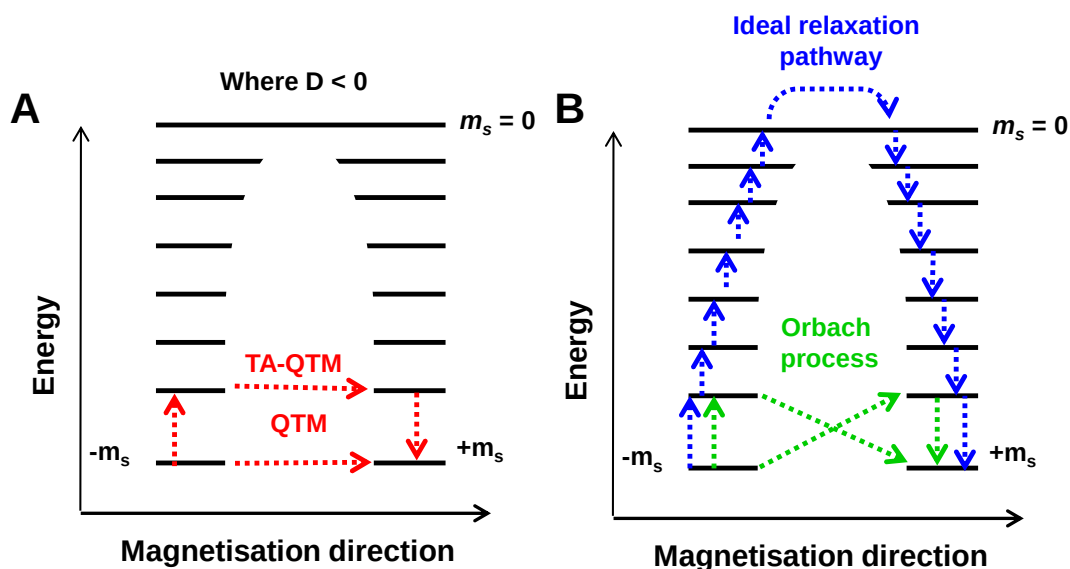


Figure 1.3. Graphical illustration of magnetic relaxation mechanisms in SMMs (where $D < 0$). Black lines represent Kramers doublets as a function of the magnetization direction (arbitrary molecule). (A) Ground-state quantum tunneling (QTM), and an example of thermally-assisted QTM (TA-QTM). (B) Thermally-assisted relaxation pathways, where the ideal situation is in blue and the most common Orbach mechanisms are in green.

In addition to suppressing ground state QTM, it has recently been demonstrated that high site-symmetry around the metal ion can facilitate magnetic relaxation via the 2nd excited

state.¹¹ Magnetic relaxation in lanthanide SMMs occurs in two ways, QTM (either ground-state or thermally-assisted) or Raman/Orbach processes (Figure 1.3). In the latter, magnetic relaxation occurs through the excited Kramers doublets (KD), however until recently only relaxation via the first excited state had been observed. Ideally magnetic relaxation would occur via all the KD's, maximizing U_{eff} (graphically depicted in figure 1.3B). Although the discussion of symmetry in SMMs usually pertains to high symmetry complexes, more recently a number of very low symmetry complexes have also shown interesting SMM behaviour. In such low-symmetry cases, SMM properties are resulting from excited state anisotropy¹²

The final design strategy pertaining to SMMs, is tailoring the ligand field to provide large zero-field splitting (ZFS) with strictly axial anisotropy.¹³ The basic predictability of obtaining axial anisotropy with different ligand field environments is discussed in detail in section 1.2.1.1. Since lanthanide SMMs have far exceeded the T_B of transition metal complexes, the following discussion will pertain to lanthanide SMMs, except where otherwise stated.

1.2 Recent Advances in Lanthanide SMMs

1.2.1 Mononuclear SMMs Exploiting 4f Anisotropy

In recent years, lanthanide-containing complexes have become the most popular class of SMMs as they exhibit exceptionally high anisotropic barriers and have far surpassed the T_B of transition metal complexes. Interestingly, the first reported lanthanide SMM ($[\text{Pc}_2\text{Ln}]^- \text{TBA}^+$ ($\text{Ln} = \text{Tb}, \text{Dy}$, $\text{Pc} = \text{phthalocyanine}$, $\text{TBA}^+ = \text{N}(\text{C}_4\text{H}_9)_4^+$))¹⁴ was also the first reported single-ion complex to exhibit slow magnetic relaxation. Since this discovery, single-ion SMMs have become so prevalent that they even have their own acronym, now commonly referred to as SIMs (single-ion magnets). Ln-SIMs are important to study due to their structural simplicity, and have greatly advanced our understanding of spin-relaxation in lanthanides. For application purposes, SIMs also represent the smallest possible magnetic unit and they have recently been investigated for uses on surfaces and in molecular-scale electronics.^{1a,15} Finally, Ln-SIMs are heavily

studied because they often exhibit remarkably high T_B particularly with high symmetry ligands including the complexes depicted in Figure 1.4.

Much of our current understanding of Ln-SIMs has come from Ishikawa's work on LnPc_2 complexes. Complex A (Figure 1.4) is the iconic TbPc_2^- sandwich complex which exhibits a remarkably high anisotropy barrier due to its high symmetry double-decker structure.¹⁴ The structural-magneto relationships of LnPc_2 SIMs with varying oxidation states and derivatized Pc ligands has been reviewed extensively.^{16,17} In 2007 we saw a significant jump in the anisotropy barrier of TbPc_2^- by the oxidation of the ligand and the addition of terminal OEt groups which caused longitudinal contraction of the coordination sphere around the Tb^{III} ion.¹⁸ The increase in U_{eff} in this case resulted from an increase in splitting between the ground and first excited state KD arising from the stronger interaction between ligand and metal electron density.¹⁸ In 2013 a study by Coronado and Torres demonstrated the effects of homo- and heteroleptic derivatization of Pc ligands using various terminal substituents.¹⁹ They discovered the highest reported anisotropy barriers to date ($U_{\text{eff}} = 653 \text{ cm}^{-1}$, 939 K), which come from a heteroleptic TbPc_2^- complex where one ligand has been derivatized with terminal tert-butylphenoxy groups that act as electron donors and ultimately cause a stronger ligand interaction between the Tb^{III} ion and the unsubstituted ring.

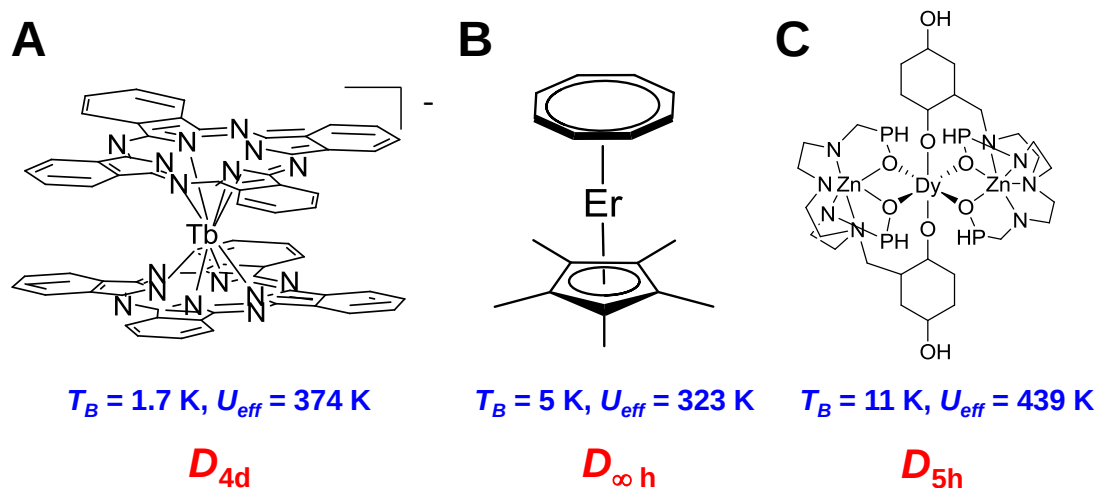


Figure 1.4. Structures of some high symmetry SIMs with the highest T_B and anisotropy barrier at $H_{\text{dc}} = 0$ labeled. (A) TbPc_2^- ,¹⁴ (B) $(\text{Cp}^*)\text{Er}(\text{COT})$,²⁰ (C) $[\text{Zn}_2\text{DyL}_2(\text{MeOH})]\text{NO}_3 \cdot 3\text{MeOH} \cdot \text{H}_2\text{O}$, $\text{L} = 2,2',2''\text{-}(((\text{nitrilo-tris(ethane-2,1-diyl))tris(azanediy))tris(methylene))tris-(4-bromo-phenol))$.²¹

Another important advance in the field of Ln-SIMs is the introduction of organometallic chemistry. Figure 1.4B depicts the structure of one of the first reported organometallic SIMs, structurally consisting of a heteroleptic sandwich complex of Er^{III} with COT (cyclooctatetraenyl) and $\text{Cp}^*(1,2,3,4,5\text{-pentamethylcyclopentadienyl})$ rings.²⁰ This very simple structure reveals one of the highest T_B 's to date (5K) and will be further discussed in relation to homoleptic COT complexes in Chapters 2 and 7. The entrance of organometallics has also influenced the design of transition metal (TM) SIMs. In particular, several linear TM-SIMs have recently been reported including a Ni(I) N-heterocyclic carbene complex $[\text{Ni}(\text{6-Mes})_2]^+$, and a linear Fe(I) complex $[\text{Fe}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$.^{4b,c} The SIM behaviour in both structures originates from the near-linear coordination environments which promote uniaxial magnetic anisotropy. A linear geometry has also been speculated to yield high U_{eff} Ln-SIMs but this theory has been limitedly explored experimentally.^{13b,c}

Ln-SMMs synthesized via coordination chemistry usually contain more than one paramagnetic metal ions; with one of the few exceptions being a Dy^{III} complex with quasi- D_{5h} geometry that exhibits the record SIM blocking temperature of 11 K (Figure 1.4C).²¹ The success of this complex results from the high local symmetry around the spin carrier which prevents certain crystal field parameters that can result in QTM.²¹ This study by Chibotaru and Tong used a reversible single-crystal-to-single-crystal transformation between the solvated and desolvated analogs to clearly demonstrate the benefit of high symmetry in promoting Ising type magnetic anisotropy in Ln-SIMs.

1.2.1.1 The Predictability of SIM Behaviour in Lanthanide Complexes

Designing new SMMs has significantly progressed from the initial serendipitous strategy.^{5,22} In addition to the trends discovered experimentally such as symmetry, geometry and electronic effects, as discussed above, in 2011 Rinehart and Long^{13a} proposed a simple but powerful electrostatic model for predicting and explaining SMM behaviour in mononuclear Ln-SIMs. The model uses the varying prolate vs. oblate asphericity of the 4f shell, quantified by Sievers in 1982.²³ Basically they postulate that oblate Ln-ions (i.e. Ce^{III} , Tb^{III} , Dy^{III}) should feel the least electrostatic repulsion with an axial crystal field, maximizing anisotropy. Likewise Ln-ions with a

prolate distribution (i.e. Er^{III} , Yb^{III}) should prefer an equatorial ligand field. This theory has been heavily debated in the literature with many exceptions being reported due to certain over-simplifications of the model.^{20,24} However it remains one of the most important predictive tools for synthetic chemists when initially targeting new SIMs. It should be noted that Soncini²⁵ recently quantified this model using an electrostatic energy integral. Their method is remarkably able to predict the anisotropy axis even in low symmetry complexes solely from X-ray structure data.²⁵

1.2.2 Multi-nuclear Lanthanide Complexes

Ln-SMMs display the highest T_B 's to date;²⁶ this is despite the fact that the majority of polynuclear Ln-SMMs display predominantly single-ion magnetic relaxation dynamics, even at very low temperatures. Polynuclear Ln-SMMs displaying a single magnetic relaxation due to a unified spin ground state is desirable. However, the poor radial extension of the 4f orbitals limits orbital overlap with bridging ligands, resulting in poor magnetic exchange and thus the major challenge with 4f-element SMMs. Tremendous effort has been put into overcoming this limitation with a particular focus on di-nuclear lanthanide complexes.

1.2.2.1 Dinuclear Lanthanide Complexes with Neutral Bridging Ligands

Several recent studies have focused on dinuclear lanthanide (Ln_2) complexes as they provide the simplest model to study magnetic interactions between two spin carriers.²⁷ Strong exchange coupling between lanthanide ions is desirable as this potentially leads to a larger spin ground state²⁸ and is known to suppress QTM in Ln_2 complexes.²⁹ The key to a strong magnetic interaction (whether dipolar interactions or exchange coupling) is the bridging ligand. The vast majority of Ln_2 complexes are oxygen-bridged due to the oxophilic nature of lanthanides, and the simplicity of coordination chemistry. Layfield and Winpenny offered a much needed diversity to oxo-bridged complexes with a series of classic organolanthanide Cp (cyclopentadienyl) complexes with the general formula $[(\eta^5\text{-Cp})_2\text{Ln}(\mu\text{-X})]$ where heteroatom bridges include Cl, bta (benzotriazolidine),³⁰ and SSiPh_3 ³¹ among others. All of these complexes were SMMs and *ab initio* calculations revealed an axial character to the ground KD's in each case.³¹ DFT calculations revealed

a weak Ln-Ln interaction in Cl- and bta-bridged complexes whereas the much softer sulfur atoms in the thiolate-bridged dimer $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Dy}(\mu\text{-SSiPh}_3)]_2$,³¹ resulted in a stronger exchange interaction and the highest U_{eff} out of the series ($U_{\text{eff}} = 133 \text{ cm}^{-1}$). The use of soft p-block bridging atoms has only been very limitedly explored but in principle, and based on the thiolate-bridged dimer discussed above, warrants more attention.³²

Prior to the work presented in this thesis, the only Ln_2 sandwich-type SMMs were bridged by Pc ligands.³³ In 2005, Ishikawa demonstrated the first f-f interaction in an SMM by carefully analysing both bis-Tb as well as Y-Tb mixed sandwich complexes.^{33a} Such complexes were composed of two Pc ligands and one terminal obPc ligand (obPc = dianion of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine), linearly stacked with either [Tb, Tb], [Tb, Y] or [Y, Tb] ions. The influence of each coordination site on the magnetic properties of Tb^{III} was determined from the diamagnetic yttrium dilution. This method also confirmed an f-f interaction between Tb^{III} ions. This study as well as a similar one on homoleptic triple decker $[\text{Tb}_2(\text{obPc})_3]$ ^{33c} complexes illustrated that in addition to a ferromagnetic dipolar interaction between Tb^{III} ions, QTM in both systems was suppressed due to the f-f interaction.

1.2.2.2 Mixed Metal 3d-4f SMMs

One way of utilizing highly anisotropic lanthanide ions, while improving the exchange interactions between metals is through mixed transition metal-lanthanide (3d-4f) complexes. In most recent reports, such mixed metal systems generally consist solely of highly anisotropic metal ions (most often containing $\text{Co}(\text{II})$).³⁴ However isotropic³⁵ as well as diamagnetic³⁶ metals have also been explored.

Some of the most interesting work in this area came from a recent report by Chibotaru and Murray³⁷ who presented two mixed $\text{Cr}^{\text{III}}_2\text{-Dy}^{\text{III}}_2$ complexes ($[\text{Cr}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\text{OMe})_2(\text{RN}\{(\text{CH}_2)_2\text{OH}\}_2)_2(\text{acac})_4(\text{NO}_3)_2]$, $\text{R} = \text{Me}, \text{Et}, n\text{Bu}$, and $[\text{Cr}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\text{OMe})_2(\text{O}_2\text{CPh})_4(\text{mdea})_2(\text{NO}_3)_2]$, $\text{mdeaH}_2 = N\text{-methyldiethanolamine}$), and compared their structural and magnetic properties to structurally analogous mixed-metal $\text{Co}^{\text{III}}_2\text{-Dy}^{\text{III}}_2$. They determined that not only does the paramagnetic Cr^{III} in place of the diamagnetic Co^{III} result in longer relaxation times, but more interestingly the anisotropy

barrier was directly correlated to the strength of the exchange interaction between metals. Although 3d-4f mixed metal complexes have yet to exhibit a T_B over a few kelvin, this area is very much under-explored. For example, the only 3d-4f SMMs reported thus far, contain Ln-ions exclusively coordinated to oxygen donor atoms.³⁸

1.2.2.3 Radical-Bridged Lanthanide SMMs

Radical-bridged Ln complexes are arguably the best strategy for achieving strong exchange coupling between lanthanide ions. Inserting a radical between two metal ions forces an antiferromagnetic Ln-radical interaction and therefore results in a ferromagnetic exchange between Ln-ions (Figure 1.5).



Figure 1.5. Graphical illustration of the typical spin alignment between lanthanide ions bridged by a neutral ligand (A), and a radical-containing ligand (B). Green circles represent Ln^{III} ions and black circle represents a radical spin.

This strategy of controlled ferromagnetic coupling was first illustrated by Sessoli in 2007 using a Dy^{III} nitronyl-nitroxide complex.³⁹ Several recent contributions by the Long group have demonstrated that incorporating a radical bridging ligand not only results in ferromagnetic exchange between lanthanide ions, but more importantly some radical-bridged complexes can facilitate extremely strong exchange coupling (J) (Figure 1.6). The best example is a N_2^{3-} radical-bridged terbium complex, $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tb}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)^-$ which holds the records for both large J and T_B values for an SMM.^{26c} In this complex and the others represented in Figure 1.6, the large J values are a result of the diffuse spin orbitals on the bridging ligands which penetrate the 4f orbitals.⁴⁰ However, in complexes C and D in Figure 1.6, we learn that just having a radical-bridged lanthanide system is not enough to guarantee SMM behaviour. In this case, the discrepancy of SMM behaviour in mono-anionic and cationic species is attributed to slight differences in symmetry.

Despite the obvious potential of radical-bridged SMMs to increase T_B , very few complexes have been reported. Many areas are unexplored including the use of more diffuse bringing ligands, and complexes containing more than two lanthanide ions. The only chain structures containing alternating lanthanides and radicals are with nitronyl-nitroxide ligands.⁴¹

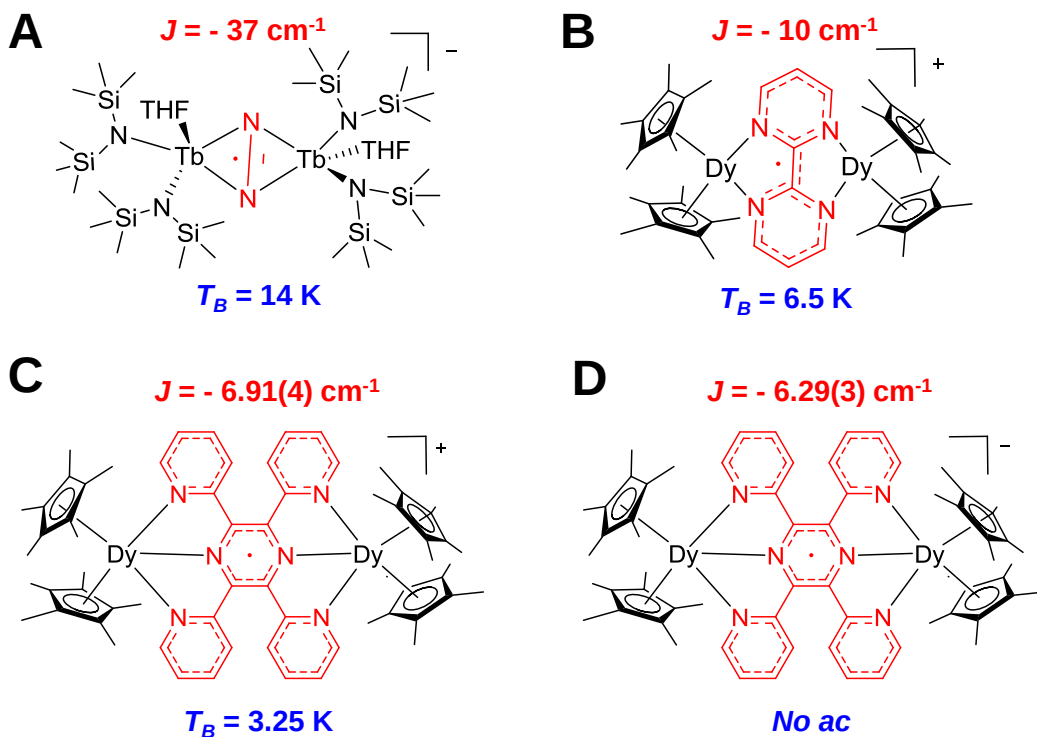


Figure 1.6. Structures of radical-bridged SMMs with bridging ligands highlighted in red. In all cases the J value was obtained from fitting the dc data of the structurally analogous Gd^{III} complex. T_B is defined here as a measurable coercive field. **(A)** $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tb}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)^{\cdot-}$,^{26c} **(B)** $[(\text{Cp}^*\text{Dy})_2(\mu\text{-bpym}\cdot)]$ (bpym = 2,2'-bipyrimidine),^{26f} **(C)** $[(\text{Cp}^*\text{Dy})_2(\mu\text{-tppz}\cdot)](\text{BPh}_4)$ (tppz = 2,3,5,6-tetra(2-pyridyl)pyrazine),⁴⁰ **(D)** $[\text{K}(\text{crypt-222})][(\text{Cp}^*\text{Ln})_2(\mu\text{-tppz}\cdot)]$ ⁴⁰.

1.3 Actinide Single Molecule Magnets

The field of SMMs has dramatically evolved particularly in the last 10 years. One of the most recent advances is the entrance of the actinides. Actinide elements combine the two most advantageous features of the transition metal and lanthanide elements; large magnetic anisotropy and covalency. Compared to the 4f orbitals, the 5f orbitals have a larger radial extension which can allow covalent interactions with bridging ligands and therefore

stronger exchange coupling.⁴² Although this is arguably the missing attribute in lanthanide SMMs, covalency comes with unique challenges. Much of the success of mononuclear lanthanide complexes is the result of unquenched orbital angular momentum which is a consequence of the core orbital nature of the 4f orbitals.^{26c} With multi-nuclear uranium complexes, stronger exchange coupling may be possible, but the magnetic properties are much more sensitive to ligand field effects where orbital angular momentum can be partially quenched.⁴² This results in a much more complicated picture of uranium magnetism and requires a higher level of rational design than lanthanide SMMs.

1.3.1 Uranium^{III} Mononuclear Complexes

The field of actinide SMMs is still very young with only a couple of dozen complexes reported, the majority of which are U^{III} mononuclear complexes. A recent report by Coronado and Gaita-Arino analyzed the magnetic properties of several published U^{III} SMMs by combining experimental data with a correlated crystal field model.⁴³ Results suggested complexes with ligand electron density along the symmetry axis as well as a trigonal prismatic geometry may provide ideal conditions to harness U^{III} SMM behavior.⁴³

This work inspired the report of numerous uranium SMMs with trigonal prismatic geometry and their results are tabulated in Table 1.1. Interestingly, none of these reported complexes display particularly strong SMMs properties. This may be due to small deviations from ideal geometry; however when looking at the whole body of reported U^{III} SMM data, an additional trend may also be a contributing factor. In more than half of reported U^{III} SMMs there is an order of magnitude discrepancy between U_{eff} and the ground and first excited state energy separation.⁴⁴ This is not the case for many lanthanide SMMs where the difference between the ground and first excited state KD frequently correlates to the experimental U_{eff} values. In lanthanide SMMs such ground state calculations are often used as an important tool for predicting the SMM properties of complexes prior to synthesis.^{45,13b,c} In U^{III} SIMs however, this discrepancy suggest an alternative spin-lattice relaxation mechanism that is not an Orbach process.⁴⁴

Table 1.1. Magnetic properties of U^{III} SMMs with trigonal prismatic geometry.

	U_{eff} (cm ⁻¹)	U_{eff} Obtained Under H_{dc}	U_{eff} (cm ⁻¹) (calculated)	Blocking Temperature	Reference
$\text{U}(\text{Ph}_2\text{BPz}_2)_3$	20	No	190	--	46
$\text{U}(\text{H}_2\text{BPz}_2)_3$	16	Yes	230	--	47
UTp_3	3.8	Yes	270	--	48
$\text{U}(\text{Bp}^{\text{Me}})_3$	--	--	--	--	49
$\text{U}(\text{Bc}^{\text{Me}})_3$	23	Yes	--	--	49

[BPz₂] = bis(pyrazolyl)borate, [Tp]⁻ = trispyrazolylborate, [Bp^{Me}]⁻ = dihydrobis(methypyrazolyl)borate, [Bc^{Me}]⁻ = dihydrobis(methylimidazolyl)borate.

Considering the experimental results of reported U^{III} SMMs, no specific trends regarding ligand field are apparent. However, Long recently demonstrated that ligand donor strength highly influences SMM performance in U^{III} mononuclear complexes.⁴⁹ The magnetic properties of two isostructural U^{III} complexes, U(Bp^{Me})₃ and U(Bc^{Me})₃ (Bp^{Me} = dihydrobis(methypyrazolyl)borate, Bc^{Me} = dihydrobis(methylimidazolyl)borate), were compared (Figure 1.7). The magnetic properties of the two complexes drastically differed where U(Bc^{Me})₃ afforded an energy barrier of 23 cm⁻¹ that increased to 33 cm⁻¹ upon magnetic dilution in a Y^{III} matrix, making it the highest energy barrier to date for a U^{III} mononuclear SMM.⁴⁴ U(Bp^{Me})₃, however, showed no slow magnetic relaxation dynamics and this difference in magnetic behaviour is due to the increased donor strength from the N-heterocyclic carbene ligands.⁴⁹ This work signifies that in addition to symmetry, ligand donor strength can dramatically influence the slow relaxation of uranium SIMs.

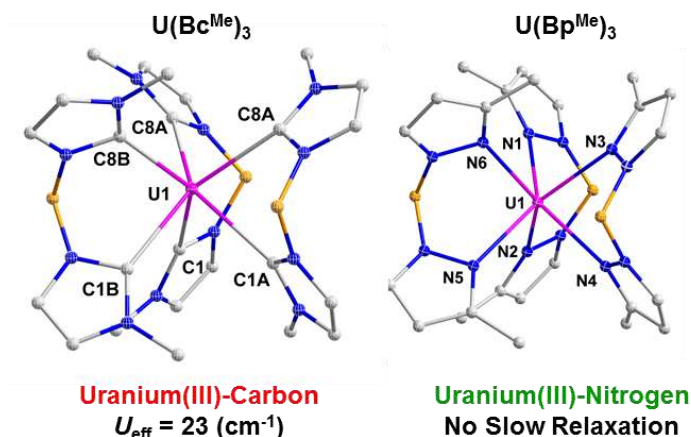


Figure 1.7. Solid state structures of U(Bp^{Me})₃ and U(Bc^{Me})₃.⁴⁹ H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Color code: uranium^{III} (pink), carbon (grey), nitrogen (blue), boron (orange).

1.4 Conclusions

The rational design of SMMs has undergone a clear shift in recent years. Mono- and dinuclear lanthanide complexes are now the most heavily studied due to their (relatively) high U_{eff} and T_B values. The vast majority of recent contributions have focused on elucidating the origins of spin relaxation in simple molecules. The three different approaches to Ln-SMM design (increasing J , symmetry, and ZFS via ligand field effects) have been extensively investigated individually. However, in order to push the T_B limit of SMMs, a more sophisticated rational design that incorporates all three of these attributes is essential, and is lacking in the field today.

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Chapter 2

Organolanthanide Sandwich Single-Ion Magnets with 1,4-Bis(trimethylsilyl)cyclooctatetraenyl Dianion Ligands*

Partial contents of this chapter have been published in: (a) J. J. Le Roy, M. Jeletic, S. I. Gorelsky, I. Korobkov, L. Ungur, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. **2013, 135, 3502. (b) J. J. Le Roy, I. Korobkov, M. Murugesu, Chem. Commun. **2014**, 50, 1602. (c) J. J. Le Roy, I. Korobkov, M. Murugesu, Dalton Trans. **2014**, 43, 2737.*

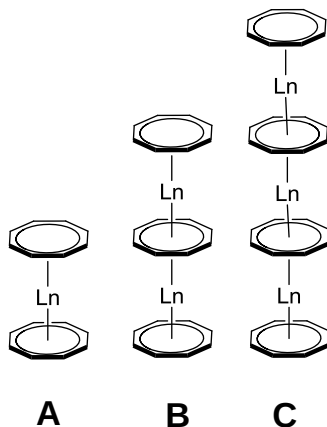
This chapter discusses the synthesis, structures and magnetic properties of a series of eight lanthanide monomers each having the general formula $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}^{\prime\prime})_2]$, ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$, $\text{DME} = 1,2\text{-dimethoxy ether}$ and $\text{COT}^{\prime\prime} = 1,4\text{-bis(trimethylsilyl)cyclooctatetraenyl dianion}$). The eight structures were confirmed to be essentially isomorphous by infrared spectroscopy and single crystal X-ray diffraction. Direct current (dc) and alternating current (ac) magnetic measurements were performed to probe the magnetic properties of all complexes. Both Dy^{III} and Er^{III} complexes exhibit zero-field SIM properties; additionally the Er^{III} complex exhibits signature magnetic remanence and coercivity characteristics in the hysteresis loops up to 8 K.

2.1 Introduction

This chapter builds upon concepts discussed in **1.2.1** pertaining to the rational design of lanthanide SIMs. In order to construct SMMs with high-energy barriers, it is essential to understand the magnetic behaviour arising from each individual metal center. This is one reason why SIMs have gained increasing attention in recent years.¹ The majority of reported SIMs are magnets due to their highly anisotropic $4f$ ions.² In such lanthanide systems, we have seen a recent synthetic trend towards sandwich complexes where among others Cp^* , $\text{COT}^{\prime\prime}$, and Pc ligands have been investigated.³ In all of these systems,

ligands are π -bonded to the central metal ion, thus the bite angle of the ligands dictates the overall coordination geometry of the complex. This chapter examines organometallic lanthanide sandwich molecules, $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}'')_2]$, where COT'' ligands are bound to the central metal center through the π -cloud.

The COT'' ligand was chosen due to its tune-ability as well as its potential to construct sandwich-type magnetic building blocks.⁴ Utilising highly tuneable ligands such as COT'' is ideal when constructing SIMs because the second coordination sphere of a molecule can have a strong effect on the magnetic anisotropy axis of an SIM.⁵ Therefore the highly tuneable COT ring is an excellent template for exploring both symmetry effects as well as electronic effects of sandwich-type SIMs. Bis(trimethylsilyl)-substituted COT was chosen for the initial study in this chapter due to its facile synthesis. Moreover, the trimethylsilyl (TMS) groups aid in the solubility of the metal complexes.⁶ The tune-ability of Ln-COT SMMs is further discussed in chapter 3.



Scheme 2.1. Different types of metallocenes. Species **A** represents the “typical” sandwich complex, species **B** and **C** are extended sandwich complexes.

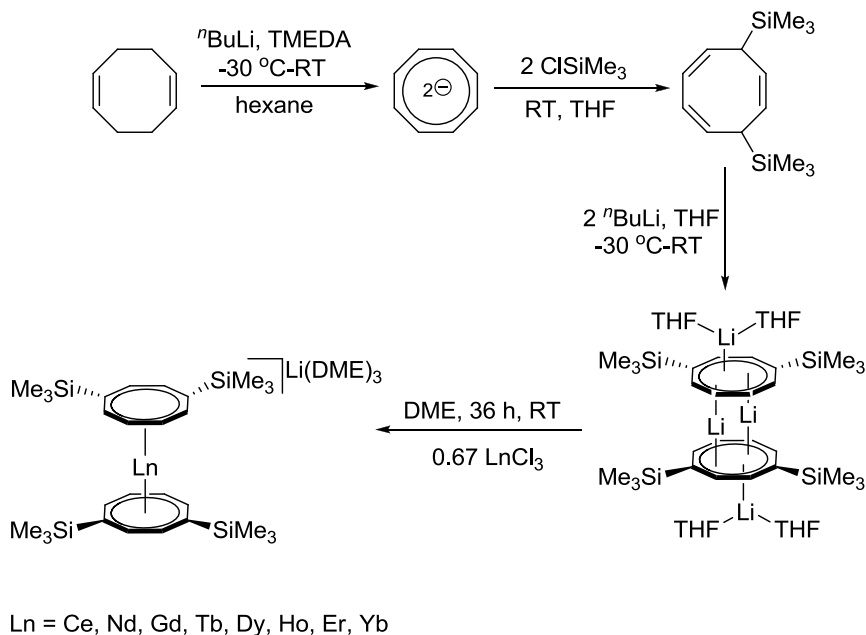
The second advantage to choosing the COT'' ligand for constructing new SIMs is the potential for these complexes to not only act as SIM's, but also as building blocks towards multi-metallic metallocenes (Scheme 2.1). There are several advantages to multi-metallic COT'' complexes including an aromatic superexchange pathway to facilitate strong J coupling between Ln^{III} ions, as well as high axial symmetry in **B** and **C** type

complexes, which may lead to strictly axial anisotropy (Scheme 2.1). Multi-metallic COT-based complexes are further discussed in Chapters 4 and 5.

In order to create high blocking temperature SMMs using multi-metallic COT'' complexes, we must first identify which lanthanide metals show the most promise in exhibiting SIM properties in the COT'' ligand field. To this extent, we have focused our attention on different Ln metals in $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}'')]_2$ sandwich complexes. Such complexes have an overall charge of -1 as the metal ions are in the +3 oxidation state and the ligands are dianionic. Herein includes the synthesis, structures and magnetic properties of a family of mononuclear organolanthanide sandwich complexes synthesized using the COT'' ligand.

2.2 Results and Discussion

2.2.1 Synthesis



Scheme 2.2. Synthetic route to $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}'')]_2$ monomers starting from 1,5-cyclooctadiene. Synthetic scheme was inspired from Ref. 6, 7 and 12.

In order to isolate sandwich type molecules, the use of planar cyclooctatetraenyl (COT) ligands has become a convenient synthetic procedure.⁷ For example, in 2011

Murugesu reported an organolanthanide sandwich complex, $[\text{Dy}(\text{COT}''')_2\text{Li}(\text{THF})(\text{DME})_3]$, where the Li atom is bound to the COT''' ring yielding an asymmetric molecule.⁸ Using a similar methodology with a slight change in crystallisation method, a series of mononuclear complexes, $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}''')_2]$, with Ln = Ce (**CeCOT'''**), Nd (**NdCOT'''**), Gd (**GdCOT'''**), Tb (**TbCOT'''**), Dy (**DyCOT'''**), Ho (**HoCOT'''**), Er (**ErCOT'''**), and Yb (**YbCOT'''**) were isolated. Scheme 2.2 displays the synthetic pathway for obtaining the aforementioned family. The general synthetic approach (inspired by Edelmann's group^{12,13,14e}) involves the reaction of one equivalent of LnCl_3 with 1.5 equivalents of the tetralithio-salt precursor, $[(\text{Li}(\text{THF})_2)\text{COT}'''\text{Li}_2\text{COT}''(\text{Li}(\text{THF})_2)]^{6,9}$, in DME for 36 h at room temperature. Recrystallizing from a concentrated solution of 1:1 DME/hexane generates large, vibrant block crystals suitable for single-crystal X-ray diffraction. As previously suggested, the formation of $\text{Ln}^{\text{III}}\text{COT}'''\text{COT}''$ anions is highly sensitive to reaction/recrystallizing conditions.¹⁰ For instance, five similar structures are now known: $[\text{DyCOT}''')_2\text{Li}(\text{THF})\text{DME}]$,⁸ $\text{Li}(\text{THF})_4[\text{Ln}(\text{COT}''')_2]$ (Ln = Y, Sm, Yb),¹¹ $[\text{Tb}(\text{COT}''')_2\text{LiDME}]$,¹⁰ $[\text{Tb}(\text{COT}''')_2\text{Li}(\text{DME})]_\infty$,¹⁰ and $\text{Li}(\text{DME})_3[\text{Tb}(\text{COT}''')_2]$.¹⁰ In our experiments, we found that the presence of DME aids in growing large crystals suitable for X-ray diffraction, whereas, when THF is employed as the primary solvent fine needle-shaped crystals of $\text{Li}(\text{THF})_4[\text{Ln}^{\text{III}}(\text{COT}''')_2]$ can be isolated. The latter crystals were too small for single crystal X-ray crystallography. Interestingly, an alternative route from $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}''')_2]$ is to first make $\text{Li}(\text{THF})_4[\text{Ln}^{\text{III}}(\text{COT}''')_2]$, and then recrystallize it in DME/hexane. The DME molecules selectively and irreversibly displace the THF molecules.

2.2.2 Solid State Structures

Single crystal X-ray crystallography studies reveal that all complexes are isostructural and crystallize in triclinic *P*-1 space group (Figure 2.1, Table 2.1). As an example, the structure of **DyCOT'''**₂ will be discussed. The molecular structure of **DyCOT'''**₂ is comprised of two silylated COT''' ligands bound η^8 to the central Dy^{III} ion. Three DME molecules surround the lithium counter-ion, providing a six coordinate octahedral environment. This geometry around lithium is not observed in other

similar LnCOT''_2^- complexes, with four coordination predominating.^{8,10-12} The shortest $\text{Li-C}_{\text{COT}''}$ distance is 5.62 Å, and is more than double that in $[\text{Dy}^{\text{III}}(\text{COT}'')_2\text{Li}(\text{THF})(\text{DME})]^\delta$ (2.33-2.51 Å), supporting that the lithium is not bound to the COT'' ring.

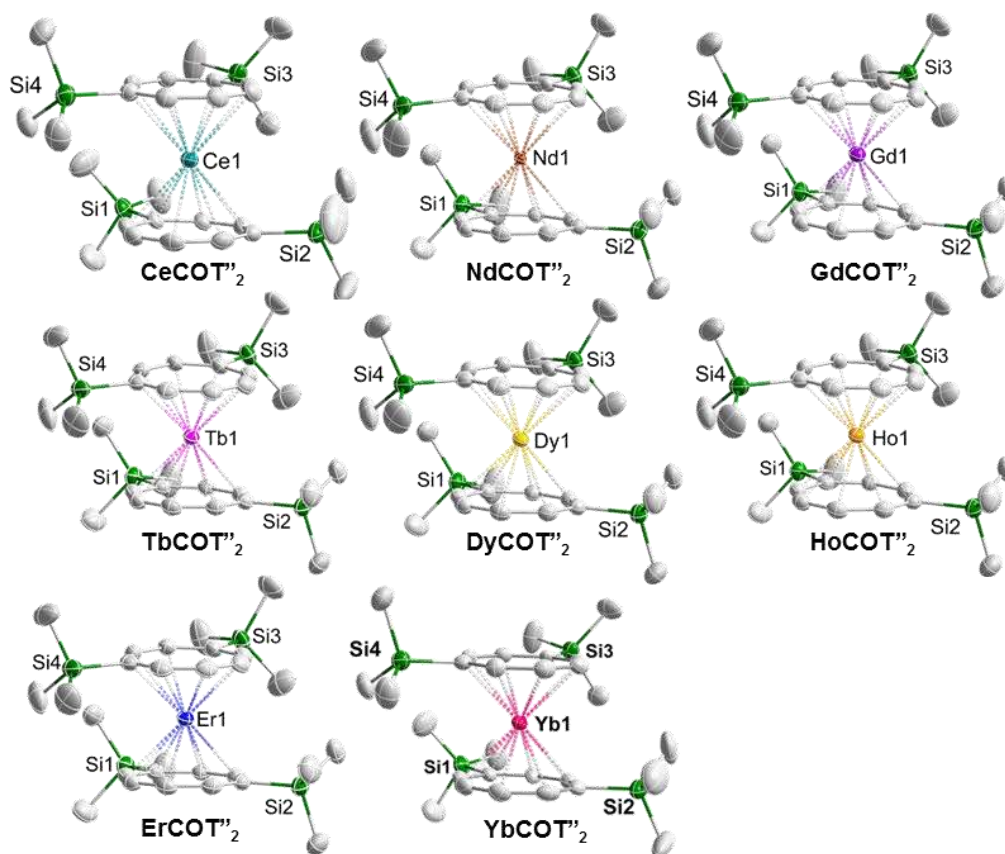


Figure 2.1. Structures of CeCOT''_2 , NdCOT''_2 , GdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 TmCOT''_2 and YbCOT''_2 . H atoms and $\text{Li}(\text{DME})_3$ counter-ion have been omitted for clarity. Thermal ellipsoids are drawn at %50 probability. Colour code: grey (C), green (Si), teal (Nd^{III}), brown (Nd^{III}), purple (Gd^{III}), pink (Tb^{III}), yellow (Dy^{III}), orange (Ho^{III}), blue (Er^{III}) and dark pink (Yb^{III}).

Based on the isostructurality, all 8 complexes exhibit comparable bond angles and distances, and unit cell parameters (Table 2.1, 2.3). For instance, the Si-C distances (1.87 Å) are identical in all 8 structures and match other similar compounds.^{8,10-11} As expected, small periodic trends are observed as a result of changing the Ln^{III} identity. The $\text{Ln}^{\text{III}}\text{-COT}''_{\text{centroid}}$ distance decreases in moving across the periodic table from Ce^{III} to Yb^{III} . The distance changes with the precision of the observed lanthanide

contraction (ionic radii). The average $\text{Dy}^{\text{III}}\text{-C}_{\text{COT}}''$ is 2.66 Å (Table 2.1) and is comparable to the $\text{Dy}^{\text{III}}\text{-C}_{\text{COT}}''$ bond distance (2.67 Å) in $[\text{Dy}^{\text{III}}(\text{COT}'')_2\text{Li}(\text{THF})(\text{DME})_3]^8$. In agreement with the Ln^{III} ionic radii trend, the average $\text{Ln}^{\text{III}}\text{-C}_{\text{COT}}''$ bond decreases in a near identical manner from $\text{Ce}^{\text{III}}\text{-Yb}^{\text{III}}$.

Table 2.1. Selected interatomic distances of CeCOT''_2 , NdCOT''_2 , GdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 and YbCOT''_2 .

	Nearest $\text{Li-C}_{\text{COT}}''$ (Å)	Average M-COT'' (centroid) (Å)	Average $\text{M-C}_{\text{COT}}''$ (Å)	Tilt angle (°)	Nearest M-M intermolecular distance (Å)
CeCOT''₂	5.65	2.06	2.78	3.6	10.43
NdCOT''₂	5.63	2.01	2.73	3.8	10.39
GdCOT''₂	5.61	1.94	2.69	3.7	10.39
TbCOT''₂	5.60	1.92	2.67	3.7	10.38
DyCOT''₂	5.62	1.91	2.66	3.7	10.40
HoCOT''₂	5.62	1.89	2.65	3.7	10.39
ErCOT''₂	5.60	1.88	2.64	3.5	10.39
YbCOT''₂	5.60	1.86	2.62	3.4	10.36

Unexpectedly, the tilt angle does not periodically change as a function of the lanthanide identity. All of the complexes exhibit a 3.4° to 3.8° tilt angle. The proximity of the lithium counter-ion is 5.60-5.65 Å, and the unit cells of the 8 complexes exhibit nothing peculiar that could serve as a reason for the almost 0.4° difference. Notably, the difference in tilt angle between **DyCOT''₂** (3.68°) and $[\text{Dy}^{\text{III}}(\text{COT}'')_2\text{Li}(\text{THF})(\text{DME})_3]^8$ (3.59°) is almost 0.1°. In this case, the binding of the Li-ion may pull enough electron density (by binding η^2) from one COT'' ring to alter the tilt angle. Each of the 8 structures contain two units per unique crystallographic cell. Detailed inspection of the packing arrangement reveals the closest intermolecular M...M distance range from 10.36-10.52-Å, therefore intermolecular magnetic interactions should be negligible.

2.2.3 Electrochemistry of CeCOT''_2 ¹³

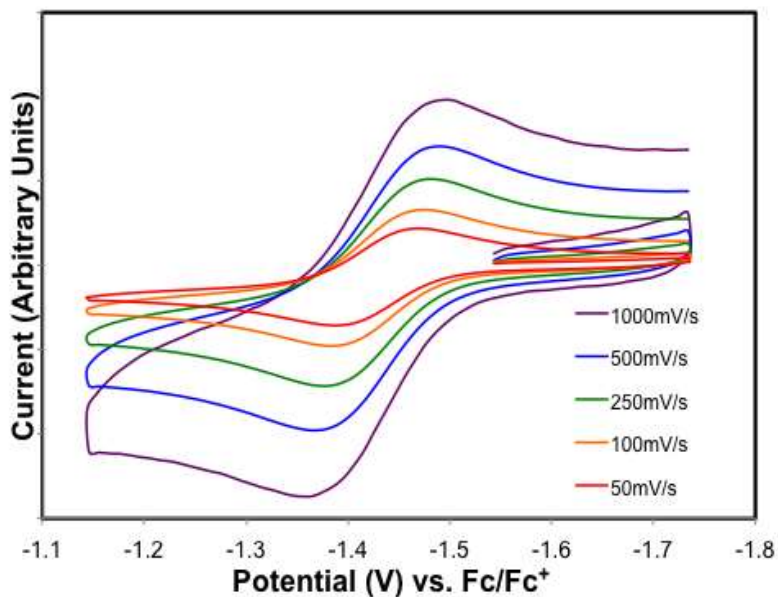


Figure 2.2. Cyclic voltammograms for CeCOT''_2 displaying the scan rate dependence of the formally $\text{Ce}^{\text{III/IV}}$ reversible redox couple recorded in THF. Potentials were referenced to a Fc/Fc^+ internal standard with 0.1 M $[\text{nPr}_4\text{N}][\text{BAr}^{\text{F}}_4]$ supporting electrolyte and ~ 1 mM analyte concentration.¹⁴

The well reported strong reducing power of $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, inspired us to investigate the redox properties of CeCOT''_2 . Electrochemical measurements performed on CeCOT''_2 revealed a one-electron oxidation at -1.43 V *versus* Fc/Fc^+ with a peak-to-peak separation of 80 mV (Figure 2.2); the scan rate dependent behaviour of the wave indicated a reversible electrochemical process as judged by a Randels-Sevcik analysis.¹⁴ This result is consistent with the reported electrochemical behaviour of $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, which exhibited a single electron oxidation at -1.4 V *versus* Fc/Fc^+ .¹⁵ A wider potential scan between $+0.6$ and -3.0 V revealed an irreversible oxidation at $E_{p,a} = +0.1$ V and an irreversible reduction at $E_{p,c} = -2.4$ V.¹⁴ As with $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, the result for CeCOT''_2 indicates a strongly reducing Ce^{III} complex.

2.2.4 Direct Current (dc) Magnetic Susceptibility

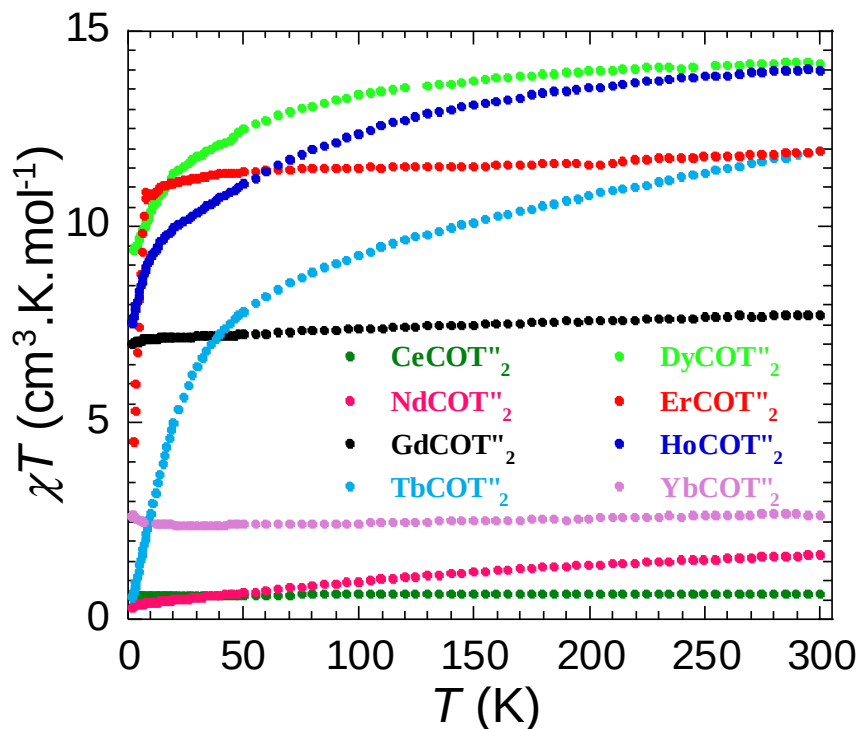


Figure 2.3. Temperature dependence of the χT product under a 1000 Oe applied field for CeCOT''_2 , NdCOT''_2 , GdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 and YbCOT''_2 (with χ being the molar susceptibility per dinuclear complex defined as M/H).

Table 2.2. Dc magnetic susceptibility data for CeCOT''_2 , NdCOT''_2 , GdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 and YbCOT''_2 .

	χT product 300 K ($\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)	Theoretical χT product 300 K ($\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)	χT product 1.8 K ($\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)	Magnetisation 7 T, 1.8 K (μB)	Theoretical magnetisation 7 T, 1.8 K (μB)
CeCOT''_2	0.66	0.80	0.60	1.11	2.54
NdCOT''_2	1.64	1.64	0.33	0.85	3.62
GdCOT''_2	7.74	7.88	7.00	7.89	7.94
TbCOT''_2	11.93	11.82	0.55	2.16	9.72
DyCOT''_2	14.17	14.17	9.22	4.75	10.63
HoCOT''_2	13.98	14.07	7.55	5.76	10.60
ErCOT''_2	11.92	11.48	2.32	4.15	9.59
YbCOT''_2	2.67	2.57	2.63	2.63	4.54

The dc magnetic susceptibilities of **CeCOT**"₂, **NdCOT**"₂, **GdCOT**"₂, **TbCOT**"₂, **DyCOT**"₂, **HoCOT**"₂, **ErCOT**"₂ and **YbCOT**"₂ were investigated using a squid magnetometer under an applied dc field of 1000 Oe and in the temperature range of 1.8-300 K. The χT vs. T plot is shown in Figure 2.3 and the field dependence of the magnetisation for all complexes can be seen in Figures 2.4-2.5. For all complexes, the observed paramagnetic behaviours arise exclusively from the 4f Ln^{III} ions. At room temperature (300 K), the χT values of all complexes are in good agreement with the theoretical value for one respective lanthanide ion (Table 2.2). For **GdCOT**"₂, the χT product remains fairly constant from 300 K down to 1.8 K to reach a minimum of 7.00 cm³·K·mol⁻¹ with a slight negative deviation around 2 K due to weak intermolecular interactions. Such linear non-variation behaviour is due to the absence of spin-orbit coupling in isotropic Gd^{III} ions. The χT products of **CeCOT**"₂, **NdCOT**"₂, **TbCOT**"₂, **DyCOT**"₂ and **HoCOT**"₂ decrease slowly from 300 K down to 50 K with a sharper decrease below 50 K (minimum χT values are reported in table 2.2). This behaviour could originate from the large inherent magnetic anisotropy in these Ln^{III} ions, and/or the depopulation of the excited states. The observed steeper decrease below 50 K is primarily due to the large inherent magnetic anisotropy of Ln^{III} ions and not intermolecular interactions (Ln-Ln distances range from 10.36-10.43 Å), confirmed by the lack of a low temperature deviation in the isotropic reference compound, **GdCOT**"₂. The χT product of **YbCOT**"₂ shows near linear behaviour from 300-20 K, however, interestingly below 20 K there is a sharp increase to reach a maximum value of 2.63 cm³ K mol⁻¹ at 1.8 K which indicates the presence of a dominant ferromagnetic interaction between the spin carriers. The χT product of **ErCOT**"₂ decreases slowly from 300 K down to 50 K, then rapidly decrease below 50 K. Such an abrupt low temperature drop is attributed to significant anisotropy as seen in some other highly anisotropic complexes.¹⁶

Field dependence of the magnetisation and reduced magnetisation of all complexes are presented in Figure 2.4-2.5. The magnetisation of **GdCOT**"₂ under an applied field of 7 T displays near saturation at 7.92 μ B, close to the theoretical value of 7.94 μ B as expected for the isotropic Gd^{III} metal.

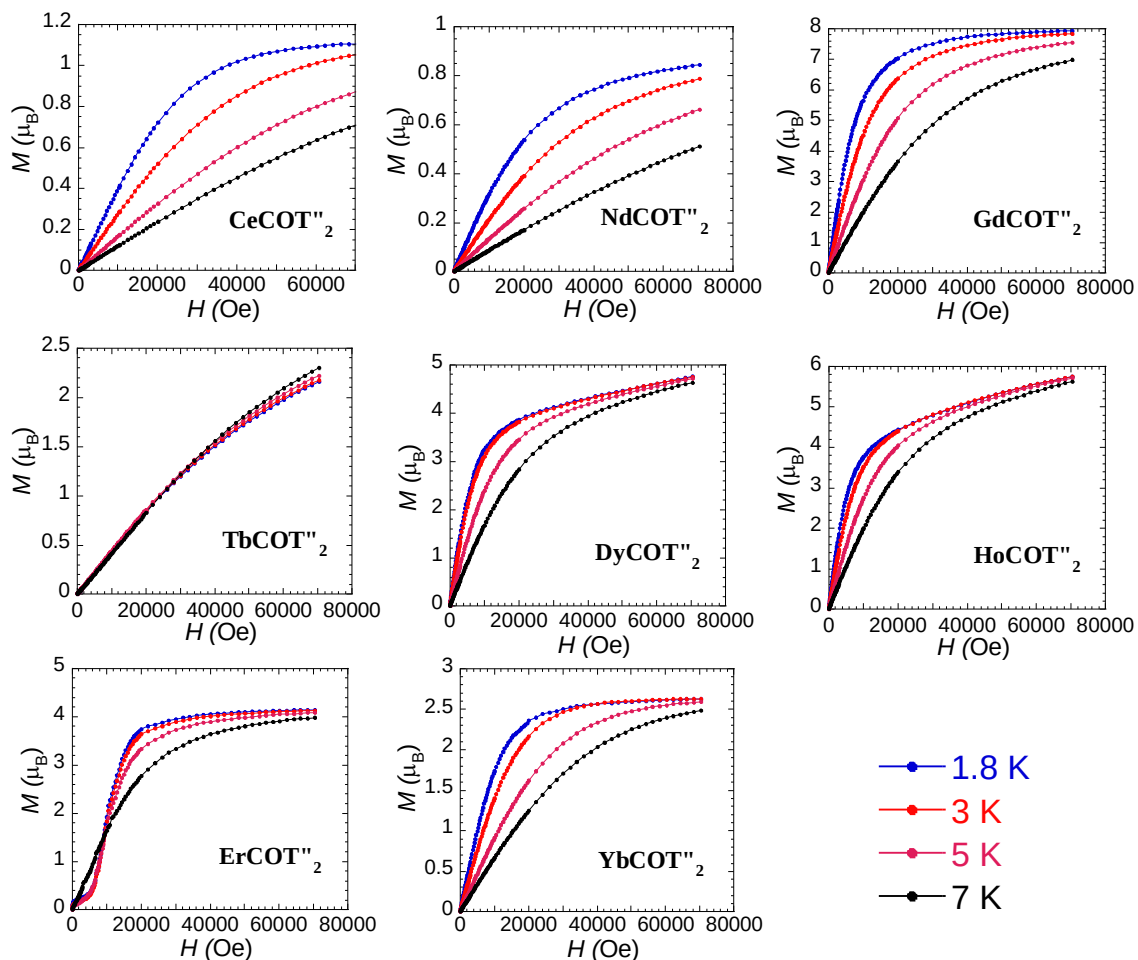


Figure 2.4. Field dependence of the magnetisation for **CeCOT''₂**, **NdCOT''₂**, **GdCOT''₂**, **TbCOT''₂**, **DyCOT''₂**, **HoCOT''₂**, **ErCOT''₂** and **YbCOT''₂** at 1.8, 3, 5, and 7 K.

Field dependent magnetisation measurements for **ErCOT''₂** reveal a rapid and steady increase of the magnetization at 7 K without clear saturation at 7 T. At temperatures below 5 K there is a sinusoidal character observed at applied fields below 1 T. Such a signature feature can be due to quantum tunnelling of the magnetization (QTM) or intermolecular interactions. In **ErCOT''₂** metal centers are separated by at least 10.39 Å, thus, intermolecular interactions are negligible. The magnetisation of **CeCOT''₂**, **NdCOT''₂**, **TbCOT''₂**, **DyCOT''₂**, **HoCOT''₂**, and **YbCOT''₂** shows a rapid increase below 1 T followed by a slow, near linear increase without reaching saturation (maximum values are reported in Table 2.2). As expected, these non-saturation values are lower than the theoretically derived saturation values, which can be attributed to significant magnetic anisotropy or low-lying excited states, which

are inherent to the subsequent Ln^{III} ions. The former considerations also explain the temperature dependence observed in the M vs. $H T^{-1}$ plots. For CeCOT''_2 , NdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 and YbCOT''_2 the curves do not superimpose on a single master curve, also indicative of magnetic anisotropy and/or the presence of low-lying excited states.

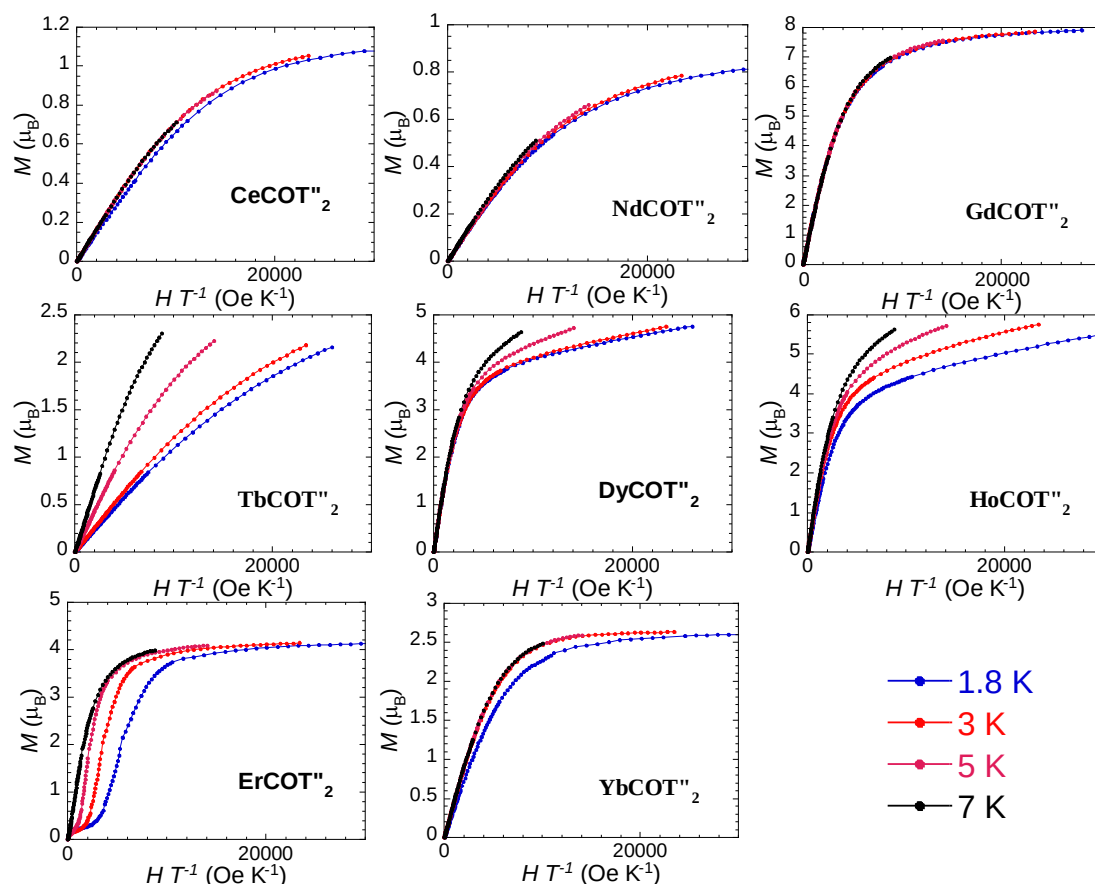


Figure 2.5. Field dependence of the reduced magnetisation for CeCOT''_2 , NdCOT''_2 , GdCOT''_2 , TbCOT''_2 , DyCOT''_2 , HoCOT''_2 , ErCOT''_2 and YbCOT''_2 at 1.8, 3, 5, and 7 K.

To further investigate blocking of the magnetization, temperature dependent hysteresis measurements were carried out between -5 to 5 T and 1.8 to 10 K (Figure 2.6). Only ErCOT''_2 displayed remanent hysteresis at 1.8 K. At a fixed sweep rate of 22 Oe S^{-1} and at 1.8 K the appearance of a clear hysteresis with coercivity is observed for ErCOT''_2 . Remarkably, at $M = 0$ a large coercive field of $\sim 6250 \text{ Oe}$ can be seen at 1.8 K. Upon increase of the temperature, coercivity decreases and closes at $M = 0$ around 8 K. Above 8 K, phonon bottleneck-type hysteresis with small openings can

be seen which disappear above 9 K. Such a large blocking temperature and coercive field is among the highest reported for any SMM regardless of the nuclearity (the vast majority of complexes only behave as SMMs at very low temperatures (>1.8 K)). Moreover, at $H = 0$ remnant magnetization can be seen in the hysteresis of **ErCOT**"₂, which is an essential quality a magnet must possess for information storage applications. It is noteworthy that the step-like feature at ~ 4500 Oe is most likely arising from thermally-assisted quantum tunnelling of the magnetisation (QTM) behaviour while the step at zero field is due to ground state tunnelling. Although ground state QTM is expected to be suppressed for a Kramer system, environmental degrees of freedom as well as hyperfine and dipolar coupling via transverse field components can result in non-negligible QTM.¹⁷

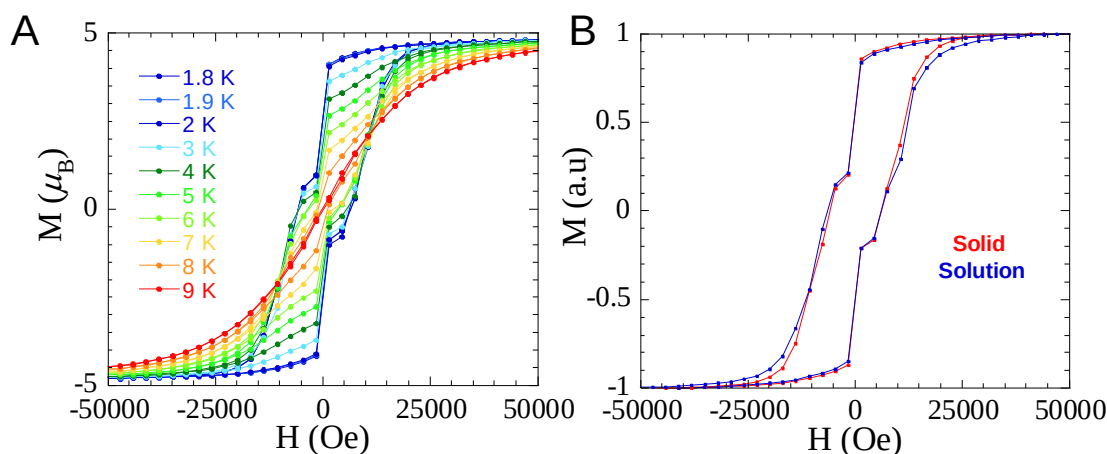


Figure 2.6. (A) Magnetic hysteresis data for **ErCOT**"₂ between 1.8-10 K. Data was collected at an average sweep rate of 22 Oe.s^{-1} . In all measurements data was collected starting at $H = 0$ Oe, sweeping to $H = 50$ kOe and then cycling to $H = -50$ kOe and back to $H = 50$ kOe. Solid lines are guides for the eye. In **ErCOT**"₂, coercivity is observed up to 8 K. (B) Solid-state magnetic hysteresis data for **ErCOT**"₂ (●) and a 4 mM cyclopentane solution of **ErCOT**"₂ (●) in toluene at 1.8 K using an average sweep rate of 22 Oe.s^{-1} . The similarity between solid-state data and frozen solution data confirms the molecular origin of the observed hysteresis. Solid lines are guides for the eye.

QTM can be minimized in complexes with high symmetry around the metal center.¹⁸ The presence of trimethylsilyl groups in **ErCOT**"₂ lowers the molecular symmetry of the molecule, therefore, removal of such groups may yield an even larger coercive field. This further confirms the intricacies of secondary coordination environments on

the local anisotropy of lanthanide molecules.^{17,19} Further single crystal studies are required to confirm potential fine structures in the hysteresis as well as tunnel-crossing levels.

2.2.5 Alternating Current (ac) Magnetic Susceptibility

In order to probe any SMM behaviour of **CeCOT**"₂, **NdCOT**"₂, **TbCOT**"₂, **DyCOT**"₂, **HoCOT**"₂, **ErCOT**"₂ and **YbCOT**"₂, ac magnetic susceptibility studies were performed. The absence of magnetic anisotropy in Gd^{III} averts the possibility of SMM behaviour in **GdCOT**"₂. **TbCOT**"₂, and **HoCOT**"₂ display no temperature or frequency dependent χ'' signal, precluding SMM behaviour in these complexes. As each of **CeCOT**"₂, **NdCOT**"₂, **DyCOT**"₂, **ErCOT**"₂ and **YbCOT**"₂ displayed an out-of-phase χ'' signal, a comprehensive magnetic analysis for each complex is provided (vide infra).

CeCOT"₂

Kajiwarra recently reported the first Ce^{III} coordination complex exhibiting SMM behaviour.²⁰ This linear Zn^{II}-Ce^{III}-Zn^{II} complex exhibits an energy barrier against magnetization reversal (U_{eff}) of 21.2(6) K under zero applied dc field. The SMM properties were surprising due to the (4f¹) spin source; the authors stipulated that the large barrier was due to the predominant axial ligand field provided by four phenoxo oxygen bridging atoms. The ground state of Ce^{III} contains a single unpaired electron in the 4f_{x(x²-3y²)} orbital.²⁰ Recently, Rinehart and Long²¹ predicted a strictly axial ligand field environment would be ideal to prevent quenching of orbital angular momentum for this configuration. The use of planar COT" ligands in **CeCOT**"₂ provides a strictly axial coordination environment around the spin carrier, therefore SMM behaviour is plausible.

The magnetic relaxation dynamics of **CeCOT**"₂ was probed using ac magnetic susceptibility measurements. Under a zero applied dc field, no ac signal was observed. Under an optimal 400 Oe applied DC field and 3 Oe ac field, a strong temperature and frequency-dependent out-of-phase (χ'') signal was observed. Frequency-dependent χ''

data revealed full frequency-dependent peaks with peak maxima shifting towards lower frequency consistent with field-induced slow relaxation of the magnetisation (Figure 2.7). Interestingly, at temperatures below 3.5 K the peaks gradually broaden, and below 2.5 K a secondary lower frequency peak is apparent. Multiple peak maxima in χ'' versus frequency data suggest multiple magnetic relaxation processes are occurring at the spin center. Such intricate magnetic behaviour for single-ion complexes has previously been observed only in complexes of Dy^{III} and U^{III} .^{8,19,22}

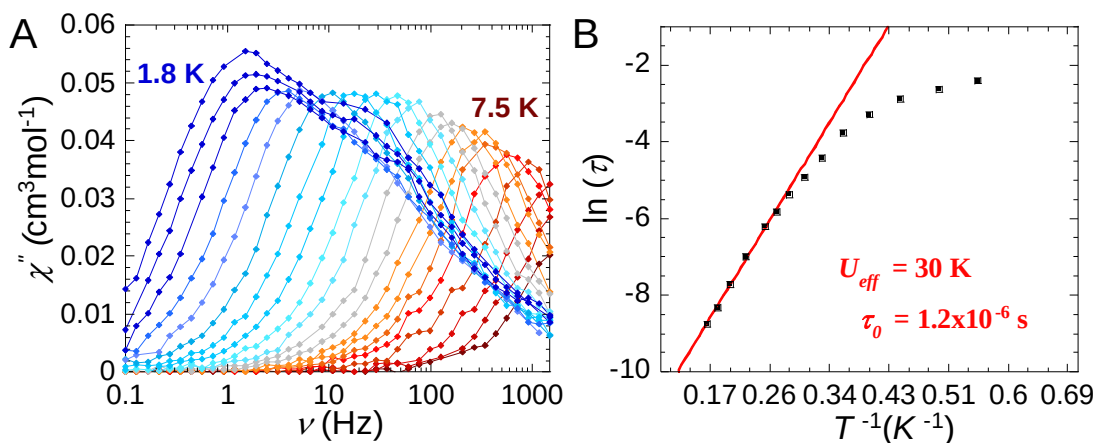


Figure 2.7. Dynamic magnetic data for CeCOT''_2 . **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for CeCOT''_2 in the temperature range 1.8-7.5 K under 400 Oe applied dc field. **(B)** An Arrhenius plot of τ (the natural log of the relaxation time) versus inverse temperature. Relaxation times are extracted from the frequency dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The red line indicates the fit to the data between 6-3.75 K and affords the $U_{\text{eff}} = 30$ K (21 cm^{-1}) with $\tau_0 = 1.2 \times 10^{-6}$ s, determined via the Arrhenius equation.

To confirm this low temperature phenomena is a result of two relaxation modes, we utilized the Cole-Cole (χ'' vs. χ') plot and generalized Debye model, $\chi(\omega) = \chi S + (\chi T + \chi S)/(1 + i\omega\tau)^{1-\alpha}$, where $\alpha = 0$ corresponds to a single relaxation process (Figure 2.8).²³⁻²⁴ Cole-Cole plots between 6-4 K show good agreement with the Debye model with alpha values between 0.02 and 0.06, consistent with one relaxation time. From 3.75 K to 2.5 K the Debye model for a single relaxation cannot be fit to the experimental data. Below 2.5 K two clear peaks are observed, which can each be fit to the Debye model, with α values ranging from 1.2 to 3.7. The clear multiple peak maxima observed in the Cole-Cole plot at 1.8 K confirms that at least two relaxation processes are

occurring from the Ce^{III} ($4f^1$) ion. The poor separation of peaks is expected if a narrow distribution of relaxation times is occurring.

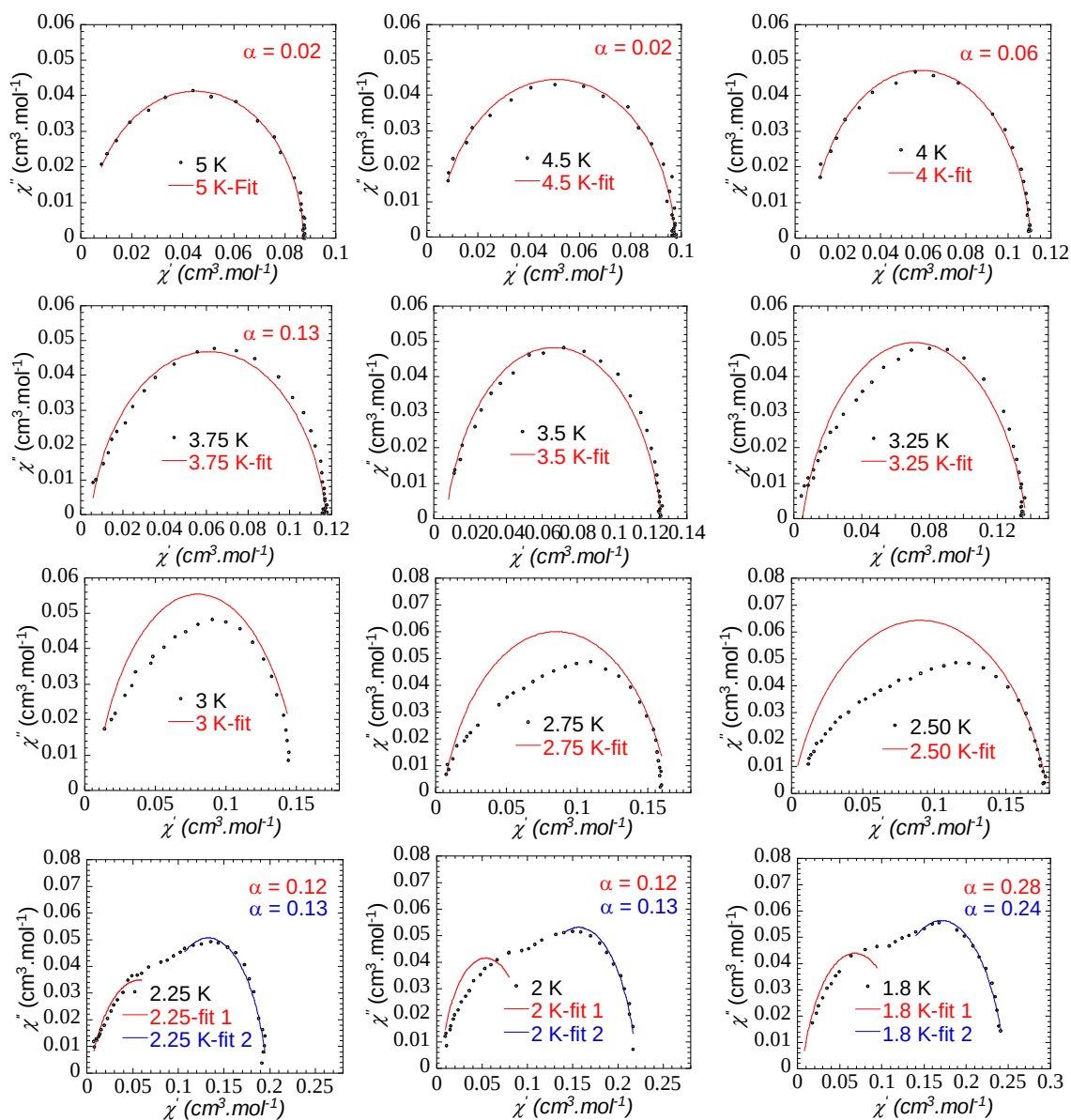


Figure 2.8. Cole-Cole plots from ac susceptibility data of CeCOT''_2 under a 400 Oe applied dc field, solid lines correspond to the fit(s).

An effective energy barrier of 30 K (21 cm^{-1}) with a pre-exponential factor (τ_0) of 1.2×10^{-6} s was extracted from the ac data above 3.5 K (Figure 2.7). The small U_{eff} value is likely the result of multiple relaxation processes.

NdCOT"₂

Under zero dc field, no ac signal was observed for **NdCOT**"₂, consistent with all previously reported neodymium SMMs.²⁵ Under a small dc field (1000 Oe) frequency dependent studies reveal a strong frequency dependent in-phase (χ') and out-of-phase magnetic susceptibility (χ'') in **NdCOT**"₂ indicative of slow relaxation of the magnetisation (Figure 2.8). An effective energy barrier of 21 K (15 cm⁻¹) with a pre-exponential factor (τ_0) of 5.5x10⁻⁵ s was extracted from the ac data. The obtained U_{eff} of 21 K (15 cm⁻¹) for **NdCOT**"₂ is significantly higher than the 2.8 cm⁻¹ previously reported for a Nd^{III} SMM.²⁵

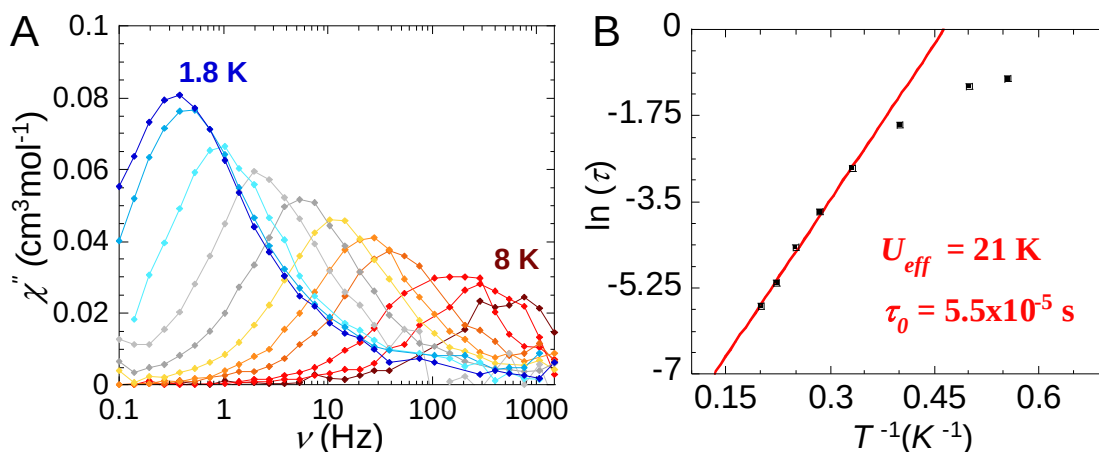


Figure 2.9. Dynamic magnetic data for **NdCOT**"₂. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for **NdCOT**"₂ in the temperature range 1.8-8 K under 1000 Oe applied dc field. **(B)** An Arrhenius plot of τ (the natural log of the relaxation time) versus inverse temperature. Relaxation times are extracted from the frequency dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The red line indicates the fit to the data between 5-3 K and affords the $U_{\text{eff}} = 21$ K (15 cm⁻¹) with $\tau_0 = 5.5 \times 10^{-5}$ s, determined via the Arrhenius equation.

DyCOT"₂

In order to probe any SIM behaviour of **DyCOT**"₂, both frequency and temperature dependent ac magnetic susceptibility measurements were carried out. The data reveals a strong temperature and frequency dependent in-phase (χ') and out-of-phase magnetic susceptibility (χ'') under a zero applied dc field and 3 Oe ac field below 15 K (Figure

2.9). In the frequency dependent data full frequency-dependent peaks can be observed in the temperature range of 4.5-9 K, where the intensity of the χ'' increases with decreasing temperature and frequency (Figure 2.9). Such slow relaxation of the magnetization is indicative of SIM behaviour. Between 2-4.5 K a full peak is observed but there is no frequency dependence of the χ'' , confirming QTM for **DyCOT**² under zero dc field. The anisotropic barrier was determined, $U_{eff} = 25$ K, (18 cm^{-1}) $\tau_0 = 6 \times 10^{-6}$ s, calculated from the Arrhenius equation ($\tau = \tau_0 \exp(U_{eff}/kT)$); this relatively small barrier is expected due to the presence of significant QTM (Figure 2.9). Recent studies on a related $[\text{Dy}^{\text{III}}(\text{COT}^{\text{2-}})_2\text{Li}(\text{THF})(\text{DME})_3]^8$ exhibited similar frequency dependent behaviour in the same temperature range with $U_{eff} = 18$ K (13 cm^{-1}), $\tau_0 = 6 \times 10^{-6}$ s under 0 dc field.

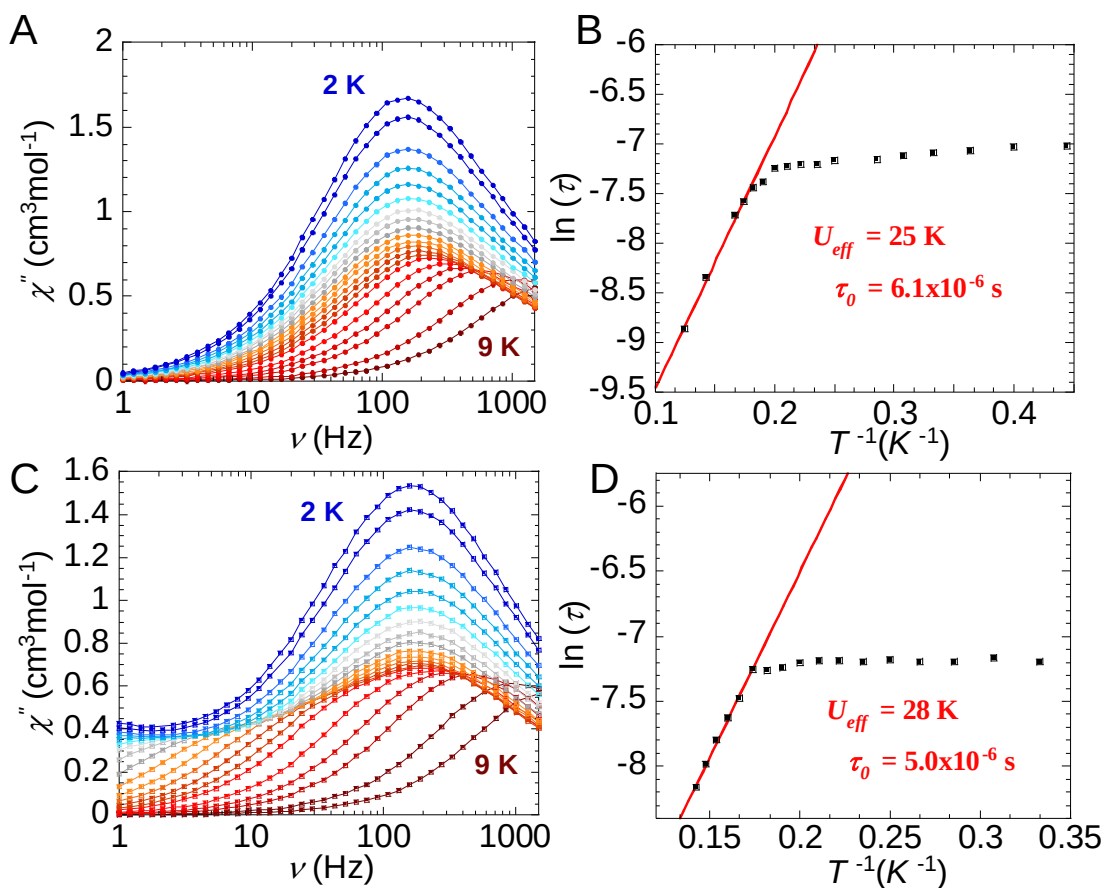


Figure 2.9. Dynamic magnetic susceptibility of **DyCOT**². Out-of-phase component χ'' for **DyCOT**² under 0 Oe (A) and 100 Oe (C) applied dc fields, compounds measured in the frequency range 0.1 Hz-1.5 kHz, between indicated temperatures; Arrhenius treatment of χ'' data for **DyCOT**² under 0 Oe (B) and 100 Oe (D) with the solid red lines indicating the fit of the data.

This reported Li-bound mononuclear sandwich molecule was also found to have unusual relaxation dynamics where multiple field-dependent relaxation processes were observed.¹⁰ We performed field-dependent studies to elucidate whether similar relaxation dynamics are inherent to **DyCOT''₂**. In the plot of χ'' vs. ν (Figure 2.9 C) under 100 Oe applied dc field, the peak with a maximum at 110 Hz under 0 Oe dc field, decreases and slightly shifts right under a 100 Oe dc field. Also under a 100 Oe applied dc field a secondary tail appears at low frequency. Such relaxation dynamics are nearly identical to those observed with the Li-bound monomer (U_{eff} = 24 K (17 cm^{-1}), τ_0 = 3×10^{-6} s).⁸ This suggests that the presence of the Li bound to the COT'' ring has only a slight effect on the relaxation dynamics of the Dy^{III} -COT'' sandwich complex due to structural distortions.

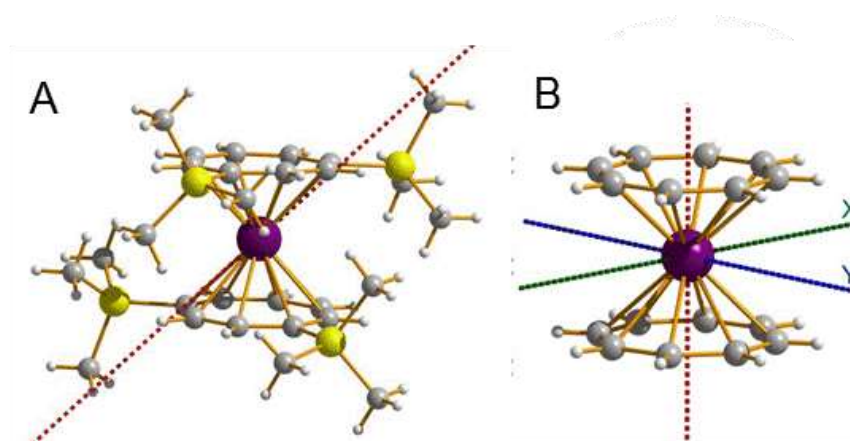


Figure 2.10. Orientation of the main magnetic axes of the ground Kramers doublets on the Dy^{III} center of the initial complex **DyCOT''₂** (A) and a symmetrized $\text{Dy}^{\text{III}}(\text{COT}'')_2$ complex (B).

To further understand the intricate magnetic behaviour of **DyCOT''₂**, the magnetic anisotropic axes and the low-lying electronic levels (Kramers doublets) on the Dy^{III} site have been calculated *ab initio* with the MOLCAS7.6 package²⁶ in different structural and basis set approximations.²⁷ The direction of the main magnetic axes on the Dy^{III} site of **DyCOT''₂** is shown in Figure 2.10 A. We can see that the direction of the local magnetic axes is far from the axis connecting the two COT'' centroids. We also considered one single symmetric $\text{Dy}^{\text{III}}(\text{COT}'')_2$ unit and interestingly we see a much more axial direction of the anisotropy axes. This proves the strong effect on the distant silyl groups on the direction of anisotropy axis. This is in line with previous findings that have also demonstrated the strong effect of the second coordination sphere on the magnetic

anisotropy axis of strongly anisotropic metal ions in a Co^{II} complex²⁶ and Dy^{III} complexes.²⁷ The analysis of the magnetic anisotropy of local Kramers doublets shows that the highest one is very axial. This suggests that a replacement of Dy^{III} by Er^{III} might result in a strong SMM effect of the complex.

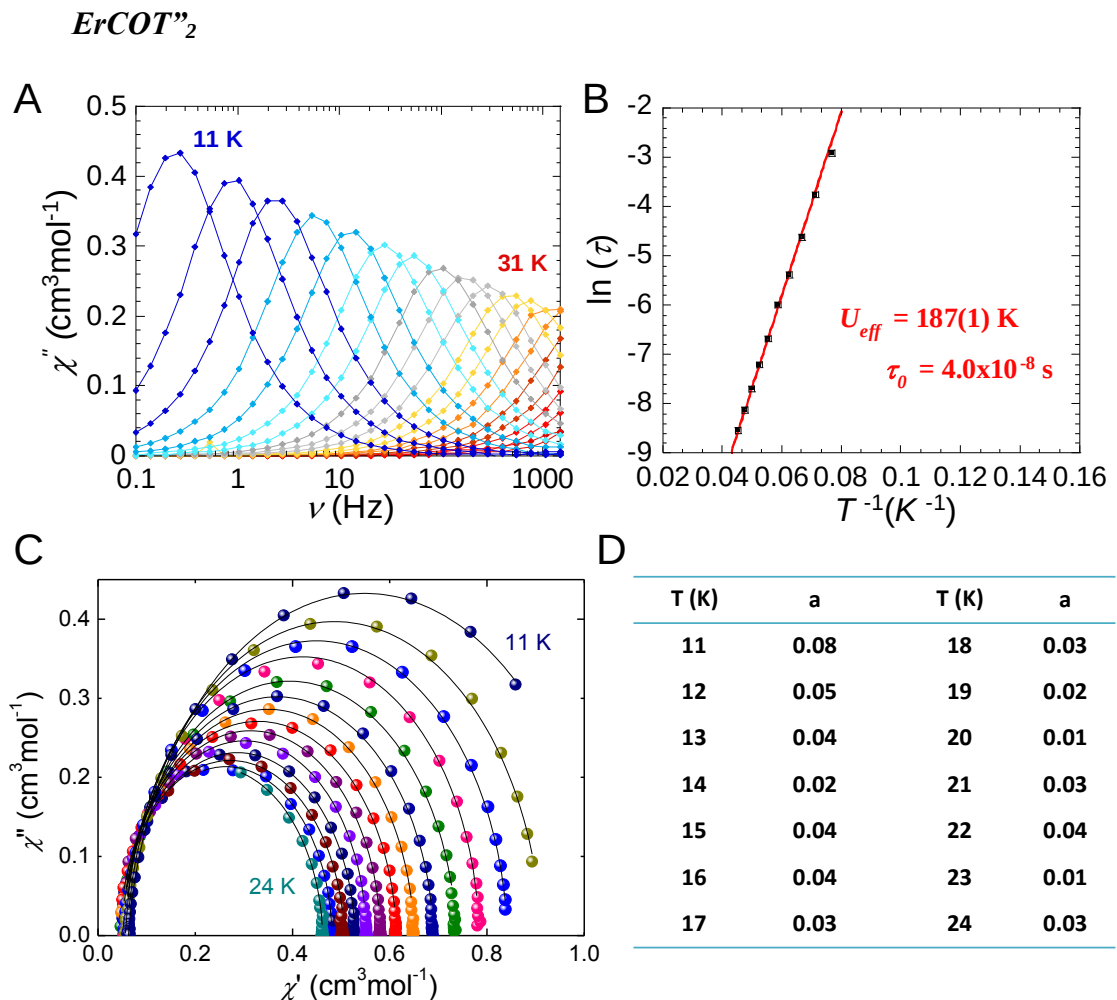


Figure 2.11. Dynamic magnetic susceptibility of **ErCOT''₂**. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for **ErCOT''₂** in the temperature range 11-31 K at 0 dc field. **(B)** Arrhenius treatment of χ'' data for **ErCOT''₂** under 0 Oe. **(C)** Cole-Cole plot for ac susceptibility of **ErCOT''₂** collected between 11-24 K. Experimental data points are represented by circles and the solid black line represents a fit to the data. Small α^2 values with a narrow distribution (0.010 to 0.080) confirm the magnetic susceptibility of **ErCOT''₂** is unique to a single relaxation process **(D)**.

Ac susceptibility measurements were performed to gain insight into the dynamics of magnetization relaxation of **ErCOT''₂**, using an oscillating field of 3 Oe (figure 2.10).

Below 31 K a frequency dependent in-phase (χ') and out-of-phase (χ'') component of the ac signal was observed confirming SIM behaviour. Using the maximum out-of phase susceptibility (χ'') between 11-25 K and the Arrhenius law, an effective energy barrier of 187(1) K (129 cm⁻¹) with a $\tau_0 = 4.0 \times 10^{-8}$ s was obtained. It is noteworthy that this barrier is significantly larger than the 25 K energy barrier obtained for **DyCOT**"₂. Moreover, there is only one clear relaxation process apparent, in contrast to **DyCOT**"₂ where multiple relaxations were observed. Competing relaxation mechanisms are likely the cause of the small energy barrier observed in **DyCOT**"₂. Likewise the graphical representation of χ'' vs. χ' (Cole-Cole plot) between 11-24 K undoubtedly confirms the single relaxation process occurring in **ErCOT**"₂. This data was fit using a generalized Debye model, which led to small α parameter with a narrow distribution (0.010 to 0.080).

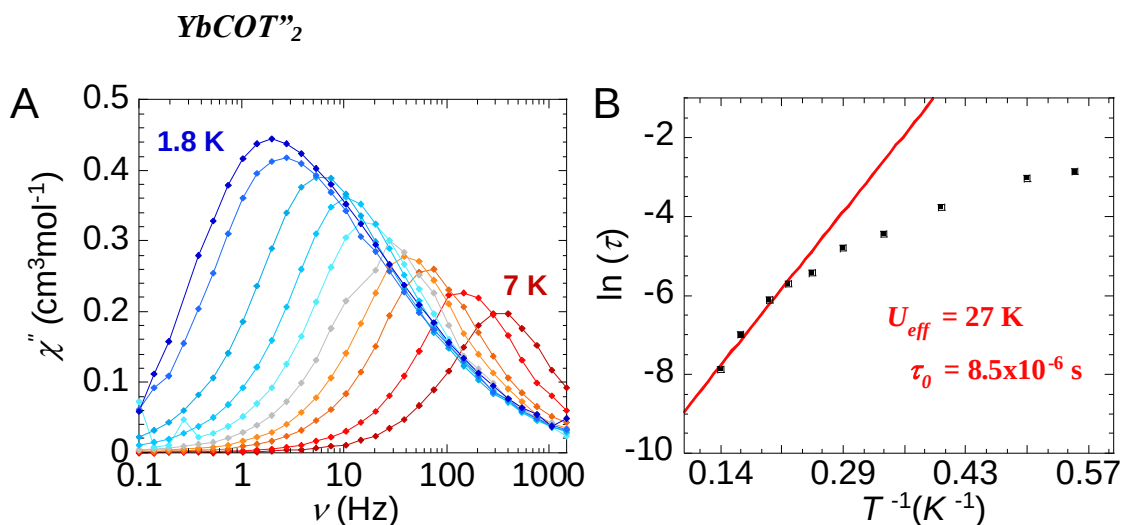


Figure 2.12. Dynamic magnetic data for **YbCOT**"₂. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for **YbCOT**"₂ in the temperature range 1.8-7 K under 1200 Oe applied dc field. **(B)** An Arrhenius plot of τ versus inverse temperature. Relaxation times are extracted from the frequency dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The Red line indicates the fit to the data between 7-5.5 K and affords the $U_{eff} = 27$ K (19 cm⁻¹) with $\tau_0 = 8.5 \times 10^{-6}$ s, determined via the Arrhenius equation.

In 2011 Rinehart and Long predicted Yb^{III} complexes should display SMM behaviour if an appropriate ligand system is applied.²¹ Ac susceptibility studies of **YbCOT**"₂ revealed no zero field magnetic susceptibility in the χ'' plot; therefore this complex is not an SMM. Under a small dc field of 1200 Oe, full frequency and temperature dependent

peaks are observed in the χ'' susceptibility from 1.8-7 K (Figure 2.12). Using the χ'' peak maxima and the Arrhenius law, an effective energy barrier of 27 K (19 cm⁻¹) with a $\tau_0 = 8.5 \times 10^{-6}$ s (Figure 2.12 B) was obtained, indicating field-induced SMM behaviour.

2.3 Conclusions

The synthesis, structures and magnetic properties of a family of mononuclear organolanthanide sandwich complexes synthesised using COT²⁻ ligands has been investigated. Each of **CeCOT²⁻₂**, **NdCOT²⁻₂**, **DyCOT²⁻₂**, **ErCOT²⁻₂** and **YbCOT²⁻₂** display interesting magnetic properties. Both **CeCOT²⁻₂** and **NdCOT²⁻₂** display slow magnetic relaxation; this is only the second report of such magnetic behaviour in Ce^{III} and Nd^{III} complexes. In the case of **NdCOT²⁻₂**, the energy barrier of $U_{\text{eff}} = 21$ K (15 cm⁻¹) is significantly higher than the 2.8 cm⁻¹ previously reported for NdTp₃ (Tp⁻ = trispyrazolylborate).²⁵ Therefore a more in depth investigation into optimizing the ligand field around Nd^{III} may lead to interesting results and stronger Nd^{III} molecular magnets. These results incite the use of early lanthanide ions in the future preparation of molecular magnetic materials.

DyCOT²⁻₂ demonstrates slow magnetic relaxation where multiple relaxation pathways are accessible through the application of various dc fields. Multiple relaxation pathways are common in complexes which have more than one structural conformer such as [(COT)Er(Cp*)].^{3a} In contrast, the X-ray structure of **DyCOT²⁻₂** clearly demonstrates the presence of a single conformer yet it exhibits multiple relaxation pathways. This is surprising due to a single metal center, however, this result is not unique as similar behaviour has previously been observed for a Dy^{III} SIMs.¹⁰ The zero field energy barrier for **DyCOT²⁻₂** is small in comparison to the highest performing SIMs, results indicate this may be due to the presence of TMS groups on the COT ring. *Ab initio* calculations performed on **DyCOT²⁻₂** demonstrate that both the COT ligand and the TMS groups perturb the ligand field enough to influence the anisotropy axis of the complex. Calculations show the orientation of the main magnetic axes of a completely symmetrized Dy^{III}(COT²⁻)₂ complex is much more axial than in **DyCOT²⁻₂**. This

important result inspired an additional investigation into unsubstituted COT sandwich complexes which is discussed in Chapter 3.

ErCOT²⁻ has one of the highest blocking temperatures of any SMM. At the time of this study, hysteresis loops with large coercive fields had only been observed in polynuclear metal complexes and radical-bridged SMMs. In comparison with [Cp*Er(COT)]^{3a}, the better performance of **ErCOT**²⁻ most likely arises from more equivalent ligand donation above and below the xy plane, and thus higher axial orientation of the anisotropy axis. Results also suggest that the significant enhancement in the energy barrier against spin reversal of **ErCOT**²⁻ in comparison to **DyCOT**²⁻ may also be attributed to the orientation of the anisotropy axis. This comparison highlights that although isostructural compounds can be obtained in late lanthanide chemistry, the magnetic anisotropy axis of each individual metal ion leads to unique behaviour. This small SIM with magnet-like behaviour clearly suggests that if such inherent anisotropy can be harnessed in single ions, better performing SMMs are achievable. The observed features of remanence and coercivity are signature characteristics of permanent magnets; thus, the remarkable performance of this SIM makes it viable for application in high-density data storage.

An isostructural series, such as the one discussed in this Chapter, provides a unique opportunity to motivate discussion on structural-magneto correlation in lanthanide chemistry. One of the main challenges of single-molecule magnetism is predictability. When trying to design strong SMMs, researchers have historically employed a serendipitous approach due to the lack of reliable models. With the help of computational chemistry, several recent theories have emerged including one by Long²¹ which claims that Ln^{III} ions with an oblate ground state electron distribution (Ce^{III}, Pr^{III}, Nd^{III}, Tb^{III}, Dy^{III}, Ho^{III}) favour an axial crystal field such as a sandwich complex, while Ln^{III} ions with a prolate electron distribution (Pm^{III}, Sm^{III}, Er^{III}, Tm^{III}, Yb^{III}) favours an equatorial crystal field.²¹ The isostructurality of **CeCOT**²⁻, **NdCOT**²⁻, **TbCOT**²⁻, **DyCOT**²⁻, **HoCOT**²⁻, **ErCOT**²⁻ and **YbCOT**²⁻ provides an excellent template for examining such a claim. Unfortunately no trend can be observed between quadrupole approximations of the electron distribution of the Ln^{III} ions and the ligand field provided by the COT²⁻ rings, even when considering only Kramers ions. Additionally

the total spin of the Ln^{III} center does not seem to influence SMM behaviour either. Additional calculations of the ground state splitting of these complexes may aid our understanding of the origin of magnetic behaviour in this series.

2.4 Experimental

General Considerations. All manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware were oven dried (120 °C, 6 h) before use. Hexanes and dimethoxyethane (DME) were dried using activated alumina and stored over 3 Å molecular sieves. Anhydrous LnCl_3 salts were purchased from Strem and used as received. All other reagents were purchased from Thermo Fisher Scientific and used without further purification. $(\text{LiTHF}_2)\text{COT}'''\text{Li}_2\text{COT}''(\text{LiTHF}_2)$ was synthesized using a previously published procedure.^{9a} ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Advance instrument at room temperature (21-23 °C). Chloroform- d and THF- d_8 were degassed using repeated freezing-evacuating-thawing cycles, and stored over 4 Å molecular sieves. IR data were collected on a Varian 640 FT-IR spectrometer.

CeCOT''_2 . CeCOT''_2 was obtained as a green polycrystalline powder (0.167 g, 67%) from CeCl_3 (0.045 g, 0.183 mmol) and $(\text{LiTHF}_2)\text{COT}'''\text{Li}_2\text{COT}''(\text{LiTHF}_2)^{9a}$ (0.218 g, 0.274 mmol). Reagents were stirred in 5 mL of THF for 36 hours, 2 mL of hexanes were then added and the resulting solution was then filtered using a fine fritted funnel. Large green block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. CCDC 944915. Selected IR data (cm^{-1}): 2950 (br), 2892 (m), 1447 (w), 1244 (s), 1079 (w), 1049 (s), 979 (w), 932 (m), 907 (w), 834 (s), 749 (m), 722 (m), 680 (w), 635 (w). ^1H NMR (300 MHz, THF- d_8) 5.4 (br), δ 1.7 (br), δ 0.7 (br), δ -0.1 (br) ppm. ^{13}C NMR (300 MHz, δ 64.55(q), δ 22.43(q), THF- d_8) δ 69.9 (br), δ 56.0 (br), δ 2.3 (br) ppm.

NdCOT''_2 . As described for CeCOT''_2 , NdCOT''_2 was obtained as an orange polycrystalline powder (0.211 g, 60%) from NdCl_3 (0.063 g, 0.25 mmol) and $(\text{LiTHF}_2)\text{COT}'''\text{Li}_2\text{COT}''(\text{LiTHF}_2)^{9a}$ (0.300 g, 0.38 mmol). Large block crystals suitable

for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. CCDC 992620. Selected IR data (cm^{-1}): 3001 (w), 2950 (br), 2895 (w), 1597 (w), 1455 (w), 1243 (s), 1086 (w), 1051 (m), 980 (w), 936 (w), 833 (s), 749 (w), 727 (w). Anal. Calc. for $\text{C}_{40}\text{H}_{78}\text{LiO}_6\text{Si}_4\text{U}$ ($M_r = 918.56$): C, 52.30; H, 8.56. Found: C, 49.39; H, 8.18.

GdCOT''₂. As described for **CeCOT''₂**, **GdCOT''₂** was obtained as a yellow polycrystalline powder (0.309 g, 53%) from GdCl_3 (0.130 g, 0.493 mmol) and $(\text{LiTHF}_2)\text{COT}''\text{Li}_2\text{COT}''(\text{LiTHF}_2)^{9a}$ (0.500 g, 0.627 mmol). Large block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. CCDC 863401. Selected IR data (Nujol mull, cm^{-1}): 2991 (br), 1458 (m), 1373 (m), 1241 (s), 1188 (m), 1079 (w), 1047 (w), 927 (s), 834 (w), 713 (w), 633 (w).

TbCOT''₂. As described for **CeCOT''₂**, **TbCOT''₂** was obtained as a bright yellow polycrystalline powder (0.502 g, 66%) from TbCl_3 (0.222 g, 0.837 mmol) and $(\text{LiTHF}_2)\text{COT}''\text{Li}_2\text{COT}''(\text{LiTHF}_2)^{9a}$ (1 g, 1.26 mmol). Large bright-yellow block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. CCDC 863402. Selected IR data (Nujol mull, cm^{-1}): 2970 (br), 1458 (s), 1374 (m), 1239 (s), 1120 (m), 1081 (s), 1052 (s), 930 (s), 827 (s), 747 (s), 711 (s), 632 (m).

DyCOT''₂. As described for **CeCOT''₂**, **DyCOT''₂** was obtained as an orange polycrystalline powder (1.63 g, 57%) from DyCl_3 (0.823 g, 3.06 mmol) and $(\text{LiTHF}_2)\text{COT}''\text{Li}_2\text{COT}''(\text{LiTHF}_2)^{9a}$ (3.66 g, 4.59 mmol). Large orange block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. CCDC 863403. Calcd. (%) for $\text{C}_{40}\text{H}_{78}\text{DyLiO}_6\text{Si}_4$: C 51.28, H 8.39 Found: (%) C 51.19, H 8.03. Selected IR data (Nujol mull, cm^{-1}): 2970 (br), 1458 (s), 1374 (m), 1239 (s), 1120 (m), 1081 (s), 1052 (s), 930 (s), 827 (s), 747 (s), 711 (s), 632 (m).

HoCOT''₂. As described for **CeCOT''₂**, **HoCOT''₂** was obtained as an orange polycrystalline powder (0.622 g, 69%) from HoCl₃ (230 mg, 0.848 mmol) and (LiTHF₂)COT''Li₂COT''(LiTHF₂)^{9a} (1 g, 1.25 mmol). Large orange block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C). The isolated crystals were extremely air and moisture sensitive. CCDC 863404. Selected IR data (Nujol mull, cm⁻¹): 2958 (br), 2842 (br), 1450 (s), 1370 (m), 1235 (s), 1081 (m), 1048 (m), 930 (w), 834 (s), 747 (w), 711 (s). ¹H NMR (300 MHz, THF-d₈) δ 14.4 (br), δ 4.8 (br), δ 4.5 (br), δ 2.9 (br), δ 1.5 (br) ppm.

ErCOT''₂. As described for **CeCOT''₂**, **ErCOT''₂** was obtained as a red-orange polycrystalline powder (446 mg, 53%) from ErCl₃ (230 mg, 0.898 mmol) and (LiTHF₂)COT''Li₂COT''(LiTHF₂)^{9a} (1 g, 1.25 mmol). Large red-orange block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C). The isolated crystals were extremely air and moisture sensitive. CCDC 863405. Selected IR data (Nujol mull, cm⁻¹): 2967 (br), 1551 (s), 1377 (m), 1240 (s), 1123 (m), 1083 (s), 1051 (s), 931 (s), 830 (s), 745 (w), 713 (s), 628 (m). ¹H NMR (300 MHz, CDCl₃) δ 7.2 (br), δ 4.7 (br), δ 4.3 (br), 1.1 (br), δ 0.7 (br), δ -0.1 (br) ppm.

YbCOT''₂. As described for **CeCOT''₂**, **YbCOT''₂** was obtained as a blue polycrystalline powder (220 mg, 65%) from YbCl₃ (0.100 g, 0.358 mmol) and (LiTHF₂)COT''Li₂COT''(LiTHF₂)^{9a} (0.428 g, 0.537 mmol). Large blue block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1; DME/hexane) at -35 °C. The isolated crystals were extremely air and moisture sensitive. ¹H NMR (300 MHz, THF-d₈) δ 1.7 (br), δ 1.6 (br), δ 1.4 (br), δ -0.1 (br), δ -1.9 (br) ppm.

X-ray Crystallography. For all complexes a suitable prism-shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).²⁸ The crystal structure was solved and

refined using the SHELXTL²⁹ program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. All published crystal structures have been deposited at the Cambridge Crystallographic Data Centre.

Magnetic Measurements. The magnetic analysis was performed on crushed polycrystalline samples wrapped in a polyethylene membrane sealed in a glove box under N₂ to prevent any sample degradation. The direct current (dc) magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Alternating current (ac) susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetization data were collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

Electrochemistry.¹³ Voltammetry experiments were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N₂ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, platinum disc (2 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced on scanning > 0 V versus ferrocene (Fc) to prevent the build-up of oxidized product on the electrode surfaces. Solutions employed during the CV studies were ~1 mM in analyte and 0.1 M in [ⁿPr₄N][B(3,5-(CF₃)₂-C₆H₃)₄] ([ⁿPr₄N][BAr^F₄]). Potentials were reported *versus* Fc, which was added as an internal standard for calibration at the end of each run. All data were collected in a positive-feedback IR compensation mode. The THF solution cell resistances were measured prior to each run at ~1100 Ω. Scan rate dependences of

50-1000 mV/s were performed to determine electrochemical reversibility. The ΔE_p values recorded were reproducible with variable analytes and electrolyte concentrations. Additionally, the observed ΔE_p for Fc at a scan rate of 100 mV/s was no greater than 80 mV. The Randels-Sevcik equation was plotted using associated scan rate data.

CASSCF Calculations.²⁷ All *ab initio* calculations were performed using the MOLCAS 7.6. program package and were of CASSCF/RASSI/SINGLE_ANISO level of theory. In the smallest structural fragment, all silyl groups were replaced by hydrogens at a fixed distance of 1.07 Å. In the medium fragment, the methyl groups were replaced by H, thus preserving the Si atoms in the calculation, while in the largest computational fragment, the entire molecule was kept as is. Two basis sets, both taken from the ANO-RCC basis set library, were employed for computation of the above structural models: basis 1 - small and basis 2 - large. Contractions of the employed basis sets are published in Murugesu.¹⁹ As a result, we have the following computational models: A1, A2, B1, B2, C1, and C2. The active space of the complete active space self-consistent field CASSCF method, denoted AS1, included nine electrons spanning seven orbitals from the 4*f* shell of the Dy^{III} ion. The spin-orbit coupling was computed by mixing all (21) spin sextet states, 128 out of 224 spin quartet states and 130 out of 490 spin doublet states.

Table 2.3. Unit cell parameters for **CeCOT**²⁻, **NdCOT**²⁻, **GdCOT**²⁻, **TbCOT**²⁻, **DyCOT**²⁻, **HoCOT**²⁻, **ErCOT**²⁻ and **YbCOT**²⁻.

	CeCOT ²⁻	NdCOT ²⁻	GdCOT ²⁻	TbCOT ²⁻
M_r (g/mol)	914.44	918.56	931.585	909.07
Formula	CeC ₄₀ H ₇₈ LiO ₆ Si ₄	NdC ₄₀ H ₇₈ LiO ₆ Si ₄	GdC ₄₀ H ₇₈ LiO ₆ Si ₄	TbC ₄₀ H ₇₈ LiO ₆ Si ₄
T(K)	200(2)	200(2)	200(2)	200(2)
γ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1 (2)	P-1 (2)	P-1 (2)	P-1 (2)
a (Å)	11.744(4)	11.6313(2)	11.5496(2)	11.5241(2)
b (Å)	12.376(4)	12.3221(3)	12.3152(3)	12.3017(2)
c (Å)	18.533(6)	18.4994(4)	18.5250(4)	18.5326(3)
α (deg)	99.150(7)°	99.1930(10)	99.23	99.2510(10)
β (deg)	102.147(7)°	102.2920(10)	102.24	102.1970(10)
γ (deg)	98.922(6)°	99.0690(10)	99.53	99.6120(10)
V (Å ³)	2549.75(688)	2506.33(9)	2486.73(9)	2479.00(7)
ρ_{calc} (cm ⁻³)	1.191	1.217	1.244	1.226
Z	2	2	2	2
Reflections collected	33388	39940	23125	30599
$R(\text{int})$	13751, 0.0313	12278, 0.0193	12231, 0.0118	12158, 0.0200
$R1$	0.0362	0.0260	0.0179	0.0265
$wR2$	0.0757	0.0631	0.0466	0.0666
Reflections with $I > 2\sigma(I)$	11109	11279	11422	10878
	DyCOT ²⁻	HoCOT ²⁻	ErCOT ²⁻	YbCOT ²⁻
M_r (g/mol)	936.82	939.25	941.58	947.36
Formula	DyC ₄₀ H ₇₈ Si ₄ LiO ₆	C ₄₀ H ₇₈ HoLiO ₆ Si ₄	C ₄₀ H ₇₈ ErLiO ₆ Si ₄	C ₄₀ H ₇₈ YbLiO ₆ Si ₄
T(K)	200(2)	200(2)	200(2)	200(2)
γ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
a (Å)	11.5077(7)	11.5001(2)	11.4921(12)	11.4718(3)
b (Å)	12.3057(7)	12.30790(10)	12.3172(12)	12.2988(3)
c (Å)	18.5852(11)	18.5623(2)	18.5804(19)	18.5706(5)
α (deg)	99.361(3)	99.2730(10)	99.322(2)	99.4477(17)
β (deg)	102.268(3)	102.2150(10)	102.182(2)	102.0557(16)
γ (deg)	99.657(3)	99.8100(10)	100.000(2)	100.0457(17)
V (Å ³)	2481.0(3)	2476.71(5)	2477.3(4)	2467.70(11)
ρ_{calc} (cm ⁻³)	1.254	1.259	1.262	1.275
Z	2	2	2	2
Reflections collected	35322	36469	23950	24803
$R(\text{int})$	12258, 0.0170	12288, 0.0257	12209, 0.0126	12106, 0.0599
$R1$	0.0177	0.0232	0.0177	0.0478
$wR2$	0.0467	0.0525	0.0473	0.0698
Reflections with $I > 2\sigma(I)$	11499	10880	11522	11499

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Chapter 3

Fine Tuning the Second Coordination Sphere to Enhance the Magnetic Properties of Lanthanide Cyclooctatetraenyl Complexes*

**Partial contents of this chapter have been published in: L. Ungur, J. J. Le Roy, I. Korobkov, L. F. Chibotaru, M. Murugesu, Angew. Chem. Int. Ed. 2014, 54, 1.*

SMMs display both classical and quantum mechanical mechanisms for spin reversal. Although these properties make SMMs unique, QTM also suppresses thermal magnetic relaxation, resulting in small anisotropic barriers in many lanthanide SMMs.¹ For example significant QTM was observed in **CeCOT**₂, **NdCOT**₂, **DyCOT**₂ and **YbCOT**₂, as discussed in detail in Chapter 2.^{1a-c} Since large anisotropic barriers are integral to potential applications, it is important to understand the fundamental reasoning and properties necessary to suppress QTM in lanthanide complexes. QTM is a natural phenomenon dependent on several factors including hyperfine interactions, crystal field and metal-metal interactions.² It is established that some parameters known to cause QTM will disappear in high-symmetry molecules.³ This chapter, therefore, extends the discussion in Chapter 2, and explores symmetry effects on the magnetic properties of Ln^{III}-COT SMMs. The synthesis and structure of high symmetry [K(18-C-6)][Ln^{III}(COT)₂] (Ln = Dy (**DyCOT**₂) and Er (**ErCOT**₂), 18-C-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, COT = cyclooctatetraenyl) complexes are discussed. Additionally the magnetic properties are compared to the similar silyl compounds in Chapter 2. Important findings include the high blocking temperature of **ErCOT**₂ where hysteresis loops have large coercive fields, achieving 7000 Oe at T = 1.8 K and field variation as slow as 1 h for the entire cycle. In this complex the coercivity persists up to about 5 K, while the hysteresis loops persist to 12 K. Increasing the symmetry by removing the TMS substituents enhanced the magnetic properties of **ErCOT**₂. The magnetic behavior of **ErCOT**₂ is so strong that our findings show that SIMs can be as efficient as polynuclear SMMs, thus opening new perspectives for their applications.

3.1 Introduction

It is well known that the magnetic moment of ions, such as Er^{III} and Dy^{III} , becomes blocked as a result of strong spin-orbit coupling of the metal in combination with the axial nature of the ligand environment. Therefore, when designing SMM complexes, a high axiality in the ligand field is desirable. This can be achieved through several mechanisms in complexes lacking any strict site symmetry. One example would be to have only one very short chemical bond with the metal ion, which favours significant orbital overlap between ligating atoms and the metal's electronic clouds. This strong chemical bond must dominate over all other chemical bonds at the metal site, leading to basically axial nature of the total ligand field felt by the metal ion. Synthetically this is a difficult challenge but has been seen in the case of individual Dy ions in Dy_4K_2 SMMs.⁴ Another route to obtaining an axial ligand field is to employ highly symmetrical ligands with no bonding atoms on the symmetry axis such as Ishikawa and co-workers⁵ terbium phthalocyanine compound, $(\text{Bu}_4\text{N})[\text{Tb}(\text{Pc})_2]$. In this compound the Tb^{III} ion is sandwiched between two Pc ligands resulting in a symmetry close to D_{4d} . In the case of perfect D_{4h} symmetry the quantum tunnelling of magnetization (QTM) in the ground state would be completely suppressed.⁶ However, the small deviation from ideal symmetry resulted in the diminishing of axiality which induces increased QTM.⁷ Clearly higher SIM performance could be achieved via the use of ligands with higher rotational symmetry, such as planar cyclooctatetraene (COT) systems.^{1a-b,8}

In Chapter 2, a series of isostructural complexes with formula $\text{Li}(\text{DME})_3[\text{Ln}^{\text{III}}(\text{COT}'')_2]$, were discussed. *Ab initio* calculations performed on **DyCOT''**₂, illustrate how sensitive the orientation of the main magnetic anisotropy axis is to the disilyl- TMS substituents on the COT'' ring.^{1a} With the aim of improving the SMM properties of **DyCOT''**₂ and **ErCOT''**₂ we turned our attention towards higher symmetry sandwich complexes. This Chapter presents the synthesis, structure and magnetic properties of high symmetry Ln^{III} -cyclooctatetraenyl sandwich complexes of Dy^{III} and Er^{III} .

3.2 Results and Discussion

3.2.1 Synthetic Strategy for DyCOT₂ and ErCOT₂

The preparation of sandwich-type complexes using unsubstituted cyclooctatetraene (COT) ligands is well established for lanthanide(III) chemistry and solid state structures of Ln^{III}COT₂⁻ (Ln^{III} = La, Ce, Nd, Sm, Eu, Er, Tm and Yb) have been previously established.⁹ The synthetic strategy for **DyCOT₂** and **ErCOT₂** complexes was inspired by the latter reports where the appropriate Ln^{III}Cl₃ reacts with a COT dianion (K₂COT) at low temperature in an inert atmosphere with rigorous exclusion of O₂ and water. Single crystals of **DyCOT₂** and **ErCOT₂** were obtained following the addition of excess crown ether (18-Crown-6) in a concentrated THF solution.

3.2.2 Solid State Structures

Table 3.1. Selected interatomic distances of **DyCOT₂** and **ErCOT₂**.

	DyCOT₂	ErCOT₂
Tilt angle (°)	2.40	3.57
Ln-COT_{centroid} (a) (Å)	1.893	1.852
Ln-COT_{centroid} (b) (Å)	1.918	1.891
Nearest K-C_{COT} (Å)	3.16	3.259
Intermolecular Ln-Ln (Å)	7.086	7.25

Solid state X-ray diffraction analyses reveal that both **DyCOT₂** and **ErCOT₂** crystallize in an orthorhombic Pnma space group. The structures are composed of two COT ligands bound η^8 to the central Ln^{III} ion, and a counter cation composed of 1 equivalent of K(18-crown-6) (Figure 3.1). In both complexes the potassium counter ion asymmetrically interacts with the COT ring, (K-C_{COT} distances between 3.16(2)-3.82(2) Å (**DyCOT₂**) and 3.259(3)-3.394(4) Å (**ErCOT₂**) which are considered weak K-C interactions through the π cloud.¹⁰ These bond lengths show a slightly higher ionic character than similar [Ce^{III}(COT₂)]⁻ and [Yb^{III}(COT₂)]⁻ complexes with average K-C bond lengths of 3.16(3) Å^{9b} and 3.02(2) Å^{9g} respectively. The near linear structure is reflected in the COT_{centroid}-Ln^{III}-COT_{centroid} angle which deviates from perfect linearity (180°) by 1.96° (**ErCOT₂**) and 6.15° (**DyCOT₂**). However a distinct tilt angle (3.57° (**ErCOT₂**) and 2.4°

(**DyCOT₂**)) as well as inequivalent ligand donation from each COT ring ($\text{Ln-COT}_{\text{Centroid}}$ distances (1.85(2), 1.89(1) (**ErCOT₂**); 1.89(3), 1.91(8) (**DyCOT₂**)) are a result of the interacting counter ion.

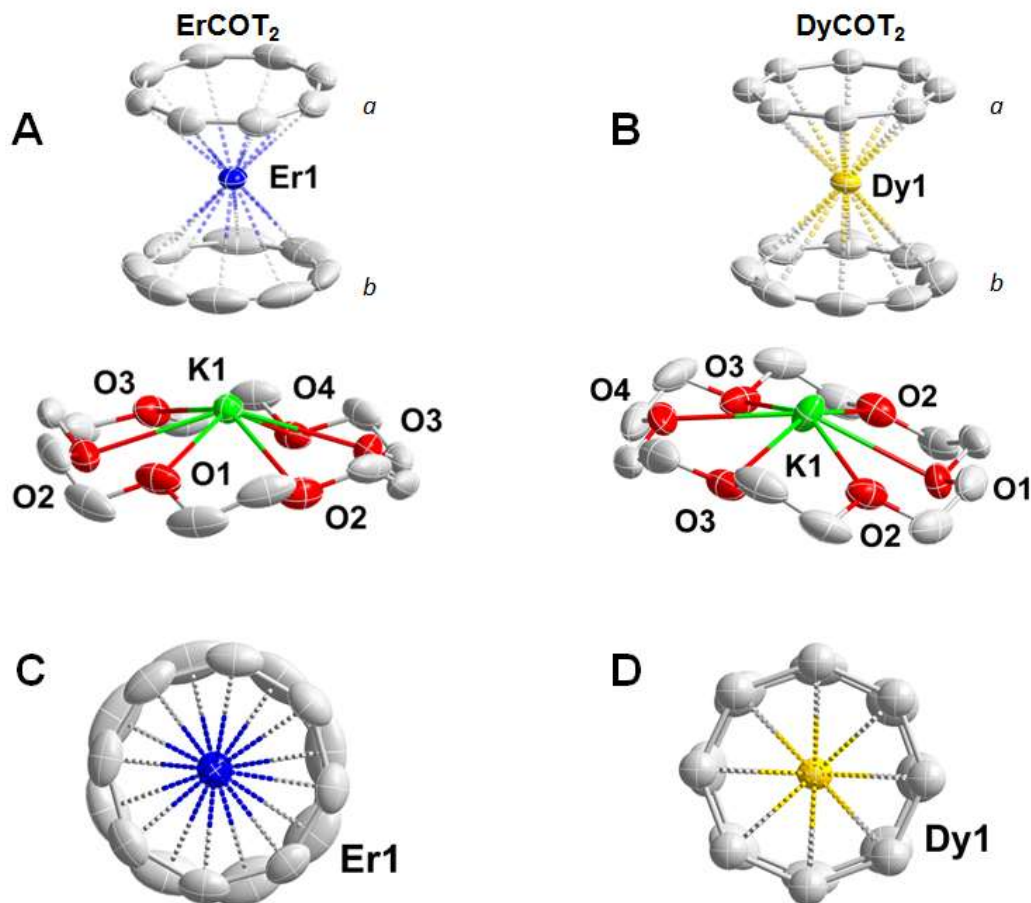


Figure 3.1. Solid state structures of **ErCOT₂** (A) and **DyCOT₂** (B). H atoms are omitted for clarity. (C) Illustrates the staggered arrangement of carbon atoms between COT layers in **ErCOT₂**. (D) Illustrates the eclipsed arrangement of carbon atoms between COT layers in **DyCOT₂**. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), light green (K), red (O), blue (Er^{III}), yellow (Dy^{III}). (Note: the difference in C and D may be an artefact of the poor crystal quality of **DyCOT₂**).

Structural parameters of **DyCOT₂** and **ErCOT₂** are located in Table 3.1, and refinement details are located in Table 3.2. The eightfold symmetry axis of the COT groups and their parallel arrangement preserve the high symmetry axis in both complexes. The **ErCOT₂** complex is close to a D_{8d} symmetry, while the **DyCOT₂** compound is more eclipsed, being closer to D_{8h} . In both complexes, the axial symmetry is higher than in previously

synthesized SIMs,^{6,4,7,11} therefore, we believe higher magnetic blocking performance can be achieved through our molecular approach.

3.2.3 Dc Magnetic Susceptibility

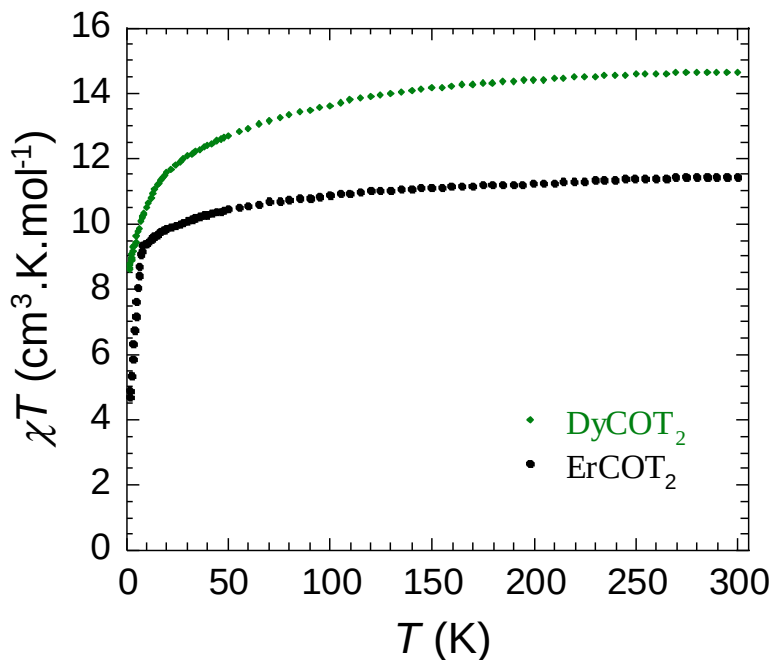


Figure 3.2. Temperature dependence of the χT product under 0.1 T for **DyCOT₂** and **ErCOT₂** with χ being the molar susceptibility per complex defined as M/H .

Magnetic susceptibility measurements were performed using a SQUID magnetometer on freshly prepared polycrystalline samples of **DyCOT₂** and **ErCOT₂** sealed under N₂ to prevent sample degradation. Dc magnetic susceptibility measurements were conducted in the temperature range of 1.8-300 K under a 0.1 T applied dc field. The room temperature χT value of 14.63 cm³·K·mol⁻¹ (**DyCOT₂**) and 11.43 cm³·K·mol⁻¹ (**ErCOT₂**) are in good agreement with the theoretical values of 14.17 cm³·K·mol⁻¹ and 11.48 cm³·K·mol⁻¹ respectively for a mononuclear Dy^{III} (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$) and Er^{III} (⁴I_{15/2}, $S = 3/2$, $L = 6$, $g = 6/5$) complexes (Figure 3.2). In both cases the χT product remains nearly linear from 300 K to 50 K, then decreases below 50 K reaching minimum values of 8.619 cm³·K·mol⁻¹ and 4.681 cm³·K·mol⁻¹ for complexes **DyCOT₂** and **ErCOT₂** respectively. This behaviour is typical for highly anisotropic Ln^{III} complexes.¹²

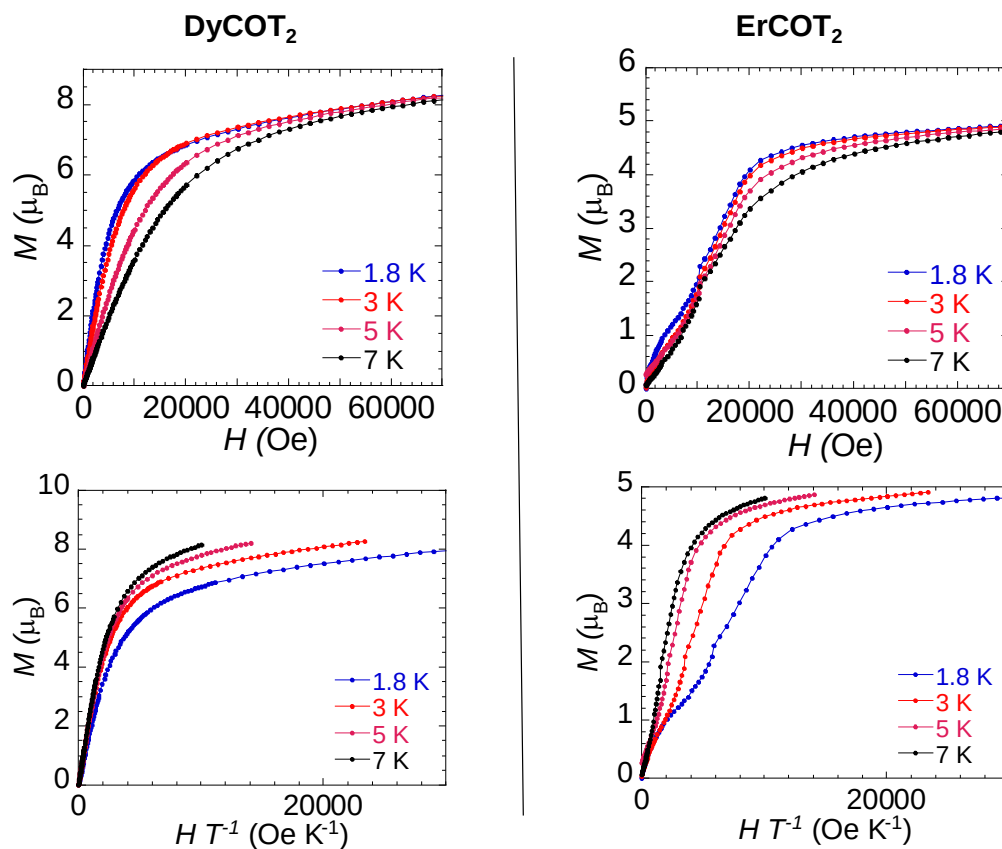


Figure 3.3. Field dependence of the magnetization (**top**) and reduced magnetization (**bottom**) for DyCOT_2 and ErCOT_2 at the indicated temperatures.

Field-dependent magnetization measurements were carried out to confirm magnetic anisotropy in both complexes. The non-saturation as well as the non-superimposition of iso-temperature lines in the M vs. H/T data also suggest magnetic anisotropy in DyCOT_2 and ErCOT_2 (Figure 3.3). More notably, the sinusoidal character of the H/T data for ErCOT_2 indicates either QTM or intermolecular interactions in this complex.

Hysteresis measurements were performed on DyCOT_2 and ErCOT_2 with an average sweep rate of 35 Oe.s $^{-1}$. No coercivity was observed for DyCOT_2 at 1.8 K as seen in DyCOT'_2 (Chapter 2). As shown in Figure 3.4, a hysteresis opening at $H = 0$ Oe is apparent from 1.8-5 K in ErCOT_2 . From 6-10 K a waist-restricted shape is observed

where there is no opening at $H = 0$ Oe however an opening at $H = \pm 25000$ Oe. This behaviour is consistent with a QTM pathway occurring in the magnetic relaxation.

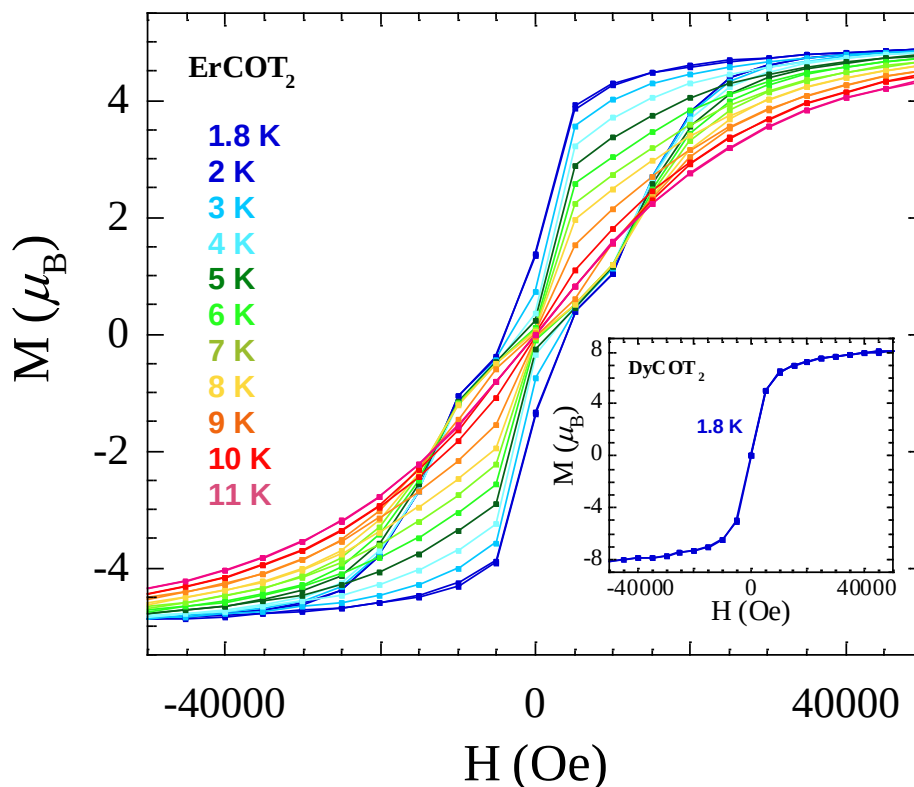


Figure 3.4. Magnetization hysteresis loops. M vs. H for **ErCOT₂** measured on a SQUID at a 35 Oe.s^{-1} sweep rate and at indicated temperatures. At $T = 1.8 \text{ K}$ the coercivity (distance between $M(H)$ points at $M=0$) is about 7000 Oe . Insert: Equivalent measurement for **DyCOT₂** at 1.8 K .

3.2.4. Ac Magnetic Susceptibility

To probe the magnetic relaxation dynamics of both complexes ac measurements were conducted. Variable temperature and variable frequency dynamics were performed (Figure 3.5-3.6). In the χ'' data of **DyCOT₂** no frequency-dependent peak is observed above 5 K . From 5 - 3.5 K peak maxima are observed which are slightly shifting towards lower frequency with decreasing temperature. Such behaviour is consistent with thermally activated spin reversal, and indicates SMM behaviour. Below 3.5 K frequency independent peaks are observed with peak intensity increasing inversely with temperature. Such behaviour indicates QTM which suppresses any thermal energy barrier. The χ'' data of complex **ErCOT₂** show frequency-independent peak maxima shifting

towards lower frequency in the temperature range of 31-12 K indicating SMM behaviour as expected.

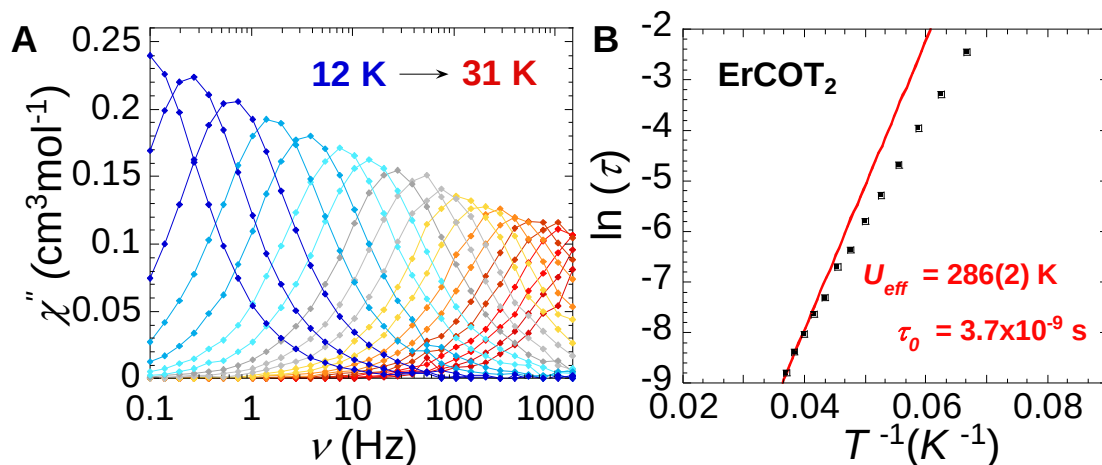


Figure 3.5. (A) Out-of-phase component χ'' for ErCOT_2 measured in the frequency range 0.1 Hz – 1.5 kHz, in zero dc field and at indicated temperatures. (B) Arrhenius treatment of χ'' data with the solid red line indicating the fit of the data. Note that below 12 K the reversal of magnetization in ErCOT_2 takes more than 10 sec. which prevents extraction of relaxation times in the low-temperature region.

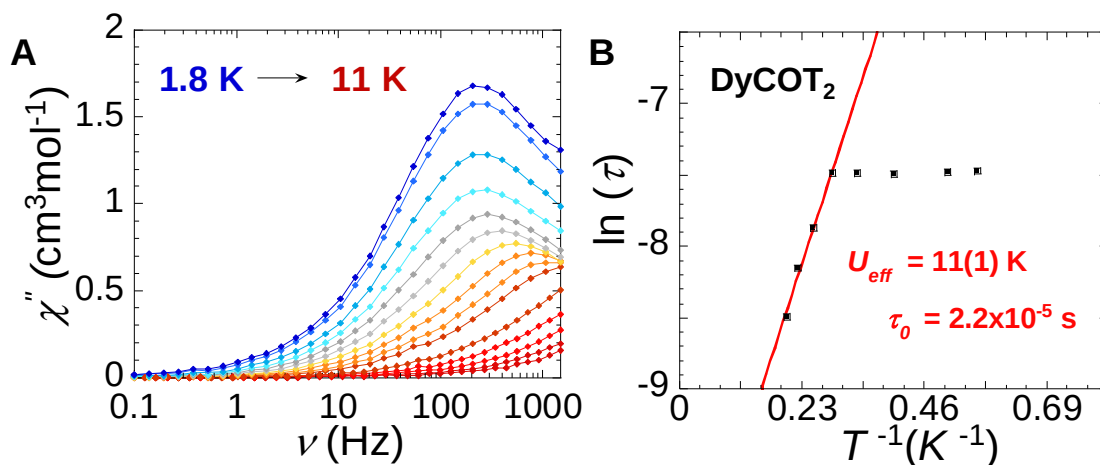


Figure 3.6. (A) Out-of-phase component χ'' for DyCOT_2 measured in the frequency range 0.1 Hz – 1.5 kHz, in zero dc field and at indicated temperatures. (B) Arrhenius treatment of χ'' data for DyCOT_2 with the solid red line indicating the fit of the data.

To probe the magnetic relaxation dynamics of both complexes ac measurements were conducted. Variable temperature and variable frequency dynamics were performed (Figure 3.5-3.6). In the χ'' data of DyCOT_2 no frequency-dependent peak is observed

above 5 K. From 5-3.5 K peak maxima are observed which are slightly shifting towards lower frequency with decreasing temperature. Such behaviour is consistent with thermally activated spin reversal, and indicates SMM behaviour. Below 3.5 K frequency independent peaks are observed with peak intensity increasing inversely with temperature. Such behaviour indicates QTM which suppresses any thermal energy barrier. The χ'' data of complex **ErCOT₂** show frequency-independent peak maxima shifting towards lower frequency in the temperature range of 31-12 K indicating SMM behaviour as expected.

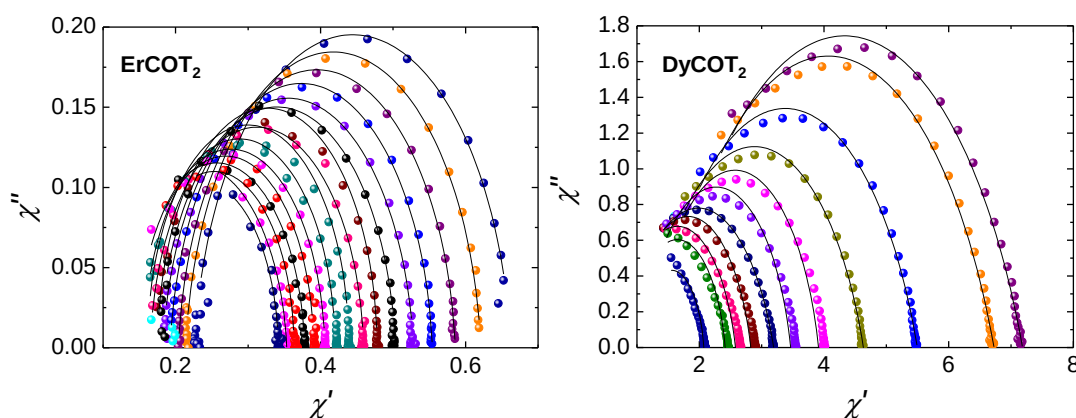


Figure. 3.7. Cole-Cole plot for zero field ac susceptibility of **ErCOT₂** (left) and **DyCOT₂** (right). Experimental data points are represented by circles and the solid black line represents a fit to the data. **ErCOT₂** α^2 values: 0.08 (15K), 0.07 (16K), 0.07 (17K), 0.06 (18K), 0.07 (19K), 0.05 (20K), 0.009 (21K), 0.05 (22K), 0.002 (23K), 0.007 (24K), 0.03 (25K), 0.008 (26K), 0.03 (27K), 0.004 (28K), 0.07 (29K), 0.02 (30K). **DyCOT₂** α^2 values: 0.43 (1.8K), 0.42 (2K), 0.39 (2.5K), 0.37 (3K), 0.23 (3.5K), 0.22 (4K), 0.36 (4.5K), 0.24 (5K), 0.24 (5.5K), 0.18 (6K), 0.13 (7K).

For both complexes, frequency dependent peaks are fit using a Gaussian function to determine the peak maxima which is represented as $\nu = (2\pi\tau)^{-1}$. This data is used in conjunction with the Arrhenius equation, $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, to calculate the U_{eff} of the magnets. For **ErCOT₂**, $U_{\text{eff}} = 212$ K (152 cm^{-1}) with $\tau_0 = 6.7 \times 10^{-8}$ s and for **DyCOT₂**, $U_{\text{eff}} = 11$ K (9 cm^{-1}) with $\tau_0 = 2.2 \times 10^{-5}$ s. The extracted blocking barriers are in good agreement with the calculated positions of the corresponding excited states through which the temperature-assisted (TA) magnetic relaxation occurs at high temperatures (Figure 3.9). Ac data for both **DyCOT₂** and **ErCOT₂** was also investigated for possible multiple relaxation behaviour (Figure 3.7). Cole-Cole plots fit using the generalized

Debye model indicate a single relaxation for **ErCOT**₂ whereas **DyCOT**₂ displayed a poor fit at some temperatures. Results are similar to those seen in **DyCOT'**₂ and **ErCOT'**₂ (Chapter 2).

3.2.5 Magnetic Properties Explained via Electronic and *Ab initio* Calculations¹³

Ab initio CASSCF/RASSI/SINGLE_ANISO calculations with MOLCAS 7.8¹⁴ predict that the ground state of **ErCOT**₂ is well separated from the low-lying excited states, and that the strong magnetic anisotropy of the ground ($g_{x,y} \approx 10^{-6}$) and of the first excited Kramers doublet have almost colinear anisotropy axes (Figure 3.8).¹³ Calculations also predict a much denser low-lying energy spectrum for **DyCOT**₂, lower degree of magnetic axiality in the lowest Kramers doublet ($g_{x,y} \approx 10^{-1}$) and non-colinear anisotropies of ground and excited states (Figure 3.8).¹³

Similar *ab initio* calculations on symmetrized models of **ErCOT**₂ with a C_8 point group revealed an energy spectrum almost independent of the relative angular positions of the COT rings, assumed parallel to each other.¹³ This confirms that the central Ln^{III} ion feels an almost perfectly rotational (i.e., described by a symmetry axis of infinite order) electronic density from a ring, a conclusion already anticipated from Figure 3.8. Studies concerning the effect of the Ln-COT distance on the low-lying electronic spectrum revealed a large domain of R(Ln-COT) for which the properties of the ground and of the few excited states reported above are similar.¹³

As found previously, the strengths of QTM and the rate of spin-phonon transitions are loosely proportional to the square of the transversal magnetic moment connecting the magnetic states of the complex.¹⁵ The blocking barrier can be defined, therefore, by the shortest paths where the values of the transversal magnetic moment are the largest.¹⁶ Figure 3.9 shows *ab initio* constructed magnetization blocking barriers for **ErCOT**₂ and **DyCOT**₂. For the former we notice the negligible value of the transversal magnetic moment in the ground state ($\approx 10^{-6} \mu_B$) which explains why the QTM is suppressed at low temperature for this compound. The transversal magnetic moment is small for the first

excited state ($\approx 10^{-4} \mu_B$); therefore, thermally-assisted QTM will be quenched for this Kramers doublet as well. Due to the colinearity of anisotropy axes of the ground and first excited Kramers doublets, the off-diagonal matrix element of the transversal magnetic moment between their components of opposite magnetization is also small ($\approx 10^{-5} \mu_B$) and the corresponding Orbach process¹⁷ is suppressed. As a result, magnetic relaxation in the **ErCOT**₂ compound can only occur via the second excited state, which allows significant thermally-assisted tunneling (Figure 3.9B). This effect was recently found to increase significantly the height of blocking barriers in lanthanide SMMs.⁴ In contrast, **DyCOT**₂ has a significantly larger value of the transversal magnetic moment already in the ground state ($\approx 10^{-1} \mu_B$), therefore allowing a fast QTM. Moreover, the tunneling in the excited state is also allowed ($\approx 10^{-1} \mu_B$), enhancing overall the reversal of magnetization at higher temperatures.

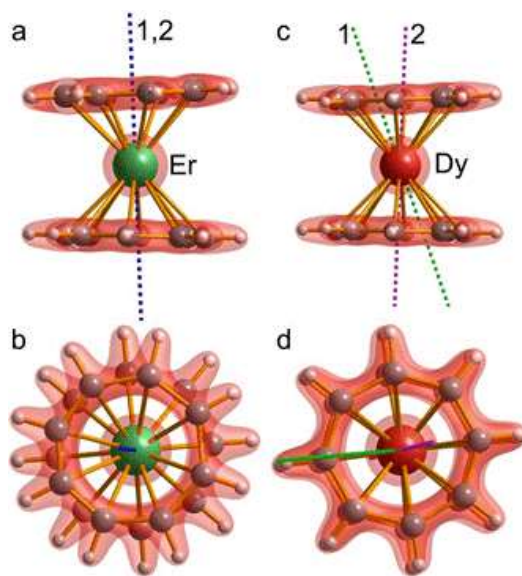


Figure 3.8. Molecular structures of **ErCOT**₂ and **DyCOT**₂. (A) Side and (B) top view for **ErCOT**₂; (C) side and (D) top view for **DyCOT**₂. Structural details: mean eccentricity of COT rings is small: 0.11 (**ErCOT**₂) and 0.21 (**DyCOT**₂); shortest distance between two neighbouring molecules in the crystal is 7.25 Å (**ErCOT**₂); 7.09 Å (**DyCOT**₂). Transparent red surface shows the calculated electronic density in the ground state. Note the high rotational symmetry of the electronic cloud close to the Ln ion. Dashed lines show the calculated orientation of the main magnetic axis on Ln ions in the ground (1) and first excited (2) Kramers doublet. For **ErCOT**₂: $g_{x,y}=3.5 \times 10^{-6}$, $g_z=17.96$ for the ground doublet and $g_{x,y}=5.4 \times 10^{-4}$, $g_z=15.53$ for the first excited doublet; the angle between corresponding g_z axes is $\sim 1.0^\circ$. For **DyCOT**₂: $g_{x,y}=1.6 \times 10^{-1}$, $g_z=12.64$ for the ground doublet (green dashed line) and $g_{x,y}=5.8 \times 10^{-2}$, $g_z=13.84$ for the first excited doublet (purple dashed line); the angle between corresponding g_z axes is $\sim 21^\circ$.^{8c}

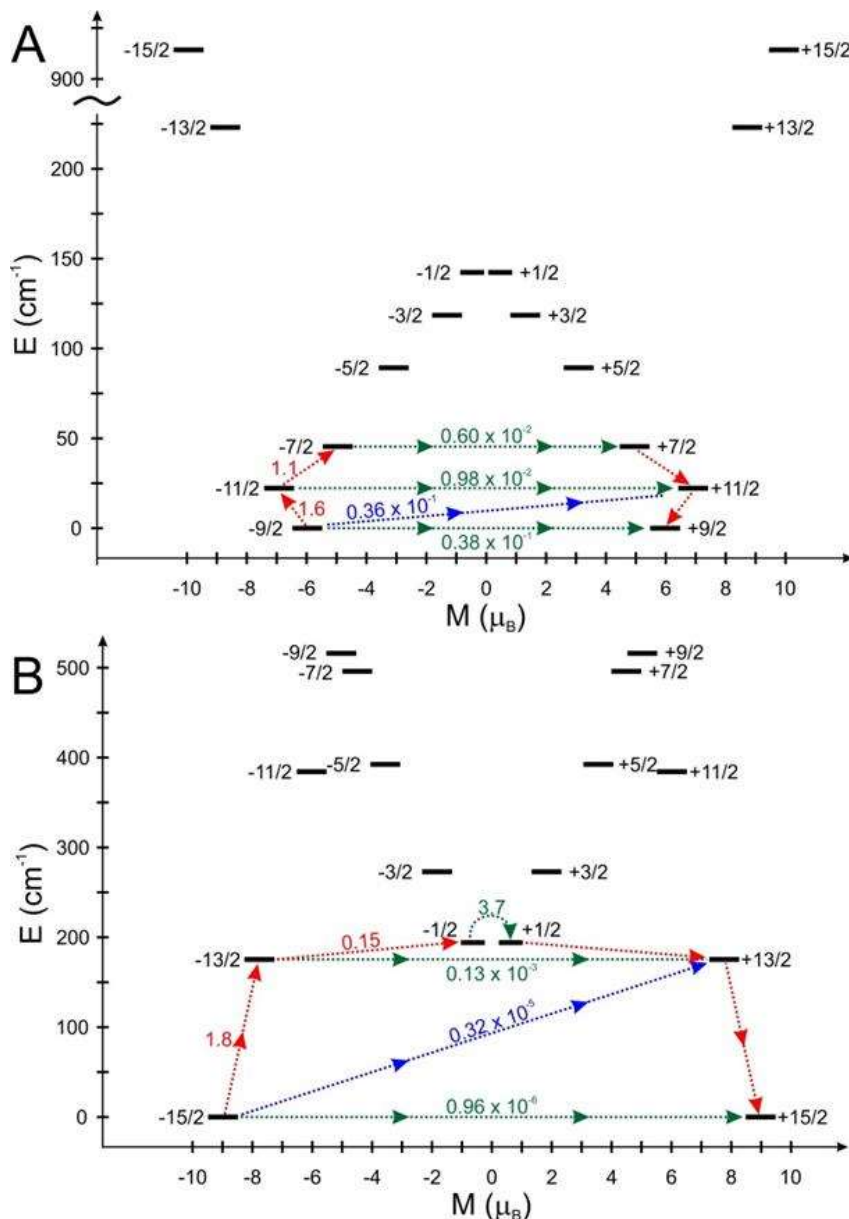


Figure 3.9. The magnetization blocking barriers in DyCOT_2 (A) and ErCOT_2 (B) compounds. The thick black lines represent the KDs as a function of their magnetic moment along the axis connecting the centres of COT rings. The green dashed lines correspond to diagonal QTM; the blue dashed lines represent possible Orbach relaxation processes. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment ($(|\mu_x|+|\mu_y|+|\mu_z|)/3$). The path shown by the red arrows represents the most probable path for magnetic relaxation in the corresponding compounds.^{8c}

In order to understand the ultimate reason for the high SIM performance of ErCOT_2 compared to DyCOT_2 , we calculated the parameters of the multiplet-specific crystal field for these compounds on the basis of *ab initio* wave functions and energies.¹³ We found

that axial parameters B_2^0, B_4^0, B_6^0 are by far the largest, while the non-axial parameters are one or more orders of magnitude smaller. The wave function of the ground state of **ErCOT**₂ is almost of pure $\pm 15/2$ type, with negligible contributions from other J -projections (weight $< 10^{-4}$). In contrast, the wave function of the ground state of **DyCOT**₂ is $\pm 9/2$ type, with significantly larger contributions from other J -projections (weight $\approx 4.5\%$). This is explained by a much larger energy gap between the ground and first excited Kramers doublet of **ErCOT**₂ compared to **DyCOT**₂. Such a large difference between the energy gaps originates from the well-known fact that the most important crystal-field parameters B_2^0 and B_4^0 have opposite signs for **ErCOT**₂ and **DyCOT**₂, which is confirmed in *ab initio* calculations.¹³ For this reason, the spectra of **ErCOT**₂ and **DyCOT**₂ compounds look as being mutually “reversed”. Indeed, the highest excited Kramers doublet obtained for **DyCOT**₂ is very axial and of $\pm 15/2$ type (Figure 3.9).

3.3 Conclusions

In contrast to the structural similarity of **ErCOT**₂ and **DyCOT**₂, their magnetic behaviour shows strong discrepancies. **ErCOT**₂ exhibits a very strong blocking of magnetization, precluding the extraction of the relaxation times for temperatures lower than 12 K between 0.1 – 1500 Hz, a phenomenon not observed in other SIM complexes. Surprisingly enough the **DyCOT**₂ complex shows much weaker magnetization blocking, with relaxation times many orders of magnitude lower than in **ErCOT**₂, despite its close structure to that of the latter. As predicted, increasing the symmetry of **ErCOT**₂, discussed in Chapter 2, increased the magnetic blocking temperature of **ErCOT**₂ (to 12 K). The structure of **ErCOT**₂ deviated from perfect D_{8d} symmetry presumably due to the unsymmetrical interaction with the K[18-C-6] counter cation. Therefore, replacing the counter cation with something less likely to interact with the COT²⁻ ring (such as 2.2.2-Cryptand) is expected to further enhance the magnetic properties of [Er(COT)₂].

In conclusion, the exceptional magnetic properties of the reported SIM complex containing one Er^{III} ion sandwiched between two planar COT ligands (the large coercive field up to 7000 Oe at 1.8 K and magnetic remanence up to 6 K) makes the reported compound comparable to polynuclear SMMs. The large remanence and coercivity at $H =$

0 Oe in **ErCOT₂** are key properties of permanent magnets. Besides showing unprecedented capability for magnetization blocking, the present **ErCOT₂** complex certainly possesses the ability to be uniformly attached *via* π - π stacking to various surfaces such as graphene or metal surfaces. This provides a pathway for employment of the present **ErCOT₂** compound in spintronics and other applications, such as information storage, thus requiring a significant magnetic blocking capacity at helium temperatures.¹⁸

3.4 Experimental

General considerations. All manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware was oven dried (120°C, 6h) before use. Tetrahydrofuran (THF) and toluene were dried using activated alumina and stored over 3Å molecular sieves. Anhydrous ErCl₃ and anhydrous DyCl₃ were purchased from Strem and used as received. C₈H₈, 18-Crown-6 and K⁺ were purchased from Sigma Aldrich and used as received. Chloroform-d was degassed using repeated freezing-evacuating-thawing cycles, and stored over 4Å molecular sieves. ¹H NMR spectra were recorded on a 300 MHz Bruker Avance instrument at room-temperature (21-23°C). Bulk ferromagnetic impurities were confirmed absent in both samples using magnetization data collected at 100 K on a SQUID Magnetometer.

ErCOT₂. C₈H₈ (0.11 mL, 1.0 mmol) was added to K⁺ (82 mg, 2.1 mmol) in 15 mL of 50:50 THF:toluene at -20 °C. The mixture was stirred at -20 °C for 4 hours, filtered, and ErCl₃ (139 mg, 0.51 mmol) was added to the filtrate. The reaction was stirred for 1 hour at -20 °C, and additionally for 3 h at room temperature before being filtered. 18-crown-6 (132 mg, 0.5 mmol) dissolved in 1 mL of THF was added. Isolated crystals of [K(18-Crown-6)][Er(COT)₂] (306 mg, 74% yield) are extremely air and moisture sensitive. CCDC: 961014. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.73 (br.s, 16H, H_{COT}), 1.81 (br.s, 24H, H18-crown-6).

DyCOT₂. Complex **DyCOT₂** was prepared in an analogous manner to **ErCOT₂** using C₈H₈ (0.11 mL, 1.0 mmol), K⁺ (82 mg, 2.1 mmol), 18-crown-6 (132 mg, 0.5 mmol), and DyCl₃ (137 mg, 0.51 mmol). Isolated crystals of [K(18-Crown-6)][Dy(COT)₂] (287 mg,

73% yield) are extremely air and moisture sensitive. CCDC: 961013. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 5.73 (br.s, 16H, H_{COT}), 1.81 (br.s, 24H, H18-crown-6).

Single crystal X-ray diffraction. For ErCOT_2 and DyCOT_2 a suitable prism-shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and refinement details are located in Table 3.2.

Table 3.2. Crystal data and structure refinement for DyCOT_2 , and ErCOT_2 .

	ErCOT₂	DyCOT₂
Formula	$\text{C}_{36}\text{H}_{56}\text{ErKO}_8$	$\text{C}_{34}\text{H}_{52}\text{DyKO}_{7.50}$
M_r (g/mol)	823.17	782.360
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma(62)	Pnma(62)
a (Å)	20.0091(5)	19.839(3)
b (Å)	11.3821(3)	11.5419(16)
c (Å)	16.3604(4)	16.297(2)
α (deg)	90.000	90.000
β (deg)	90.000	90.000
γ (deg)	90.000	90.000
V (Å³)	3726.01(16)	3731.7(9)
T(K)	200(2)	200(2)
Z	4	4
Reflections collected	42350	28888
goodness of fit	1.092	1.017
Shape and Colour	Block orange	Block orange
R1/ wR2	0.0282/0.0792	0.0712/0.1936
Size (mm)	0.24 x 0.21 x 0.11	0.31 x 0.19 x 0.15
Reflections with I > 2σ(I)	4397	3965

SQUID Magnetometry. Magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz and at 0 dc field. Hysteresis measurements were performed using hysteresis mode and in all measurements data was collected starting at H=0 Oe, sweeping to H=50 the average sweep rate calculated per cycle. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

Computational Details.¹³ All calculations were done with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type. Three structural approximations of the initial LnCOT₂K molecules were employed: **A** (small), **B** (medium) and **C** (the entire molecule). In the structural model **A**, the K atom and its surroundings were removed. The structural model **B**, included the structure of the model A and the K atom, while the surrounding of the K atom was removed. The structural model **C**, is the entire molecule as determined experimentally (taken from the CIF file). Two basis set approximations have been employed: **1** – small, **2** – large; Table 3.3 shows the contractions of the employed basis sets for all elements. All in all there are 6 computational models for each magnetic center in the considered LnCOT₂K molecule: **A1**, **A2**, **B1**, **B2**, **C1** and **C2**. Alongside the above compounds with real geometry, the symmetrized D_{8d} or D_{8d} versions of the structural model **A1** and **A2** were computed. Active space of the CASSCF method includes the electrons from the last shell spanning the 7 orbitals (4f orbitals of the Ln³⁺ ion). For Er compound all spin states were mixed by the spin-orbit coupling, while for Dy only a limited number of roots was possible to mix, namely 21 sextets, 128 quartet and 130 doublet states. On the basis of the resulting spin-orbital multiplets the SINGLE_ANISO program computed local magnetic properties (*g*-tensors, main magnetic axes, local magnetic susceptibility, Crystal-Field parameters, etc.)

Table 3.3. Contractions of the employed basis sets in computational approximations.

	Basis 1 (DZP-quality)	Basis 2 (TZP-quality)
<u>employed for models A</u>	Ln.ANO-RCC...7s6p4d2f1g. C.ANO-RCC...3s2p1d. H.ANO-RCC...2s1p.	Ln.ANO-RCC...8s7p5d3f2g1h. C.ANO-RCC...4s3p2d1f. H.ANO-RCC...3s2p1d.
<u>employed for models B</u>	Ln.ANO-RCC...7s6p4d2f1g. K.ANO-RCC...5s4p1d. C.ANO-RCC...3s2p1d. H.ANO-RCC...2s1p.	Ln.ANO-RCC...8s7p5d3f2g1h. K.ANO-RCC...6s5p2d1f. C.ANO-RCC...4s3p2d1f. H.ANO-RCC...3s2p1d.
<u>employed for models C</u>	Ln.ANO-RCC...7s6p4d2f1g. K.ANO-RCC...5s4p1d. O.ANO-RCC...3s2p. C.ANO-RCC...3s2p1d.(close) C.ANO-RCC...3s2p.(distant) H.ANO-RCC...2s1p. (close) H.ANO-RCC...2s. (distant)	Ln.ANO-RCC...8s7p5d3f2g1h. K.ANO-RCC...6s5p2d1f. O.ANO-RCC...3s2p. C.ANO-RCC...4s3p2d1f. (close) C.ANO-RCC...3s2p.(distant) H.ANO-RCC...3s2p1d. (close) H.ANO-RCC...2s. (distant)

Ln= Dy, Er

3.5 References

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Chapter 4

Aromatic Cyclooctatetraenyl Dianion Ligand to Promote Magnetic Interaction between Lanthanide ions*

Partial contents of this chapter have been published in: (a) J. J. Le Roy, M. Jeletic, S. I. Gorelsky, I. Korobkov, L. Ungur, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. **2013, 135, 3502. (b) J. J. Le Roy, L. Ungur, I. Korobkov, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. **2014**, 136, 8003.*

As highlighted in previous chapters, fine-tuning the ligand field and local symmetry around individual lanthanide ions has been a successful strategy to increase the blocking temperatures of lanthanide SIMs.¹ Further fine-tuning of local symmetry could no doubt result in SIMs with higher blocking temperatures, however, such a strategy has a finite ceiling for improvement. In order to significantly increase the blocking temperature of lanthanide SMMs, the total spin of the molecule needs to increase; therefore the number of paramagnetic ions needs to increase. Employing such a strategy in lanthanide SMMs is challenging due to the poor radial extension of the 4f electrons. Since significant ferromagnetic exchange between lanthanide ions is vital to increasing the spin ground state of the complex, we investigated the use of bridging COT^{2-} ligands to provide a delocalized super-exchange pathway ideal for promoting magnetic interaction between lanthanide ions.

This Chapter utilizes an organometallic building block strategy to investigate the magnetic properties of triple-decker organolanthanide SMMs. The synthesis and magnetic properties of new homoleptic $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ ($\text{Ln} = \text{Gd}$ ($\text{Gd}_2\text{COT}''_3$), Dy ($\text{Dy}_2\text{COT}''_3$), Er ($\text{Er}_2\text{COT}''_3$), $\text{COT}'' = 1,4\text{-bis}(\text{trimethylsilyl})\text{cyclooctatetraenyl dianion}$) complexes are discussed. Important findings in this chapter include DFT calculations on

$\text{Dy}_2\text{COT}^{2-}_3$, which indicate the presence of strong metal-ligand covalency and uneven donation to the Dy^{III} ions by the terminal and internal COT²⁻ rings that correlate with the respective bond distances. Interestingly, studies also point to a weak covalent interaction between the metal centers, despite a large physical separation. Such an interaction is surprising due to the core orbital nature of 4f electrons, however, this interaction significantly contributes to the strong magnetic properties of $\text{Er}_2\text{COT}^{2-}_3$. Magnetic susceptibility studies reveal that both $\text{Dy}_2\text{COT}^{2-}_3$ and $\text{Er}_2\text{COT}^{2-}_3$ behave as SMMs, and $\text{Er}_2\text{COT}^{2-}_3$ has a high magnetic blocking temperature of 12 K. Notably, the 4 K increase in the magnetic blocking temperature of $\text{Er}_2\text{COT}^{2-}_3$ over the double-decker analog (ErCOT^{2-} , Chapter 2) is attributed to an additional mechanism of magnetization blocking arising from exchange coupling between Er^{III} ions. This Chapter establishes that increasing the total spin of an SMM, while also considering local symmetry, is an effective approach to increasing the blocking temperature of lanthanide SMMs.

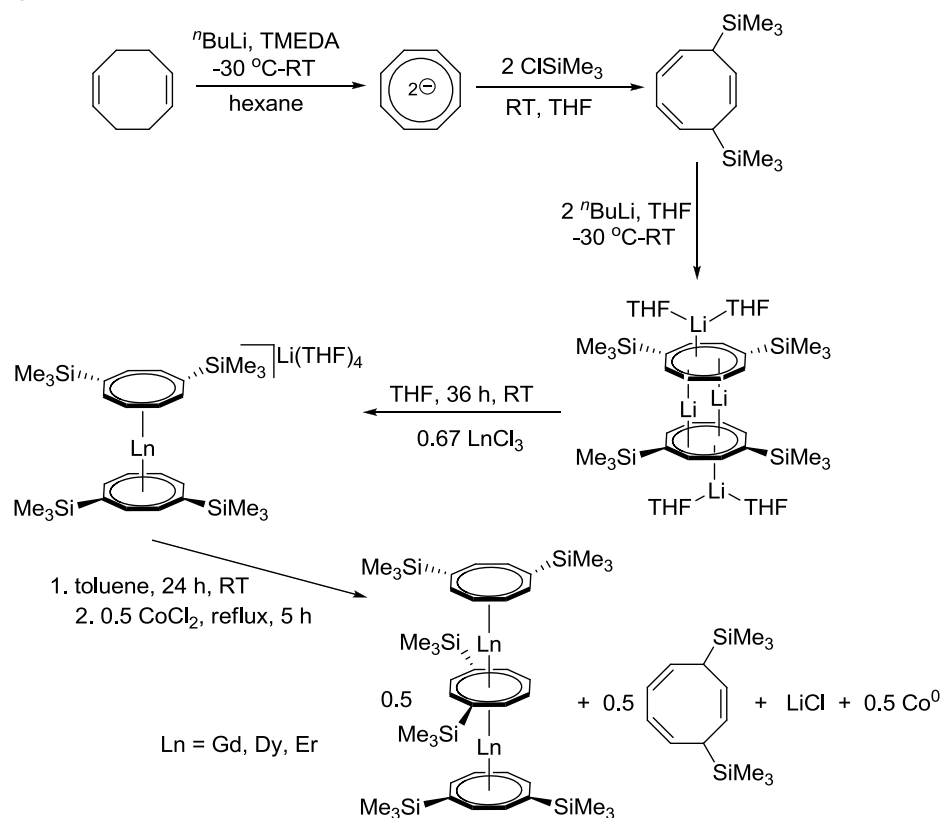
4.1 Introduction

Lanthanide SIMs, like those discussed in Chapters 2 and 3, are popular due to their large intrinsic magnetic anisotropy, however they still fail to surpass the record blocking temperatures set by polynuclear SMMs.² Theoretically speaking, larger energy barriers are expected for polynuclear complexes as they possess many spin carriers, and when coupled ferromagnetically could lead to a large spin ground state. The study of multi-metallic coordination clusters has greatly advanced the field of SMMs, yet an underlying problem still exists; oxygen and nitrogen bridged coordination complexes have limited orbital overlap with the shielded 4f orbitals. Therefore, multinuclear lanthanide SMMs usually display predominantly single-ion based relaxation dynamics. Several strategies have been explored to increase exchange coupling between lanthanide ions; including the use of heavier elements with more diffuse orbitals,³ as well as bridging radicals^{2,4} as potentially efficient superexchange pathways. The radical approach has been the most successful in obtaining strong exchange coupling constants between two lanthanide ions due to the presence of an unpaired electron on the ligand, however, extending this methodology to larger molecules involving multiple metal centers/radicals is synthetically very difficult and has, thus, led to limited application of this approach.

Therefore, research efforts towards achieving stronger metal-metal coupling as well as significant spin interactions were directed towards organometallic complexes where the metal centers are bridged by large aromatic COT'' rings. These complexes take advantage of the π electron cloud created by the multiple carbon atoms to facilitate efficient overlap with the metal f orbitals, subsequently leading to non-negligible interactions. This Chapter examines lanthanide COT''²⁻ sandwich complexes as building blocks to construct polynuclear SMMs. The synthesis, structure and magnetic properties of organopolylanthanide complexes of general formula, $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$, are discussed as well and a magnetic comparison with their respective mononuclear building block units (Chapter 2).

4.2 Triple Decker Lanthanide-COT'' Complexes

4.2.1 Synthesis



Scheme 4.1. Synthetic route to the Ln^{III} homoleptic triple-decker sandwich complexes starting from 1,5-cyclooctadiene.

Our synthetic strategy for the design of organopolymetallic SMMs is inspired from Edelmann and co-worker's methodology.⁵ The strategy consists of a building block approach whereby $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ complexes are built from the bottom up. Monometallic sandwich complexes, $[\text{LnCOT}'']_2$, can be isolated from planar COT''^{2-} ligands as discussed in Chapter 2.^{5c,6} The isolated complexes are ideal charged building blocks where an oxidation of the ligand leads to a coupling of the monomer units resulting in triple decker sandwich complexes, $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$.^{5e,7} In these bimetallic structures a central COT'' ring bridges both metal centers, thus providing an ideal delocalized super-exchange pathway for magnetic interactions. The synthesis of all $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ complexes was conducted in an analogous fashion, where two equivalents of $[\text{LnCOT}'']_2\text{Li}(\text{THF})_4$ ^{6a} reacts with 1 equivalent of CoCl_2 to generate the desired $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ complex as well as an equivalent of 1,4-bis(trimethylsilyl)cyclooctatetraene, 2 equivalents of LiCl and 1 equivalent of Co^0 metal (Scheme 4.1). The similar reactivity and common oxidation states of lanthanide ions prove to be useful in the isolation of isostructural compounds from the lanthanide series and therefore allow the use of similar/identical synthetic methodologies.

4.2.2 Structural Characterization

Single crystal X-ray diffraction studies reveal that each of $\text{Gd}_2\text{COT}''_3$, $\text{Dy}_2\text{COT}''_3$ and $\text{Er}_2\text{COT}''_3$ are isostructural and crystallize in the tetragonal *I*-4 space group (Figure 4.1, Table 4.1 and 4.4). As an example, the structure of $\text{Dy}_2\text{COT}''_3$ will be discussed in detail. The neutral $\text{Dy}_2\text{COT}''_3$ molecule is a homoleptic triple-decker sandwich complex containing two Dy^{III} centers that bind to opposing sides of the COT'' rings. The outer COT'' ligands coordinate in an η^8 manner to Dy^{III} ions with $\text{Dy}^{\text{III}}\text{-C}$ bond distances ranging from 2.54-2.62 Å, whereas the central ring serves as $\mu\text{-}\eta^8\text{:}\eta^8$ bridging ligand with a $\text{Dy}^{\text{III}}\text{-C}$ bond distance range of 2.73-2.79 Å. The $\text{Dy}^{\text{III}}\text{-Dy}^{\text{III}}$ distance is 4.14 Å. The distance between the outer COT'' centroid and Dy^{III} ion is 1.79 Å, whereas the inner $\text{COT}''_{\text{centroid}}\text{-Dy}^{\text{III}}$ distance is significantly longer (2.07 Å). This differs from DyCOT''_2 (Chapter 2) where a more symmetrical arrangement was observed with an average

COT''_{centroid}-Dy^{III} distance of 1.90 Å. The reasons for this will be discussed in the computational section (4.2.3).

Table 1. Structural parameters for **Gd₂COT''₃**, **Dy₂COT''₃** and **Er₂COT''₃**.

	Gd₂COT''₃	Dy₂COT''₃	Er₂COT''₃
Intramolecular			
Ln-Ln (Å)	4.207	4.139	4.111
Ln-COT''_{centroid} (terminal) (Å)	1.814	1.788	1.745
Ln-COT''_{centroid} (bridging) (Å)	2.104	2.070	2.057
Ln-COT''_{centroid}-Ln (°)	176.9	176.0	175.7
Intermolecular Ln-Ln (Å)	9.034	9.197	9.195

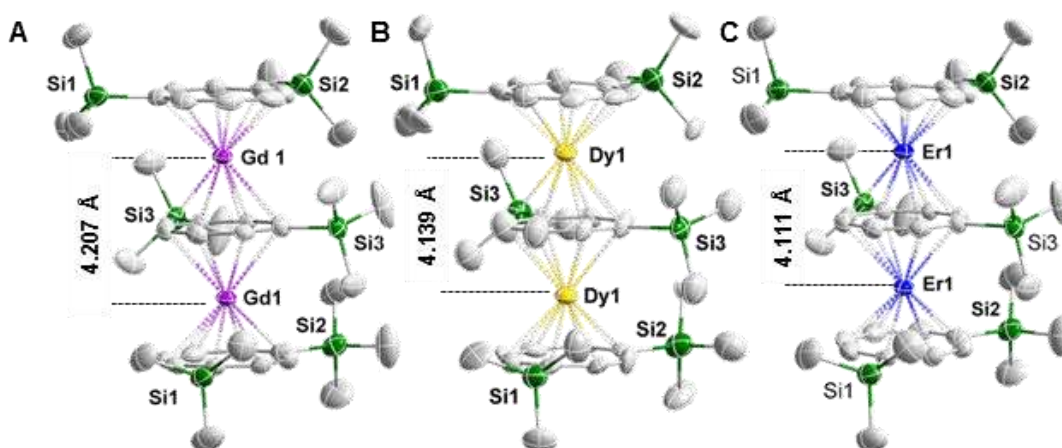


Figure 4.1. Solid state structures of **Gd₂COT''₃** (A), **Dy₂COT''₃** (B) and **Er₂COT''₃** (C). H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), green (Si), purple (Gd^{III}), yellow (Dy^{III}) and blue (Er^{III}).

The outer COT'' rings are in near parallel arrangement with the central ring with a slight tilt angle of 1.86°, and the angle between the three COT'' centroids is 177°. The presence of TMS groups most likely distorts the structure from a perfect parallel arrangement. This type of near parallel ring arrangement is rare in multinuclear organolanthanide chemistry.⁸ Also of interest, when viewing the structure of **Dy₂COT''₃** from above, the carbon atoms in each layer are staggered. This staggering effect is most likely dictated by the sterics of the bulky silyl groups, while specific orbital coordination arrangements around the central Dy^{III} ion could also influence this arrangement. Close inspection of the

packing arrangement of **Dy₂COT''₃** reveals the closest intermolecular Dy^{III}-Dy^{III} distance is 9.197 Å and the complex packs orthogonal with respect to itself in the previous layer. Overall **Dy₂COT''₃** (as well as **Gd₂COT''₃** and **Er₂COT''₃**) is structurally analogous to the previously reported Nd^{III} complex.^{5e}

4.2.3 Electronic Structure Calculations of **Dy₂COT''₃**⁹

The electronic structure of **Dy₂COT''₃** was probed using DFT calculations at the spin-unrestricted B3LYP¹⁰/TZVP¹¹ level (the SDD¹² basis set and effective core potential for Dy^{III}) using the crystal structure geometry. The TMS groups were replaced by protons and all C-H bond distances were adjusted from the X-ray model values to 1.07 Å in order to simplify the calculations, while still providing an accurate bonding picture. In **Dy₂COT''₃** each Dy^{III} ion interacts with the terminal and the central COT'' ligands. The net charges of the terminal and central COT'' ligands are -0.30 a.u. and -0.12 a.u., respectively. These charges indicate that the terminal dianionic COT'' ligands donate 1.70 e⁻ to each Dy^{III} ion. The central dianionic COT'' ligand donates larger electron density to the Dy^{III} ions (1.88 e⁻), but because there are two Dy^{III} ions, each receives only 0.94 e⁻. The Mayer bond orders¹³ for the stronger Dy^{III}-ligand interactions (2.3 for the interaction with the terminal COT'' and 1.2 for the interaction with the central COT'') confirm this finding. Thus, stronger terminal COT''→Dy^{III} charge donation explains the shorter Dy^{III}-C_{centroid} distances for the terminal COT''-Dy^{III} fragment. The analysis of the wavefunction in terms of contributions from fragment orbitals indicates that only charge donation from the COT'' ligands to Dy^{III} contribute to the covalent bonding in this complex. Eight occupied orbitals of the central COT'' dianionic ligand participate significantly (change in orbital population is greater than 3%) in covalent bonding with the two Dy^{III} ions (Figure 4.2B). Most of the donated electron density comes from four π orbitals (HOMO, HOMO-1, HOMO-2 and HOMO-3). Thus, the whole superexchange interaction *via* the central COT'' ligand plays a major role in defining the spin interaction between the two Dy^{III} ions. There is also a weak direct Dy^{III}-Dy^{III} covalent interaction with a bond order of 0.04. Although this value is relatively small, it is still surprising to observe such direct Dy^{III}-Dy^{III} covalent interaction. Further spectroscopic studies are currently underway in order to validate this interaction.¹⁴

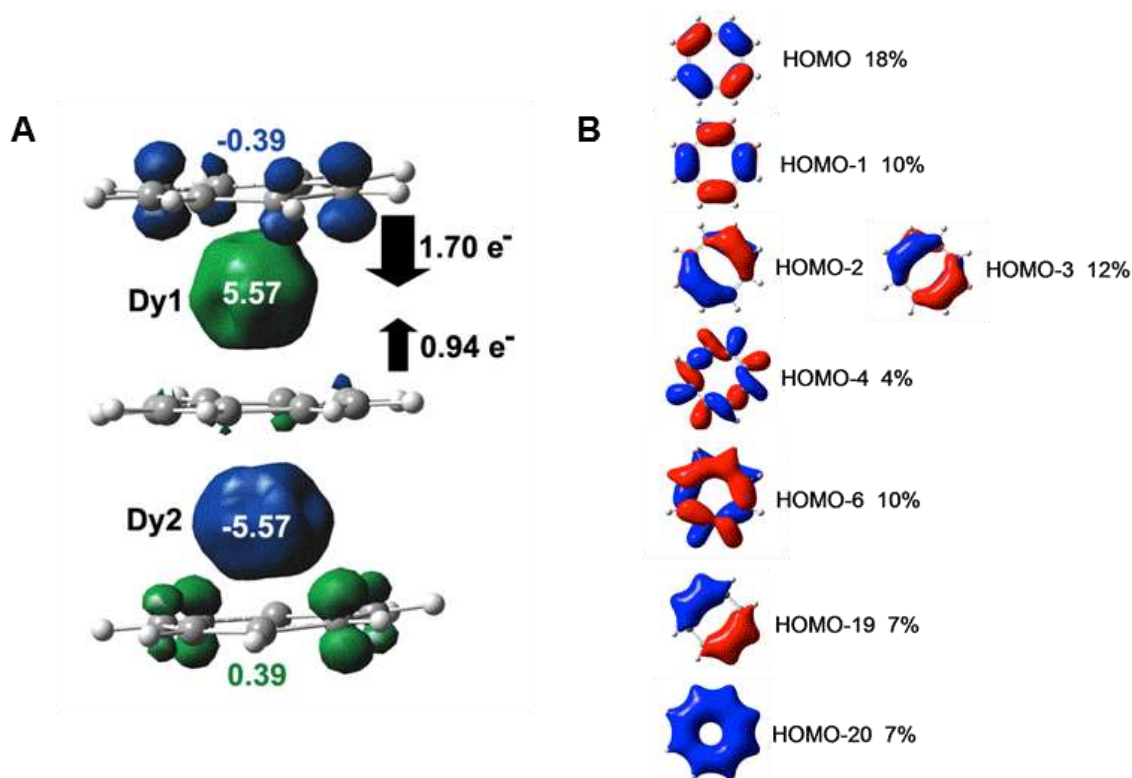


Figure 4.2.⁹ Electronic structure calculations of $\text{Dy}_2\text{COT}''_3$. (A) Spin density distribution of the BS singlet state of $\text{Dy}_2\text{COT}''_3$. Green and blue indicate the regions of positive and negative spin densities, respectively. Black arrows indicate charge donation from the dianionic COT'' ligands to Dy^{III} ions. (B) Fragment molecular orbitals of the central COT'' dianionic ligand that contribute significantly (>3% change in occupancy) to the bonding in $\text{Dy}_2\text{COT}''_3$. % Changes in occupancy upon bonding in the complexes are shown. Isosurface value of 0.04 was used for visualization of the orbitals.

4.3 Magnetic Properties of $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ Complexes

Chapters 2 and 3 described the magnetic properties of both ErCOT''_2 and ErCOT_2 building block units, in which magnetic blocking temperatures of 8 K and 10 K were determined, respectively.^{1a,6d} Our current objective is to enhance the magnetic properties of Lanthanide-COT sandwich complexes by increasing spin through dimerization, while maintaining strictly axial anisotropy. $\text{Ln}^{\text{III}}_2(\text{COT}'')_3$ complexes are ideal due to linearity and high axial symmetry around the spin sources. In such complexes a strong magnetic interaction between Ln^{III} ions is expected due to close M-M distances ($\text{Dy}_2\text{COT}''_3$: 4.139 Å, $\text{Er}_2\text{COT}''_3$: 4.111 Å). To evaluate the effect of promoting a strong magnetic interaction through an aromatic COT''²⁻ ring, the magnetic properties of $\text{Gd}_2\text{COT}''_3$,

Dy₂COT''₃ and **Er₂COT''₃** were investigated using a SQUID magnetometer and compared to their respective monomer building blocks.

4.3.1 Dc Magnetic Susceptibility

Dc magnetic susceptibility measurements were performed in the temperature range of 1.8-300 K under an applied dc field of 1000 Oe (Figure 4.3) and dc magnetic susceptibility data is located in Table 4.2. The magnetic properties of **Er₂COT''₃** were additionally investigated in a 4 mM cyclopentane frozen solution to probe any intermolecular magnetic interactions.

Table 4.2. Dc magnetic susceptibility data for **Gd₂COT''₃**, **Dy₂COT''₃**, and **Er₂COT''₃**.

	χT product 300 K (cm ³ ·K·mol ⁻¹)	Theoretical χT product 300 K (cm ³ ·K·mol ⁻¹)	χT product 1.8 K (cm ³ ·K·mol ⁻¹)
Gd₂COT''₃	15.08	15.76	9.22
Dy₂COT''₃	27.92	28.34	10.42
Er₂COT''₃	22.45	22.96	0.55

The room temperature χT values for **Gd₂COT''₃**, **Dy₂COT''₃**, and **Er₂COT''₃** are all in agreement with the theoretical values for two non-interacting Gd^{III} (⁸S_{7/2}, $S = 7/2$; $L = 0$, $g = 2$), Dy^{III} (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$) and Er^{III} (⁴I_{15/2}, $S = 3/2$, $L = 6$, $g = 6/5$) ions (Table 4.2). For all complexes, the χT value gradually decreases from the room temperature value with a faster decrease below 50 K. For **Dy₂COT''₃**, and **Er₂COT''₃** this behavior could originate from a combination of the large inherent magnetic anisotropy in Ln^{III} ions, and the thermal depopulation of the excited states. In both complexes, the observed steeper decrease below 50 K indicates either a non-negligible contribution from antiferromagnetic interactions between metal centers or intermolecular interactions. To rule out any intermolecular interactions we performed frozen solution measurements in 4 mM cyclopentane for **Er₂COT''₃** in the 1.8-100 K temperature range. The χT product again shows a steep drop at low temperatures reaching a minimum value of 1.62 cm³·K·mol⁻¹, thus confirming the low temperature decrease is not due to intermolecular influence. Although interactions are hard to quantify between highly anisotropic Dy^{III} and

Er^{III} ions, antiferromagnetic interactions are expected to be non-negligible due to the presence of eight occupied orbitals of the central COT²⁻ dianionic ligand acting as a superexchange pathway as well as the weak direct $\text{Dy}^{\text{III}}\text{-Dy}^{\text{III}}$ (for $\text{Dy}_2\text{COT}^{2-}_3$) covalent interaction (section 4.2.3).

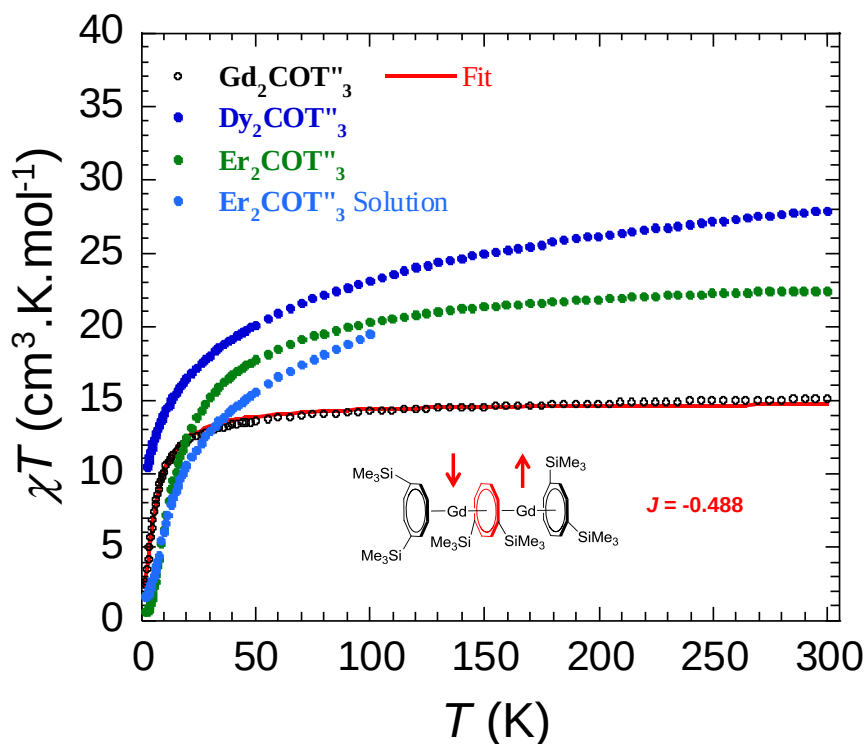


Figure 4.3. Temperature dependence of the χT product at 1000 Oe for $\text{Gd}_2\text{COT}^{2-}_3$, $\text{Dy}_2\text{COT}^{2-}_3$ and $\text{Er}_2\text{COT}^{2-}_3$, with χ being the molar susceptibility per dinuclear complex defined as M/H . The solid red line corresponds to the best fit for $\text{Gd}_2\text{COT}^{2-}_3$.

For $\text{Gd}_2\text{COT}^{2-}_3$, the χT product remains relatively constant down to 50 K and then decreases sharply at low temperature. Such behavior of the isotropic Gd^{III} system indicates the final decrease is primarily due to antiferromagnetic coupling between the metal centers. To quantify the strength of this interaction application of the van Vleck equation to the Kambe's vector coupling method¹⁵ was applied using the isotropic spin Hamiltonian $H = -JS_a \cdot S_b$ with $S_a = S_b = 7/2$, which was used to fit the variation of χT vs. T . The best-fit parameters obtained are $J = -0.448(1) \text{ cm}^{-1}$ and $g = 2.00(0)$. Although this J value is relatively small, it has been previously demonstrated that even much smaller coupling leads to significant effects on relaxation mechanisms.¹⁶ Moreover, it is important

to note that this value is larger than the obtained value of $-0.178(1) \text{ cm}^{-1}$ for a phenoxide bridged dinuclear Gd_2 complex with much shorter Gd-Gd distances ($3.82 \text{ \AA}$ vs. $4.21 \text{ \AA}$ for $\text{Gd}_2\text{COT}^{2-}_3$).^{16a} Fukuda and co-workers have demonstrated that solid state f-f interactions are non-negligible even at distances up to $6.8 \text{ \AA}$.¹⁷ Here the observed intermolecular $\text{Ln}^{\text{III}}\text{-Ln}^{\text{III}}$ distances of $9.034 \text{ \AA}$ (for $\text{Gd}_2\text{COT}^{2-}_3$), $9.197 \text{ \AA}$ (for $\text{Dy}_2\text{COT}^{2-}_3$) and $9.195 \text{ \AA}$ (for $\text{Er}_2\text{COT}^{2-}_3$) are much larger. Therefore, it is reasonable to assume the intramolecular antiferromagnetic interactions play a significant role in the negative deviation of the χT product for all three complexes. This illustrates that the interaction through the delocalized π cloud and the weak direct $\text{Ln}^{\text{III}}\text{-Ln}^{\text{III}}$ covalent interactions are significant.

To investigate the blocking of the magnetization, magnetic hysteresis measurements were performed between fields of 5 and -5 T. To directly compare the magnetic blocking of $\text{Er}_2\text{COT}^{2-}_3$ to ErCOT^{2-}_2 (Chapter 2) a sweep rate of 22 Oe.s^{-1} was employed, consistent with the monometallic complex (Figure 4.4).^{6d} $\text{Er}_2\text{COT}^{2-}_3$ displays clear hysteresis at 1.8 K with a coercivity at $M = 0 \text{ Oe}$. Interestingly, contrary to the monomer (Chapter 2), we do not observe a step in the hysteresis at $H = 0 \text{ Oe}$.^{6d} However, distinct steps appear at $\sim \pm 1500 \text{ Oe}$ most likely arising from an intramolecular antiferromagnetic interaction between Er^{III} ions.^{16b,17} Upon raising the temperature, clear coercivity at $H = 0 \text{ Oe}$ is observed up until 7 K and s-shaped hysteresis loops remain open until 12 K .^{7b} This signifies a 4 K increase in the magnetic blocking temperature in comparison to the mononuclear analog.^{6d} This substantial increase is surprising due to the antiferromagnetic nature of the Er-Er interaction as demonstrated in the χT plot. This is most likely due to the fact that the magnetic moments on the Er^{III} ions are not fully compensated as in the case of an antiferromagnetically coupled system. As a result, we observe the blocking of the small uncompensated magnetic moment.

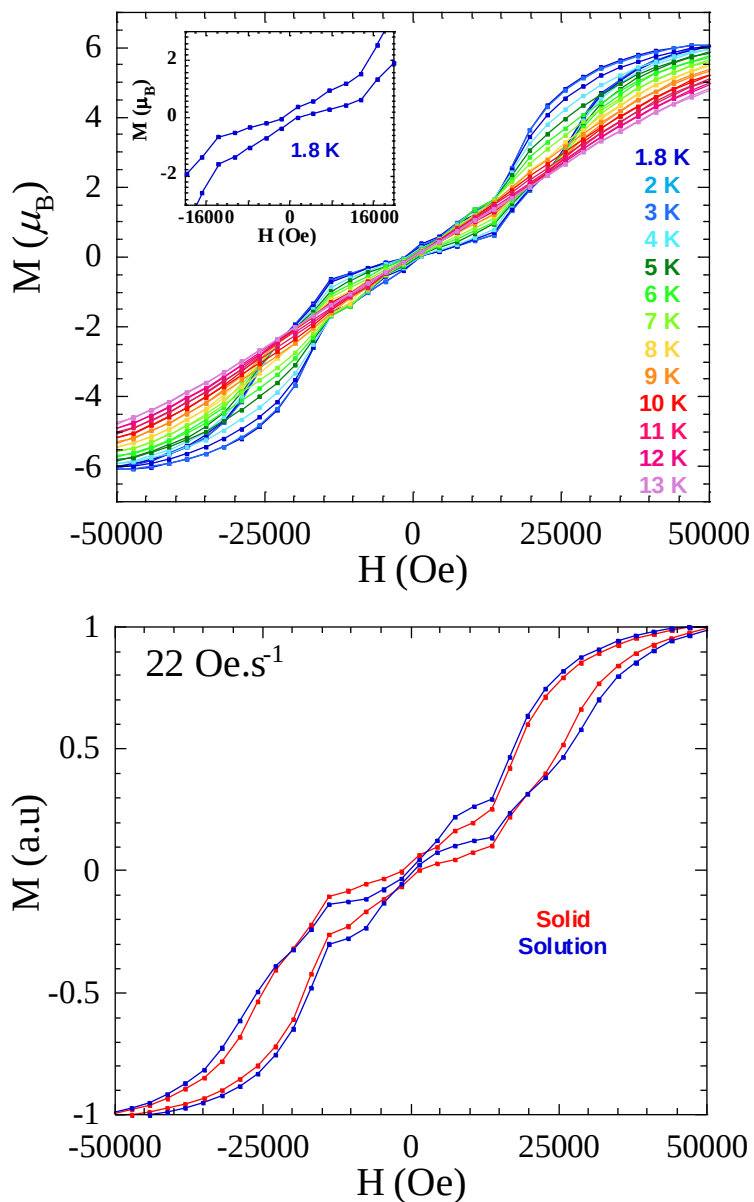


Figure 4.4. Top: Magnetic hysteresis of $\text{Er}_2\text{COT}''_3$ with an average sweep rate of 22 Oe.s^{-1} . Inset: Zoomed in hysteresis loop at 1.8 K for $\text{Er}_2\text{COT}''_3$. **Bottom:** Solid state magnetic hysteresis data for $\text{Er}_2\text{COT}''_3$ (●) and a 4 mM cyclopentane frozen solution of $\text{Er}_2\text{COT}''_3$ (●) at 1.8 K using an average sweep rate of 22 Oe.s^{-1} . Solid lines are guides for the eye.

To probe any intermolecular influence on the hysteresis of $\text{Er}_2\text{COT}''_3$, solution measurements were performed under identical conditions. At 1.8 K the hysteresis of $\text{Er}_2\text{COT}''_3$, measured as a bulk solid and in a 4 mM frozen solution of cyclopentane, show near identical behavior (Figure 4.4 bottom), therefore distinct steps at $\sim \pm 15 \text{ kOe}$ are molecular in origin and not the result of intramolecular interactions. Solution studies

reveal slight improvement in the hysteresis, where openings at $H \neq 0$ Oe are observed up until 14 K possibly due to the dilution of intermolecular antiferromagnetic interactions.^{7b} This high temperature for blocking of the magnetization clearly shows how highly anisotropic Er^{III} ions can exhibit remarkable performance when subjected to the appropriate crystal field.

4.3.2 Ac Magnetic Susceptibility

$\text{Dy}_2\text{COT}''_3$

In order to probe the SMM behavior of $\text{Dy}_2\text{COT}''_3$, both temperature and frequency dependent ac magnetic susceptibility measurements were carried out. Figure 4.5 depicts the frequency dependent studies under a zero static dc field from 2.5-9 K and plotted as χ'' vs. ν . Observation of shifting peak maxima under 5 K indicate SMM behavior. From the Arrhenius equation ($\tau = \tau_0 \exp(U_{\text{eff}}/kT)$), the calculated anisotropic barrier is $U_{\text{eff}} = 9$ K (6 cm^{-1}), $\tau_0 = 1.8 \times 10^{-5} \text{ s}$.

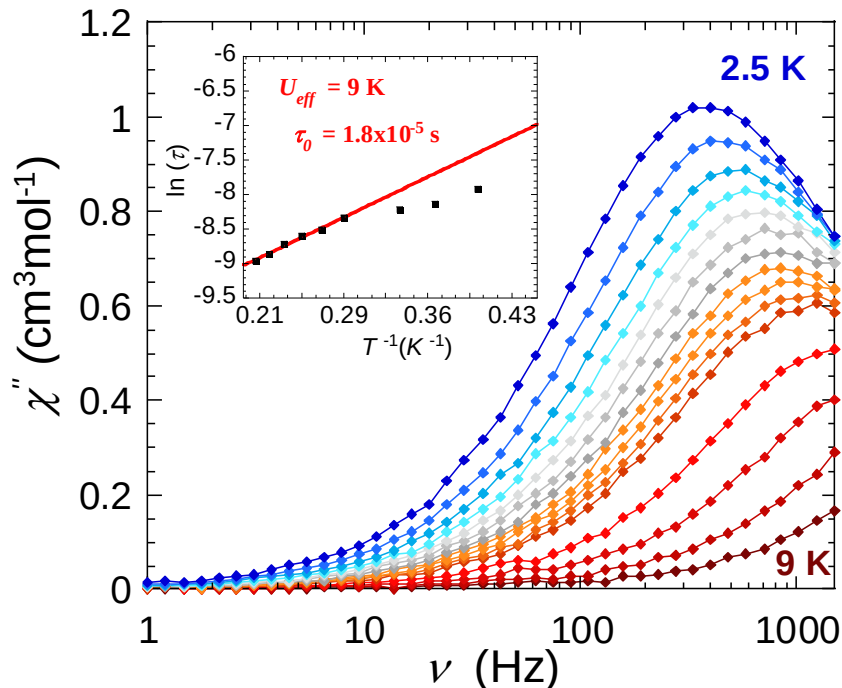


Figure 4.5. Frequency dependence of the out-of-phase (χ'') susceptibility of $\text{Dy}_2\text{COT}''_3$ at indicated temperatures under zero applied dc field. Insert: Plots of $\ln(\tau)$ vs. T for $\text{Dy}_2\text{COT}''_3$ at $H_{\text{dc}} = 0$ Oe. The solid lines represent the Arrhenius fit of the frequency-dependent data.

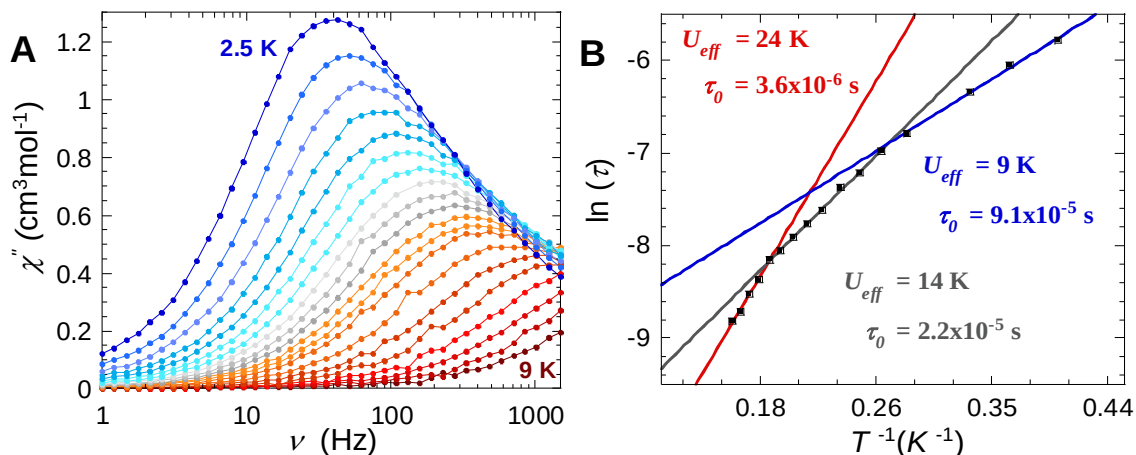


Figure 4.6. (A) Out-of-phase susceptibility (χ'') vs. frequency (ν) for $\text{Dy}_2\text{COT}''_3$ in the temperature range 2.5-9 K under an optimum applied dc field of 600 Oe. (B) Plots of $\ln(\tau)$ vs. T for $\text{Dy}_2\text{COT}''_3$ at $H_{\text{dc}} = 600$ Oe. The solid lines represent the Arrhenius fit of the frequency-dependent data.

Both the Arrhenius plot, and the broad peaks in the χ'' vs. T plot, suggests the presence of QTM in the zero-field dynamics of $\text{Dy}_2\text{COT}''_3$. As a result of applying an optimum static dc field of 600 Oe to reduce QTM, (Figure 4.6A) a frequency dependent out-of-phase (χ'') signal with shifting peak maxima towards higher temperatures is observed. The absence of overlapping peak maxima at low temperatures suggests the lack of a quantum regime, thus QTM is minimized upon application of the static dc field. In the χ'' vs. T plot, the occurrence of broad peaks spanning from 2.5-9 K above 500 Hz signals the possibility of frequency dependent multiple relaxation processes in $\text{Dy}_2\text{COT}''_3$. Figure 4.6B displays the three proposed relaxation mechanisms. From the Arrhenius equation, the calculated anisotropic barriers for the observed activated regimes are; **A:** $U_{\text{eff}} = 24 \text{ K}$, (17 cm^{-1} , $\tau_0 = 3.6 \times 10^{-6} \text{ s}$), **B:** $U_{\text{eff}} = 19 \text{ K}$, (14 cm^{-1} , $\tau_0 = 2.2 \times 10^{-5} \text{ s}$), and **C:** $U_{\text{eff}} = 9 \text{ K}$, (6 cm^{-1} , $\tau_0 = 9.1 \times 10^{-5} \text{ s}$). The unsaturated curve confirms the reduction of QTM in $\text{Dy}_2\text{COT}''_3$ under the applied optimum dc field. The presence of multiple relaxation barriers was further explored using a graphical representation, χ' vs. χ'' (Cole-Cole plot), calculated using the generalized Debye model¹⁸ in a temperature range of 2.5-5.5 K (Figure 4.7). Unsymmetrical semi-circles were poorly fit with α values ranging from 0.04-0.35, indicating high amounts of disorder and relaxation times not unique to a single relaxation mechanism.

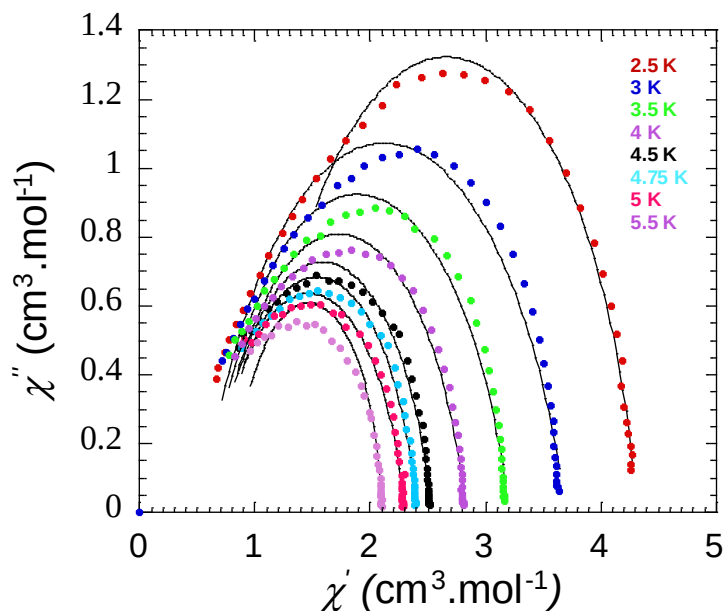


Figure 4.7. Cole-Cole plot for **Dy₂COT''₃** under 600 Oe applied dc field. Experimental data points are represented by circles and the solid black line represents the attempted fit to the data.

As was previously demonstrated from the magnetic studies of the mononuclear precursor building block unit, **DyCOT''₂**, multiple relaxation modes can exist for a mononuclear system, therefore it is not surprising that the relaxation dynamics of **Dy₂COT''₃** are not unique to a single relaxation mechanism. Hence, coupling two SIM units through a central COT'' ligand in order to create an SMM further promotes the overlap of several relaxation pathways; thus the observed complex magnetic features are expected.

Er₂COT''₃

Ac magnetic susceptibility measurements were performed to gain insight into the relaxation dynamics of **Er₂COT''₃**. Temperature and frequency dependent out-of-phase (χ'') magnetic susceptibility signals were observed under 0 Oe applied dc field (Figures 4.8A). For **Er₂COT''₃** a frequency dependent χ'' signal was observed from 26-14 K with shifting peak maxima towards lower temperatures, indicating SMM behavior. This relaxation data fits well to the Arrhenius equation to yield an effective energy barrier (U_{eff}) of 323 K (231 cm⁻¹), with a pre-exponential factor of $\tau_0 = 5.7 \times 10^{-10}$ s (Figure 4.8B). It is noteworthy that the energy barrier for **Er₂COT''₃** is among the highest reported for

an SMM^{1,2} but also that, it is significantly higher than the 187(1) K (134 cm⁻¹) barrier observed in **ErCOT**"₂^{6d} (Chapter 2). When the Arrhenius data was extrapolated to low temperature, the relaxation time was 100s at 12.5 K. Solution studies of **Er₂COT**"₃ show slightly enhanced ac susceptibility dynamics, consistent with dc measurements, with an effective energy barrier of 335(13) K (239 cm⁻¹) with a $\tau_0 = 1.9 \times 10^{-10}$ s.^{7b}

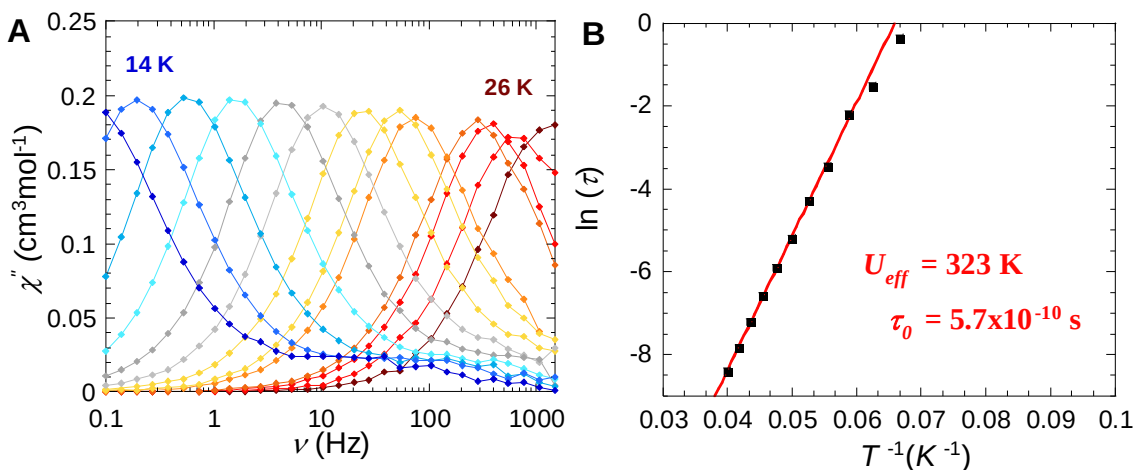


Figure 4.8. (A) Out-of phase magnetic susceptibility of **Er₂COT**"₃ under a zero applied dc field between indicated temperatures. (B) Solid-state relaxation time of the magnetization $\ln(\tau)$ vs. T^{-1} for **Er₂COT**"₃ (Arrhenius plot using ac data) under 0 Oe applied field. The solid line corresponds to the fit.

4.3.3 Magnetic Properties Explained through CASSCF Calculations¹⁹

Dy₂COT"₃

To probe the magnetic anisotropic axes of **Dy₂COT**"₃ the low-lying electronic levels (Kramers doublets) on the Dy^{III} sites have been investigated using *ab initio* calculations with the MOLCAS7.6 package²⁰ in different structural and basis set approximations.¹⁹ The energies of the eight Kramers doublets arising from the $J = 15/2$ atomic ground multiplet of Dy^{III} are given in Table 4.3. The calculation of the magnetic properties of each Kramers doublet have been done with SINGLE_ANISO module.²¹ The results for the main values of the obtained g tensors are given in Table 4.3. The directions of the main magnetic axes on the Dy^{III} sites of **Dy₂COT**"₃ are shown in Figure 4.9A. We can see in **Dy₂COT**"₃ that the directions of the local magnetic axes are far from the axis

connecting the two dysprosium ions. This provides evidence for the strong effects the distant silyl groups have on the direction of the anisotropy axis. This is in line with the direction of the anisotropic axis observed in **DyCOT**²⁻₂ as well as in previous findings, where the second coordination sphere had a direct impact on the magnetic anisotropy of highly anisotropic metal ions in Co^{II} and Dy^{III} complexes.^{22,23} For comparison, similar calculations for the symmetrized structure of **Dy₂COT**²⁻₃ were carried out, where the silyl groups were replaced by hydrogen and the Dy^{III}-C groups for each COT²⁻ were averaged to one distance so as to have the overall symmetry C_{8h} at each Dy^{III} site (Figure 4.9B). The results for the lowest eight Kramers doublets on each Dy^{III} are shown in Table 4.3. We can see that the ground state g_z roughly corresponds to $J = 9/2$, in contrary to the case of real geometry, where g_z is closer to $J = 15/2$ (as was found in many other low symmetry Dy^{III} complexes).²⁰ On the other hand the main magnetic axis on each Dy^{III} ion is now directed along the symmetry axis of the complex.

In order to get more insight into the obtained spectrum of crystal field levels on each Dy^{III} site, the calculated crystal field parameters describing the splitting of the $J = 15/2$ ground atomic multiplet with SINGLE_ANISO module of MOLCAS were calculated. Results indicate that all B_n^0 parameters are positive which means that the equatorial component of the ligand field is stronger than the axial one.¹⁹ This will lead to the stabilization of the lowest possible momentum projection ($m = \pm 1/2$) if all $B_n^m = 0$ for $m \neq 0$, because it corresponds to a prolate distribution of $4f$ electron charge density in the case of Dy^{III}.²⁴ In our case, however, all 27 B_n^m parameters are nonzero because of the lack of rotational symmetry around the chosen quantization axis (Figure 4.9A). As a result the lowest Kramers doublet on Dy^{III} sites will correspond to a combination of several projections m . On the other hand, the predominant equatorial ligand field of the two COT²⁻ ligands will strongly destabilize the doublet with highest moment $J = \pm 15/2$, because it corresponds to an oblate charge density distribution in Dy^{III}.²⁴ This is confirmed by our *ab initio* calculations (Table 4.3).

Table 4.3. The energies of the eight Kramers doublets arising from the $J = 15/2$ atomic ground multiplet of individual Dy(III) ions in **Dy₂COT₃**.

KD	A1		A2		B1		B2		C1		C2	
	<i>E</i> (cm ⁻¹)	<i>g</i>	<i>E</i> (cm ⁻¹)	<i>g</i>	<i>E</i> (cm ⁻¹)	<i>g</i>	<i>E</i> (cm ⁻¹)	<i>g</i>	<i>E</i> (cm ⁻¹)	<i>g</i>	<i>E</i> (cm ⁻¹)	<i>g</i>
1	gx		0.030		0.367		0.020		0.216		0.046	
	gy	0.000	0.058	0.000	0.445	0.000	0.057	0.000	0.271	0.000	0.080	0.000
	gz		19.74		19.00		19.70		18.61		19.64	
2	gx		0.151		1.890		0.385		2.009		0.609	
	gy	41.15	0.220	25.31	2.751	31.72	0.576	30.40	2.678	30.92	0.883	34.07
	gz		16.93		16.58		16.83		16.38		16.84	
3	gx		1.014		10.74		1.727		0.373		1.971	
	gy	82.29	1.860	52.96	6.289	71.36	3.685	55.76	4.625	69.40	4.457	58.28
	gz		13.77		0.860		13.28		10.71		12.96	
4	gx		3.055		6.960		2.611		4.349		2.252	
	gy	109.1	6.887	87.83	5.891	101.8	6.720	85.72	6.082	102.1	6.500	89.68
	gz		11.23		0.081		11.86		8.872		11.75	
5	gx		0.867		2.287		0.733		0.909		0.794	
	gy	125.4	1.232	102.4	5.123	121.3	1.008	105.4	1.747	124.7	0.936	110.1
	gz		15.57		11.83		17.38		15.46		16.92	
6	gx		0.183		0.181		0.325		0.098		0.462	
	gy	180.2	0.256	126.1	0.360	155.9	0.493	134.4	0.267	147.8	0.871	138.8
	gz		14.33		19.29		14.15		19.19		13.97	
7	gx		0.001		0.004		0.002		0.008		0.002	
	gy	423.6	0.001	302.0	0.005	385.8	0.003	282.5	0.009	370.1	0.002	286.5
	gz		17.43		17.41		17.42		17.39		17.41	
8	gx		0.000		0.000		0.000		0.000		0.000	
	gy	1126	0.000	951.1	0.000	1059.6	0.000	903.1	0.000	1036	0.000	909.2
	gz		19.89		19.89		19.89		19.89		19.89	

For the directions of local anisotropy axes, as shown in Figure 4.9, and for the calculated *g* factors (Table 4.3) the dipolar interaction between magnetic moments on Dy^{III} is rather weak, albeit antiferromagnetic. The calculated splitting of the exchange doublets in **Dy₂COT₃** due to this interaction only amounts to 1.3 cm⁻¹. This means that the main contribution to the magnetic interaction between Dy^{III} ions comes from an anisotropic exchange interaction, which is expected to be relatively large on the basis of DFT calculations discussed above.

We may conclude that for **Dy₂COT₃** the obtained large magnetic moment on the Dy^{III} ions in the ground state is due to the low symmetry environment. The analysis of the magnetic anisotropy of local Kramers doublets shows that the highest one is very axial.

This suggests that a replacement of Dy^{III} by Er^{III} in $\text{Dy}_2\text{COT}^{2-}_3$ might result in enhanced magnetic properties of the complex (as previously established in section 4.3.1).

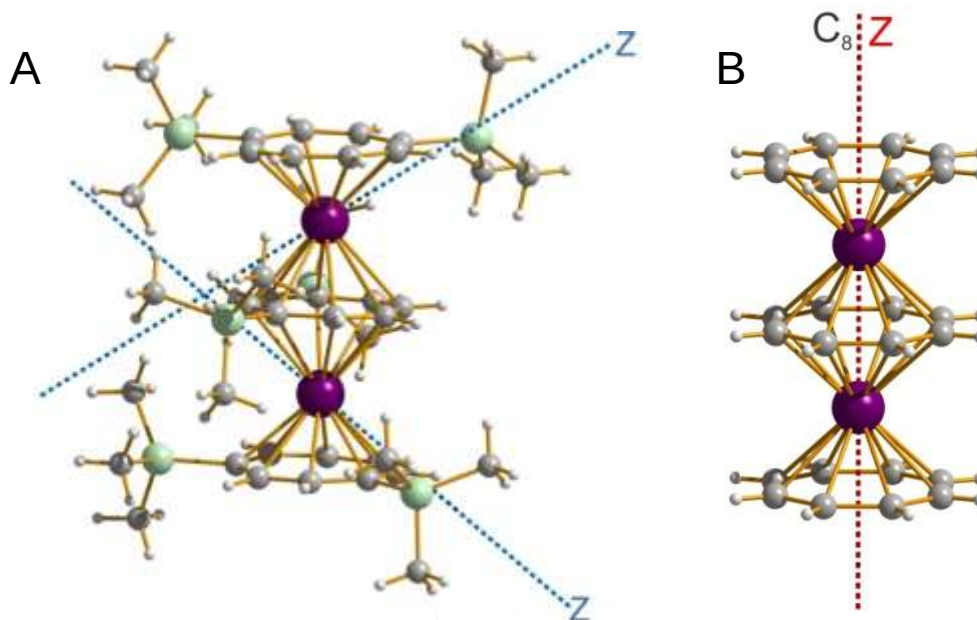


Figure 4.9. Orientation of the main magnetic axes of the ground Kramers doublets on Dy^{III} centers of (A) $\text{Dy}_2\text{COT}^{2-}_3$; (B) the symmetrized $\text{Dy}_2(\text{COT})_3$ complex.

$\text{Er}_2\text{COT}^{2-}_3$

Ab initio calculations of CASSCF/RASSI/SINGLE_ANISO type^{21b,25} reveal that the ground and first excited Kramers doublets on all Er^{III} sites in $\text{Er}_2\text{COT}^{2-}_3$ are significantly magnetically axial, similar to what was found in the ErCOT^{2-}_2 monomer (Chapter 2). The reason for strong magnetic axiality in Er^{III} ions^{1a} is the negative sign of the main crystal field parameters B_2^0 and B_4^0 , which leads to the stabilization of the Kramers doublet $|\pm 15/2\rangle$, with the projection of angular momentum on the symmetry axis of the $[\text{Er}(\text{COT})_2]^-$ unit in the ground state. Moreover, the main magnetic axis of the first excited Kramers doublet is almost parallel to the main magnetic axis of the ground state. These axes at different Er^{III} sites are almost parallel to each other (Figure 4.10) which implies a ferromagnetic dipole-dipole interaction between the magnetic moments of these sites (Figure 4.10B).

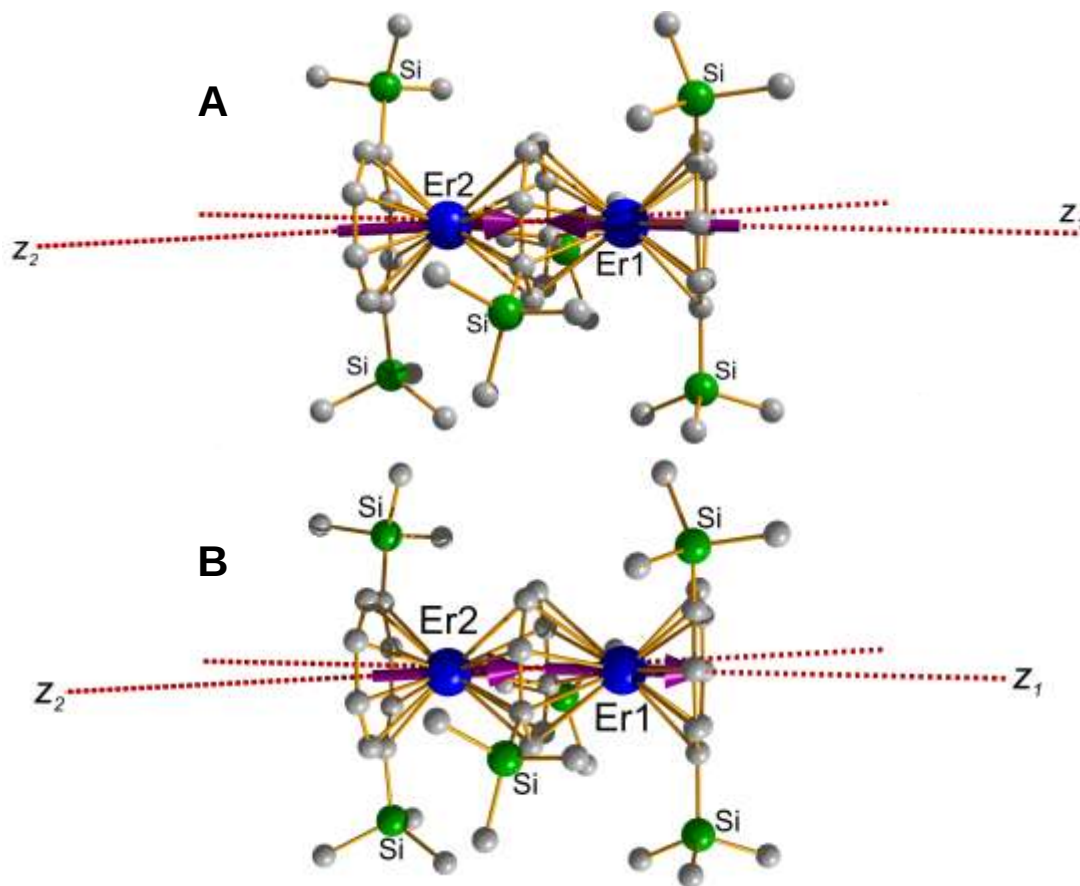


Figure 4.10. (A) Red dashed lines represent the main magnetic axes of the ground Kramers doublets on Er^{III} ions in $\text{Er}_2\text{COT}^{3-}$. Purple arrows show the strong antiferromagnetic coupling of the Er^{III} ions in $\text{Er}_2\text{COT}^{3-}$. (B) Orientations of local magnetic moments on both Er^{III} ions in the ground exchange doublet state of $\text{Er}_2\text{COT}^{3-}$ when only the intramolecular dipole-dipole interaction is considered.

Broken Symmetry-DFT calculations for $\text{Er}_2\text{COT}^{3-}$ reveal a strong antiferromagnetic exchange interaction between Er^{III} sites, significantly overcoming the ferromagnetic dipolar interaction (Figure 4.10). The calculations testify that the obtained strong antiferromagnetic coupling between Er^{III} ions in $\text{Er}_2\text{COT}^{3-}$ is promoted effectively by the delocalized π_z orbitals of the central COT^{2-} ligand. In fact, due to the non-collinearity of the main magnetic axes of Er^{III} ions in $\text{Er}_2\text{COT}^{3-}$ (the relative angle $\approx 4.2^\circ$), the ground exchange doublet has a small magnetic moment of *ca.* $0.62 \mu_B$. This is in agreement with the small slope of the magnetization curve at fields below 1.5 T (Figures 4.4). The first excited exchange doublet corresponds to ferromagnetic coupling of the magnetic moments, having a large value of the magnetic moment of *ca.* $17.94 \mu_B$. The

clear step on the magnetization curve, seen at *ca.* 1.5 T, is due to level crossing of the ground and first excited exchange state (Figure 4.11). We notice that the hysteresis is significantly enlarged in this region (Figure 4.4). Since both the ground and excited exchange doublets in **Er₂COT''₃** can efficiently block the magnetization, the hysteresis loops display distinct regions corresponding to each of them being in the ground state (Figure 4.4).

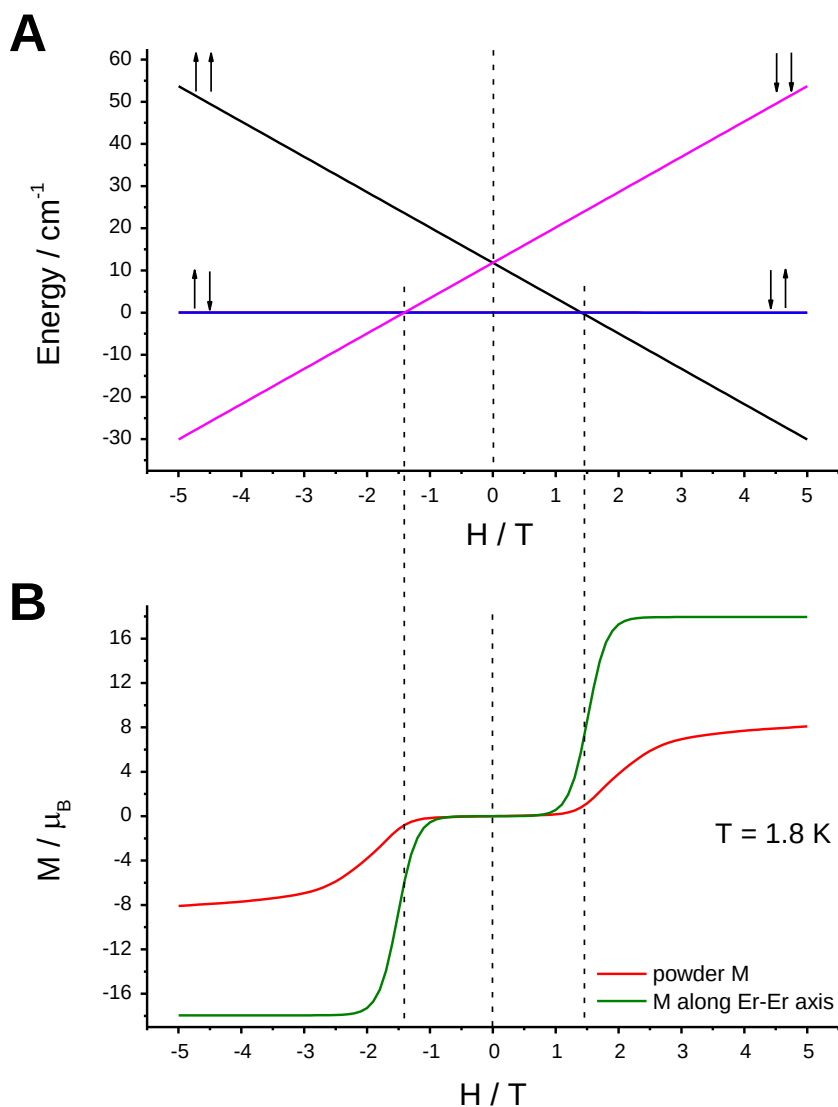


Figure 4.11. Evolution of low-lying exchange energy states in **Er₂COT''₃** in an applied magnetic field along the Er-Er axis. At fields ≈ 1.5 T the excited state holding the largest magnetic moment becomes the ground state, causing a steep rise of the molar magnetization (**B**) (Figure 4.4).

4.4 Conclusions

A unique organometallic building block approach was successfully employed to create three dinuclear triple-decker lanthanide complexes. The use of planar COT²⁻ ligands allow for access to a new coordination environment that provides a unique ligand field around the spin carrier. As such, the isolated complexes **Dy₂COT²⁻₃** and **Er₂COT²⁻₃** behave as SMMs in a distinctive ligand system. The analogous isotropic complex **Gd₂COT²⁻₃** provides further evidence of the strength and nature of intramolecular coupling in the dinuclear triple-decker complexes. In contrast to typical lanthanide complexes with weak metal-ligand covalency, the electronic structure analysis of the Dy^{III} complex demonstrates high metal-ligand covalency. This methodology promotes a delocalized superexchange pathway for magnetic interactions. Evidence of a non-negligible superexchange interaction *via* the central COT²⁻ ligand was observed through magnetic measurements as well as through DFT calculations. Surprisingly, a weak direct Dy^{III}-Dy^{III} covalent interaction is also observed. In addition, *ab initio* calculations reveal the importance of the second coordination sphere on the magnetic properties of **Dy₂COT²⁻₃**. TMS groups on the COT²⁻ ligands significantly influence the orientation of the magnetic axis, while absence of these groups led to the perfect alignment of the anisotropy axis along the idealized C₈ axis of **Dy₂COT²⁻₃**.

As predicted via *ab initio* calculation, **Er₂COT²⁻₃** exhibits a remarkably large blocking temperatures and displays magnetic hysteresis up to 12 K. Frozen solution measurements reveal slight improvement in the hysteresis, where openings at H ≠ 0 are observed up until 14 K. Such magnetic performance has never been observed in any non-radical based SMMs. **Er₂COT²⁻₃** shows an increase in magnetic blocking properties compared to the mononuclear precursor (**ErCOT²⁻₂**). The increase in the SMM properties of **Er₂COT²⁻₃** is due to the additional blocking mechanism coming from the exchange interaction between the Er^{III} sites.

The use of an aromatic bridging COT²⁻ ring provides a non-negligible Ln^{III}-Ln^{III} superexchange interaction in **Dy₂COT²⁻₃** and **Er₂COT²⁻₃**. Therefore, coupling spin sources while maintaining a similar crystal field around each spin carrier resulted in an increased

blocking temperature in **Er₂COT''₃**. The 4 K increase in the magnetic blocking of **Er₂COT''₃** over **ErCOT''₂** may have significant implications in the field of molecular magnetism if this building block methodology can be extended to create larger multideck Er^{III}-COT complexes or 1-D chains. Such complexes would take advantage of higher nuclearity, therefore increasing blocking temperature *via* increasing the total spin of the complex.

4.5 Experimental

General Considerations. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware was oven dried (120°C, 6h) before use. Hexanes, cyclopentane, toluene and tetrahydrofuran (THF) were dried using activated alumina and stored over 3Å molecular sieves. All chemicals were purchased from Thermofisher Scientific or Strem and used without further purification. The [Li₄(COT'')₂(THF)₄]^{6a} was synthesized using a previously published procedure. IR data were collected on a Varian 640 FT-IR spectrometer. ¹H spectra were recorded on a 300 MHz Bruker Advance spectrometer at room temperature (21-23 °C). Toluene-d₈ was dried using activated alumina and 3Å molecular sieves.

Dy₂COT''₃. In a 20 mL scintillation vial [DyCOT''₂]₂Li(THF)₄^{6a} (0.200 g, 0.195 mmol) and CoCl₂ (0.013 g, 0.0976 mmol) were refluxed in 5 mL toluene for 5 h. Co⁰ was filtered off as a black precipitate. The remaining solution was concentrated down to an amber oil where large block crystals of **Dy₂COT''₃** were grown by the addition of cyclopentane at -35°C with 25% yield. Individual block crystals were picked out of the oil and washed thoroughly with cold cyclopentane. Isolated crystals are extremely air sensitive. CCDC: 938031. Elemental analysis, Calcd.(%) for C₄₂H₇₂Dy₂Si₆: C 47.12, H 6.78 Found (%) C 47.35, H 6.70. Selected IR data for **2** (cm⁻¹): 2999 (w), 2957 (br), 2900 (m) 1450 (br), 1403 (w), 1247 (s), 1049 (m), 978 (w), 933 (w), 837 (s), 748 (m), 721 (w), 688 (w), 634 (w).

Er₂COT''₃. As described above [ErCOT''₂]*Li*(THF)₄ (0.200 g, 0.194 mmol) and CoCl₂ (0.013 g, 0.097 mmol) were refluxed in 5 mL toluene for 5 h. Co⁰ was filtered off as a black precipitate using a fine fritted funnel. The remaining solution was concentrated down to an amber oil where large block crystals of **Er₂COT''₃** were grown by the addition of 0.5 mL of cyclopentane at -35°C with 20% yield. Individual block crystals were picked out of the oil and recrystallized from cyclopentane. Isolated crystals are air and moisture sensitive. CCDC: 974992. Selected IR data (cm⁻¹): 2999 (w), 2957 (br), 2900 (m), 1450 (br), 1403 (w), 1247 (s), 1049 (m), 978 (w), 933 (w), 837 (s), 748 (m), 721 (w), 688 (w), 634 (w). ¹H NMR (300 MHz, toluene-d₈): δ 7.12 (br s), 7.04 (br s), 7.00 (br s), 2.11 (br s), 0.11 (br s) ppm. UV – vis (0.3 mM cyclopentane): λ max (ε) = 273(1.035).

Gd₂COT''₃. As described above, [GdCOT''₂]*Li*(THF)₄ (0.167 g, 0.164 mmol) and CoCl₂ (0.011 g, 0.0819 mmol) in 5 mL of toluene was stirred for 24 h, and refluxed for an additional 5 h. Co⁰ was filtered off as a black precipitate. The remaining solution was concentrated down to an amber oil where large orange block crystals were grown by the addition of cyclopentane at -35°C with 30% yield. Block crystals were removed and washed thoroughly with cold cyclopentane. Isolated crystals are extremely air sensitive. CCDC: 863405. Elemental analysis, Calcd.(%) for C 47.59, H 6.85 Found: (%) C 47.31 H 6.52. Selected IR data (cm⁻¹): 3031 (w), 2967 (br), 2895 (m), 1459 (br), 1400 (m), 1247(s), 1052 (s), 983 (m), 936 (w), 837 (br), 753 (w), 726 (w), 681 (w), 638 (m).

X-ray Crystallography. For all complexes a suitable prism-shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).²⁶ The crystal structures were solved and refined using the SHELXTL²⁷ program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom

positions were calculated geometrically and were riding on their respective atoms. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre.

Magnetic Measurements. The magnetic analyses were performed on crushed polycrystalline samples wrapped in a polyethylene membrane sealed in a glove box to prevent any sample degradation. The dc magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetization data were collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

Table 4.4. Unit cell parameters for $\text{Gd}_2\text{COT''}_3$, $\text{Dy}_2\text{COT''}_3$ and $\text{Er}_2\text{COT''}_3$.

	$\text{Gd}_2\text{COT''}_3$	$\text{Dy}_2\text{COT''}_3$	$\text{Er}_2\text{COT''}_3$
M_r (g/mol)	1060.04	1070.54	1080.06
Formula	$\text{Gd}_2\text{C}_{42}\text{H}_{72}\text{Si}_6$	$\text{Dy}_2\text{C}_{42}\text{H}_{72}\text{Si}_6$	$\text{Er}_2\text{C}_{42}\text{H}_{72}\text{Si}_6$
T(K)	200(2)	200(2)	200(2)
γ (Å)	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	tetragonal
Space group	I -4	I-4	I-4
a (Å)	16.9774(4)	16.898(3)	16.8620(4)
b (Å)	16.9774(4)	16.898(3)	16.8620(4)
c (Å)	20.0097(6)	20.269(4)	20.2149(5)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00
V (Å³)	5767.44(26)	5787.5(18)	5747.6(3)
ρ_{calc} (cm⁻³)	1.221	1.229	1.248
Z	4	4	4
Reflections collected	42421	42231	28967
$R(\text{int})$	7120, 0.0170	7115, 0.0396	7058, 0.0309
$R1$	0.0256	0.0324	0.0277
$wR2$	0.0755	0.0827	0.0630
Reflections with $I > 2\sigma(I)$	6978	6488	6433

4.6 References and Notes

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Chapter 5

Magnetic Exchange Coupling in Potassium Bridged Lanthanide - Cyclooctatetraenyl Sandwich Compounds*

Partial contents of this chapter have been published in: J. J. Le Roy, L. Ungur, I. Korobkov, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. **2014, 136, 8003.*

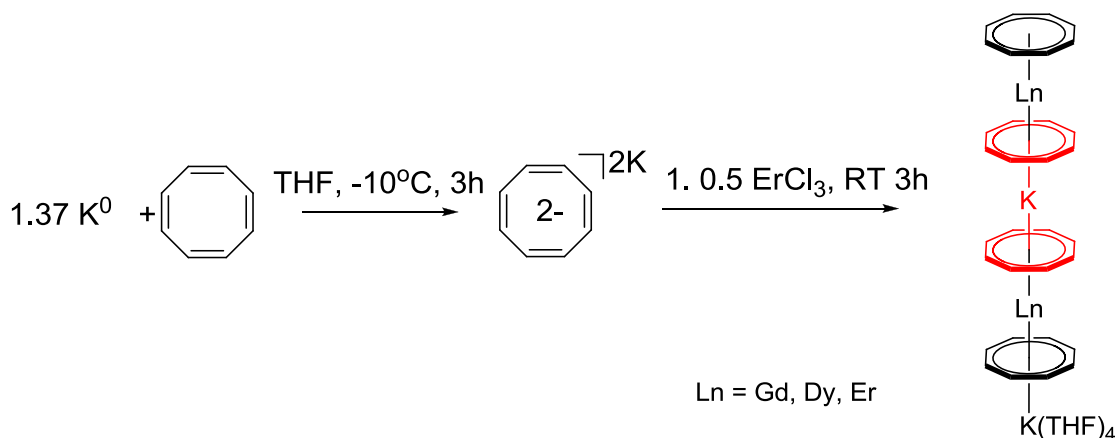
This Chapter extends the discussion of multi-decker lanthanide-COT complexes to include potassium-bridged $\text{Ln}^{\text{III}}\text{COT}_2$ dimers. The synthesis, structure and magnetic properties of three quadruple-decker COT complexes with the formula $\text{K}_2(\text{THF})_4[\text{Ln}^{\text{III}}_2(\text{COT})_4]$ ($\text{Ln} = \text{Gd}$ (**Gd₂K₂COT₄**), Dy (**Dy₂K₂COT₄**), Er (**Er₂K₂COT₄**), $\text{COT} = \text{cyclooctatetraenyl dianion}$, $\text{THF} = \text{tetrahydrofuran}$) are discussed. Both Er^{III} and Dy^{III} dimers display enhanced SMM properties over their mononuclear analogues **ErCOT₂** and **DyCOT₂** (described in Chapter 3). The Er^{III} complex behaves as an SMM and exhibits magnetic hysteresis at 12 K in the solid state. *Ab initio* calculations confirm that this 2 K increase in T_B over the mononuclear **ErCOT₂** is due to single-ion effects such as enhanced symmetry, and is not the result of exchange coupling.

5.1 Introduction

In Chapter 3, we discussed the properties that make **ErCOT₂**, among the highest T_B SIMs to date. Unfortunately 10 K is still way too low for practical applications therefore we turn towards trying to increase the T_B of COT based magnets by increasing the total spin of the molecule. As demonstrated in Chapter 5, an efficient way to increase the spin ground state of $\text{Ln}^{\text{III}}\text{COT}_2$ -type SIMs while maintaining strictly axial anisotropy is through a linear stacking arrangement.¹ Herein we present the synthesis, structure and magnetic properties of three Ln^{III} -COT quadruple-decker complexes, each consisting of two LnCOT_2 unit bridged by an alkali metal. The magnetic properties of **Er₂K₂COT₄** is carefully compared to **Er₂COT**³ (Chapter 4) to help evaluate this new coupling strategy.

5.2 Results and Discussion

5.2.1 Synthesis of Quadruple-Decker Lanthanide-COT Complexes



Scheme 1. Synthetic route to **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄**, with the Ln-Ln magnetic exchange pathway highlighted in red.

The preparation of potassium bridged Lanthanide-COT sandwich complexes was previously reported by Chen in 1991 using a 2 step procedure where (PhCH₂C₅H₄)ErCl₃·3THF is first prepared from the reaction of ErCl₃ and PhCH₂C₅H₄, and then is added to freshly prepared K₂COT.² In contrast **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄** were isolated using a direct method and commercially available precursors.¹ For all complexes, freshly cut K⁰ was added to COT to give K₂COT in a THF solution, the appropriate LnCl₃ was next added in-situ at -37 C°. X-ray quality single crystals were grown in a concentrated THF solution at -37 C° after 4 days. The isolated crystals are air and moisture sensitive.

5.2.2 Solid State Structures

Complexes **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄** are isostructural, and each crystallize in a triclinic *P*-1 space group. Table 5.1 and 5.3 contain the structural details and refinement parameters of all complexes. For simplicity, the molecular structure of **Er₂K₂COT₄** will be discussed in detail. Complex **Er₂K₂COT₄** has a tetra-layer sandwich architecture, comprised of two [Er^{III}COT₂]⁻ units bridged by a K ion bound η⁸ to both

units. An additional $\text{K}(\text{THF})_4$ counter cation is bound η^8 through the K to one COT ring as reflected in the average $\text{K1-COT}(d)$ distance of 3.20 Å. The near linear structure of $\text{Er}_2\text{K}_2\text{COT}_4$ is illustrated by Er2-K2-Er1 and K2-Er1-K1 angles of 169.57° and 179.35° respectively. The Er-Er distance of 8.82 Å is significantly longer than in $\text{Er}_2\text{COT}''_2$ (4.11 Å, Chapter 4). Uneven charge donation is apparent in Er2 (Er1-C_{COT} average distance for decks *a* and *b* is 2.58 and 2.66 Å respectively) but not Er1 (Er2-C_{COT} average distance for decks *a* and *b* is 2.61 Å), most likely due to uneven ligand donation as described for $\text{Er}_2\text{COT}''_2$ (Chapter 4).

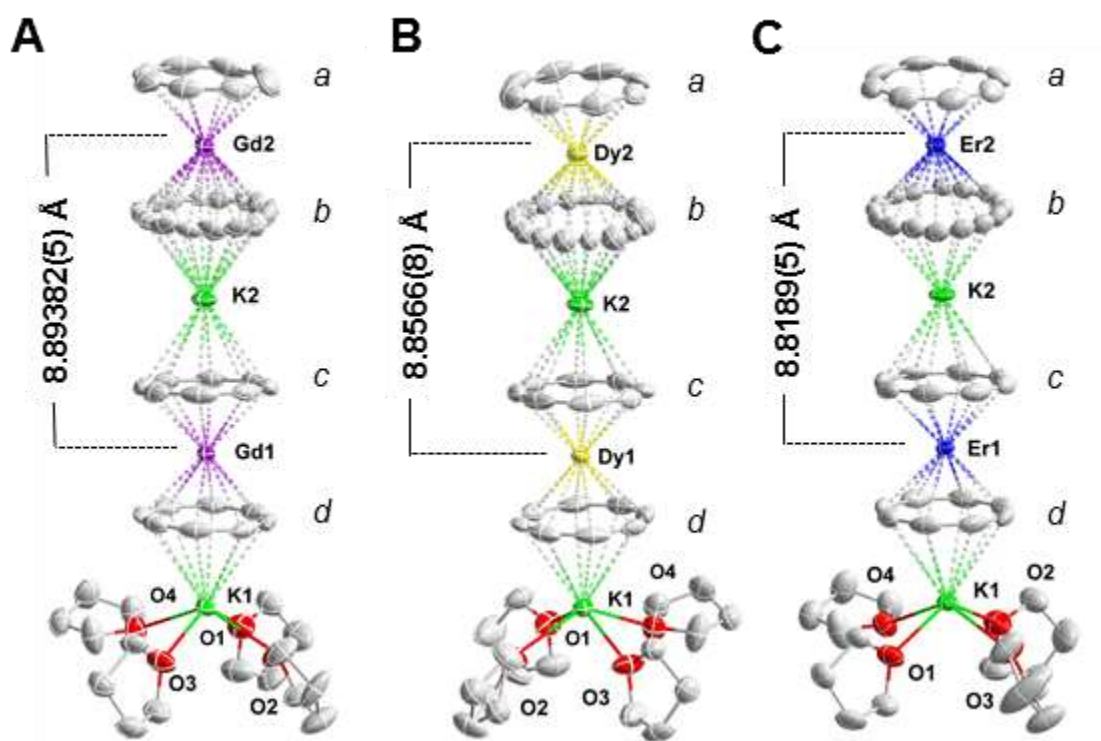


Figure 5.1. Structure of $\text{Gd}_2\text{K}_2\text{COT}_2$ (A), $\text{Dy}_2\text{K}_2\text{COT}_2$ (B) and $\text{Er}_2\text{K}_2\text{COT}_2$ (C). H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), light green (K), red (O), purple (Gd^{III}), yellow (Dy^{III}), blue (Er^{III}).

Table 5.1. Selected interatomic distances of **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄**.

	Gd₂K₂COT₄	Dy₂K₂COT₄	Er₂K₂COT₄
Intramolecular Ln-Ln (Å)	8.929	8.557	8.819
Ln2-K2-Ln1 (°)	169.6	169.6	169.6
K2-Ln1-K1 (°)	178.83	179.2	179.3
Tilt angle deck A and B	1.97	1.39	1.50
Tilt angle deck C and D	2.78	2.48	1.82
Ave. Ln2-C_{COT(a)} (Å)	2.628	2.609	2.580
Ave. Ln2-C_{COT(b)} (Å)	2.704	2.676	2.570
Ave. K2-C_{COT(b)} (Å)	3.101	3.103	3.091
Ave. K2-C_{COT(c)} (Å)	3.130	3.128	3.129
Ave. Ln1-C_{COT(c)} (Å)	2.663	2.635	2.605
Ave. Ln1-C_{COT(d)} (Å)	2.262	2.623	2.605
Ave. K1-C_{COT(d)} (Å)	3.314	3.198	3.203
Nearest Intermolecular Ln-Ln (Å)	7.126	7.402	7.193

5.2.3 Magnetic Properties

Direct Current (dc) Magnetic Susceptibility

The magnetic susceptibility of **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄** was measured using a SQUID magnetometer on freshly prepared polycrystalline samples of each complex sealed under nitrogen to prevent sample degradation. Dc magnetic susceptibility measurements were conducted in the temperature range of 1.8-300 K under a 0.1 T applied dc field (Figure 5.2). The room temperature χT values of **Dy₂K₂COT₄** and **Er₂K₂COT₄** are in good agreement with theoretical values for 2 non-interacting Dy^{III} (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$) and Er^{III} (⁴I_{15/2}, $S = 3/2$, $L = 6$, $g = 6/5$) ions respectively (Table 5.2). For **Dy₂K₂COT₄**, upon decrease of the temperature, the χT product remains fairly constant from 300 K to 150 K and below which, a gradual decrease can be seen. A further sharp decrease can be observed below 50 K to reach a minimum value of 10.42 cm³K·mol⁻¹ at 1.8 K. Such negative deviation of the χT product can arise from a combination of several factors such as intramolecular antiferromagnetic interactions, depopulation of the excited states, crystal field effects with significant magnetic anisotropy and/or intermolecular interactions.³ Similar behavior is observed in the temperature-dependent χT product of **Er₂K₂COT₄**, where fairly linear behaviour is observed from 300 K to 20 K, with a sharp decrease below 20 K to reach a minimum

value of $12.05 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$ at 1.8 K. In both **Dy₂K₂COT₄** and **Er₂K₂COT₄** complexes, the χT behavior is reminiscent of the highly anisotropic **DyCOT₂** and **ErCOT₂** monomers discussed in Chapter 3. In both of these complexes, it is reasonable to assume that intramolecular interactions are weak due to the large Ln-Ln separation (Ln-Ln distance of 8.56 Å (**Dy₂K₂COT₄**), 8.82 Å (**Er₂K₂COT₄**)). Due to the highly anisotropic nature of Dy^{III} and Er^{III} ions it is not possible to quantify the coupling strength by fitting the susceptibility data through Kambe's coupling method. Therefore, to approximate the strength of the Ln^{III}-Ln^{III} interactions in these systems **Gd₂K₂COT₄** was synthesized and analyzed to provide an ideal isotropic model.

The room temperature χT value of $15.79 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$ for **Gd₂K₂COT₄**, is in good agreement with the theoretical value of $15.76 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$ for two non-interacting Gd^{III} (⁸S_{7/2}, $S = 7/2$, $L = 0$, $g = 2$) ions. Upon decreasing the temperature the χT product remains constant with a slight decrease below 10 K to reach a minimum value of $14.30 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$ at 1.8 K. The low temperature decrease is primarily due to intramolecular anti-ferromagnetic coupling between isotropic Gd^{III} ions. To quantify the strength of Gd^{III}-Gd^{III} interaction, application of the Van Vleck equation to the Kambe's vector coupling method was calculated using the isotropic spin Hamiltonian $H = -J S_a \cdot S_b$ with $S_a = S_b = 7/2$, which was used to fit the variation of the χT vs. T data. The best fit parameters obtained are $J = -0.007(4) \text{ cm}^{-1}$ and $g = 1.99(1)$ for **Gd₂K₂COT₄**. The small J value is a consequence of the large Gd^{III}-Gd^{III} distance of 8.93 Å. These results clearly suggest that in compounds **Dy₂K₂COT₄** and **Er₂K₂COT₄** the Ln^{III} ions might behave as weakly coupled systems thus the overall magnetic behavior will most likely resemble **ErCOT₂** and **DyCOT₂** SIMs discussed in Chapter 3.

Table 5.2. Select magnetic data for **Gd₂K₂COT₂**, **Dy₂K₂COT₂** and **Er₂K₂COT₂**.

	χT 300 K $\text{cm}^3\text{K}\cdot\text{mol}^{-1}$	χT 300 K Theoretical* $\text{cm}^3\text{K}\cdot\text{mol}^{-1}$	J	τ_0 0 Oe (s ⁻¹)	U_{eff} 0 Oe (K)	T_B
Gd ₂ K ₂ COT ₂	15.79	15.76	-0.007	--	--	--
Dy ₂ K ₂ COT ₂	27.94	28.34	--	2.5×10^{-7}	50	> 1.8 K
Er ₂ K ₂ COT ₂	22.54	22.96	--	5.0×10^{-9}	306	12 K

*Theoretical values for χT (300K) were determined from the theoretical ground state and the following parameters: Gd^{III} (⁸S_{7/2}, $S = 7/2$, $L = 0$, $g = 2$), Dy^{III} (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$) and Er^{III} (⁴I_{15/2}, $S = 3/2$, $L = 6$, $g = 6/5$).

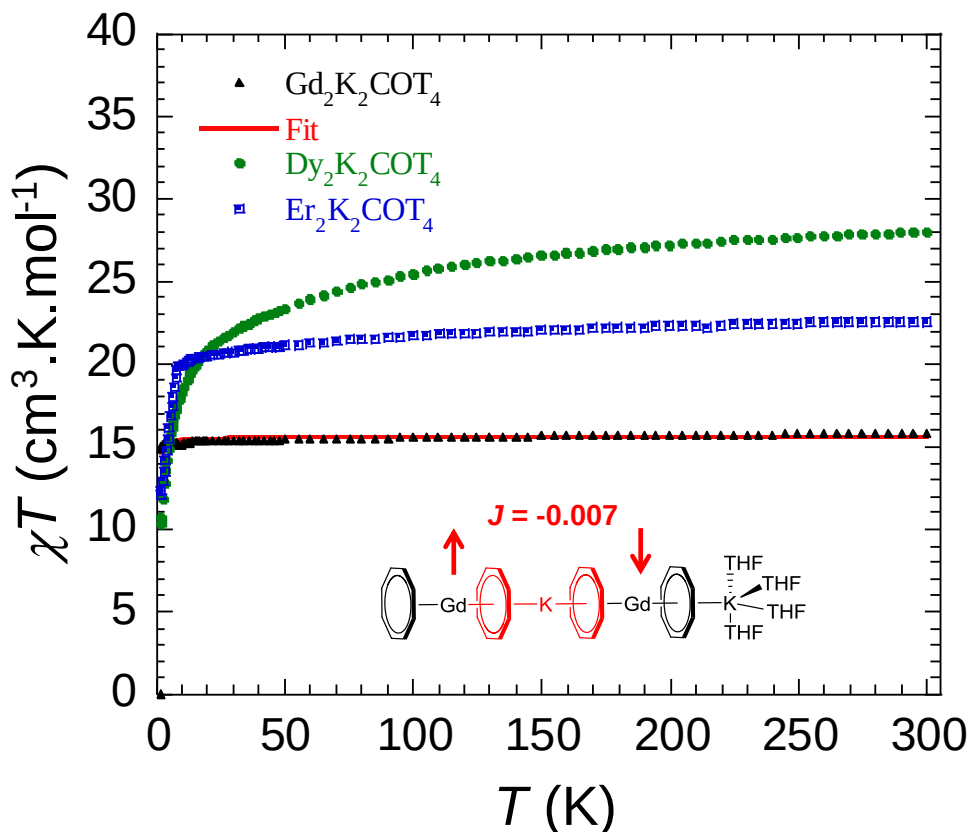


Figure 5.2. Temperature dependence of the χT product under 0.1 T for **Gd₂K₂COT₄**, **Dy₂K₂COT₄** and **Er₂K₂COT₄** with χ being the molar susceptibility per complex defined as M/H .

To investigate the blocking of the magnetization, magnetic hysteresis measurements were performed. No coercivity was observed for **Dy₂K₂COT₄** at 1.8 K similar to **DyCOT₂** (Chapter 3). To directly compare the magnetic blocking of **Er₂K₂COT₄** to the mononuclear analog, **ErCOT₂**, the same sweep rate of 0.0018 T.s⁻¹ was employed.⁴ At a fixed sweep rate of 0.0018 T.s⁻¹ and at 1.8 K the appearance of a clear butterfly-shape hysteresis is observed in **Er₂K₂COT₄** with openings at $H \neq 0$. Upon raising the temperature, openings in the hysteresis narrow, then close above 12 K (Figure 5.3). In comparison, **ErCOT₂** (Chapter 3) displays clear hysteresis and remanance at $M = 0$ Oe up to 5 K.⁴ The increase in the T_B of **Er₂K₂COT₄** over **ErCOT₂** is most likely due to single-ion effects considering the antiferromagnetic interaction between Er^{III} ions determined from the χT plot. Additionally an f-f magnetic interaction with a 8.81 Å separation between Er^{III} ions would be surprising. The longest interaction previously observed between lanthanide ions was in a Tb^{III} triple decker phthalocyanine complex reported by

Fukuda and co-workers where f–f interactions were considered non-negligible up to 6.8 Å.⁵ The perfect butterfly shape of the hysteresis curve at 1.8 K for **Er₂K₂COT₄** is devoid of steps, similar to **ErCOT₂**, thus confirming the largely single-ion nature of the relaxation.

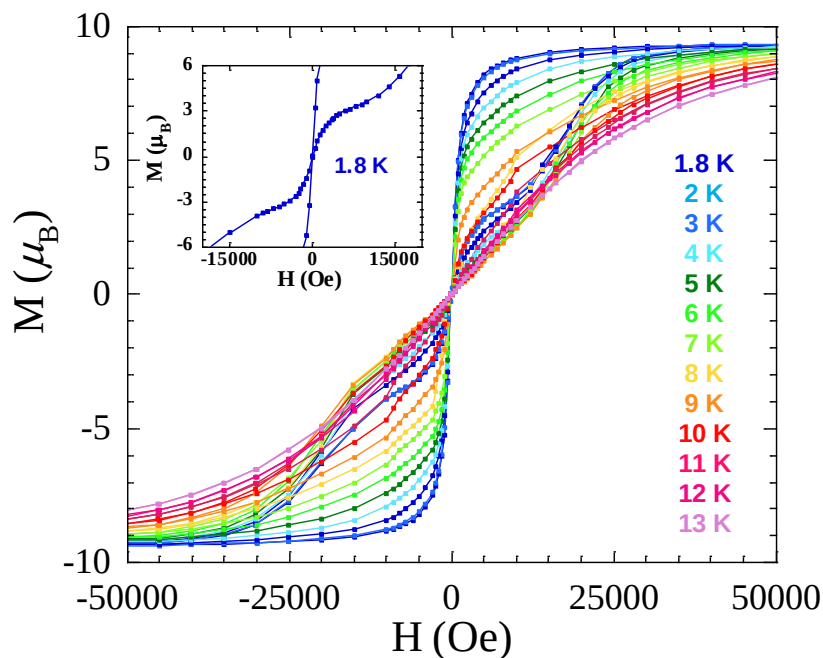


Figure 5.3. Magnetization hysteresis loops. M vs. H for **Er₂K₂COT₄** measured on a SQUID at 0.0018 T.s⁻¹ sweep rate and at indicated temperatures. Insert: Equivalent measurement for **Dy₂K₂COT₄** at 1.8 K.

Ac Magnetic Susceptibility

Dy₂K₂COT₄

A frequency dependent χ'' signal was observed for **Dy₂K₂COT₄** with two distinct relaxation processes. The lower frequency relaxation process displayed shifting peak maxima towards lower temperatures confirming **Dy₂K₂COT₄** is a zero field SMM. Using χ'' peak maxima between 8-1.8 K (Figure 5.4) and the Arrhenius law, an effective energy barrier of 50 K (36 cm⁻¹) with a $\tau_0 = 2.5 \times 10^{-7}$ s was obtained from the low frequency relaxation process. This shows a significant increase over the **DyCOT₂** complex (Chapter 3, $U_{eff} = 11$ K (8 cm⁻¹), $\tau_0 = 2.2 \times 10^{-5}$ s).

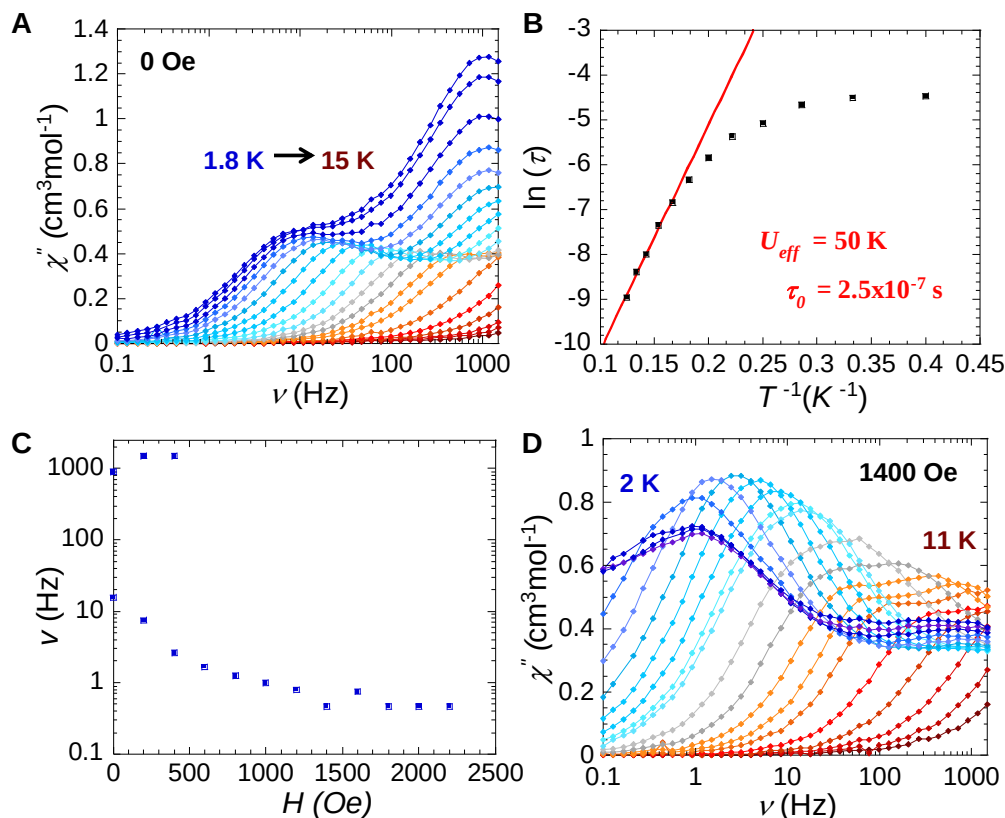


Figure 5.4. Select ac data for $\text{Dy}_2\text{K}_2\text{COT}_4$. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) in the temperature range 1.8–15 K under 0 dc field. **(B)** An Arrhenius plot of τ (the natural log of the relaxation time) versus inverse temperature. Relaxation times are extracted from the frequency dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The red line indicates the fit to the data and affords $U_{\text{eff}} = 50 \text{ K}$ (36 cm^{-1}) with $\tau_0 = 2.5 \times 10^{-7} \text{ s}$, determined via the Arrhenius equation. **(C)** Field dependence of the magnetization. **(D)** Out-of-phase susceptibility (χ'') versus frequency (ν) in the temperature range 2–11 K under 1400 Oe dc field.

The higher frequency relaxation process appears to be frequency independent suggesting QTM. To confirm QTM is occurring a small optimal dc field of 1400 Oe was applied (Figure 5.4D). The resulting data showed very complex relaxation dynamics; to help understand the multiple processes occurring, Cole-Cole plots were utilized (Figure 5.5). Figure 5.6A shows the frequency dependent χ'' data under a 1400 Oe dc field, the numbers 1-3 indicate the regions where different relaxation behaviour is apparent and each region corresponds to their respective Cole-Cole plot with the range indicated (Figure 5.5B-D). The Debye fit for Cole-Cole plots **C** and **D** show relatively high alpha

values indicating the possibility of multiple relaxation mechanisms occurring in these temperature ranges. Between 4-5.5 K (Figure 5.5B) two distinct relaxations are visibly apparent and the Debye model could not be fit to the data. In summary, at least two relaxation processes are occurring in $\text{Dy}_2\text{K}_2\text{COT}_4$ under a 1400 Oe applied dc field, possibly a consequence of the long Dy-Dy separation and the two crystallographically distinct Dy^{III} ions.

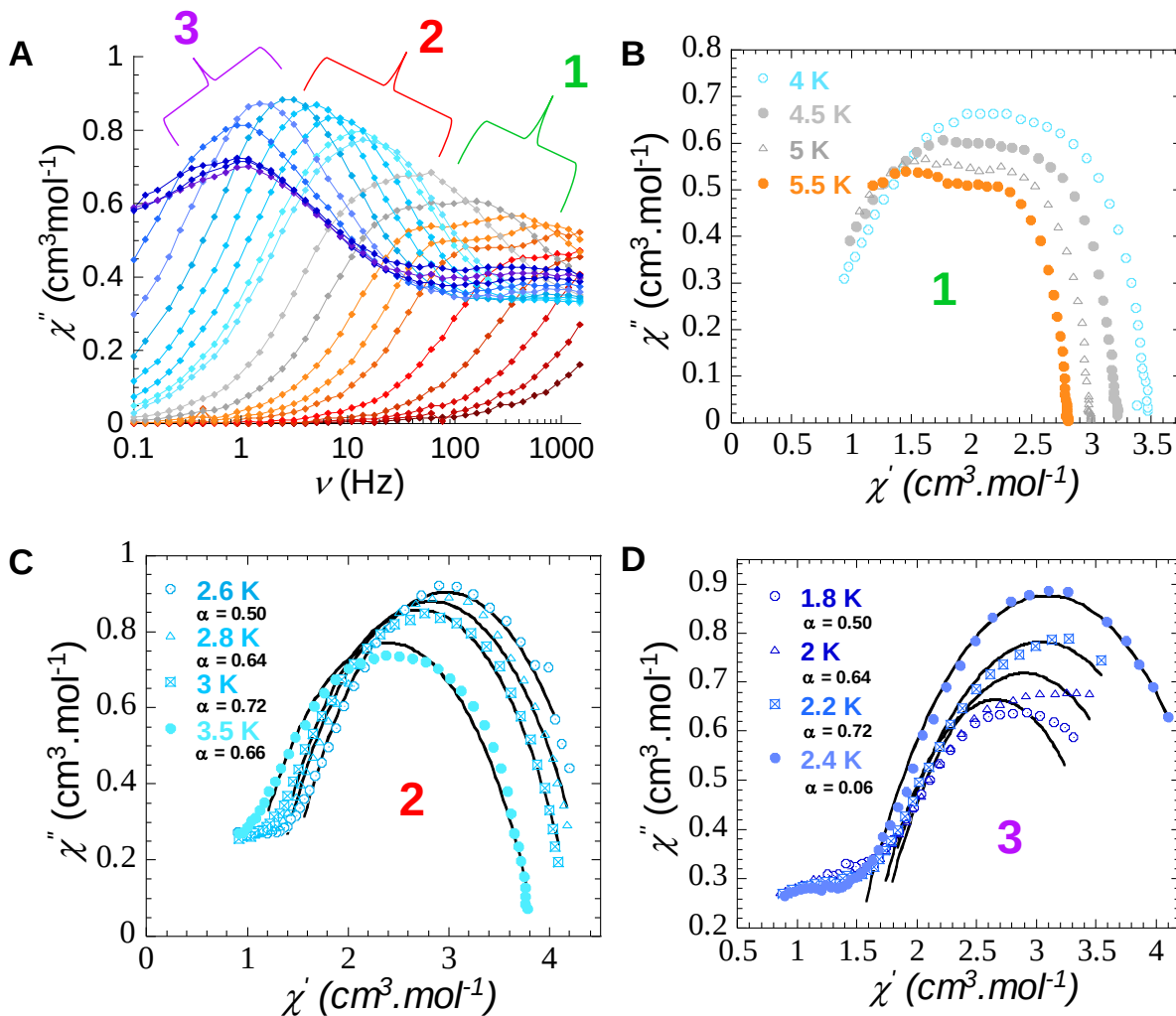


Figure 5.5. Cole-Cole plots of $\text{Dy}_2\text{K}_2\text{COT}_4$ under 1400 Oe applied dc field. (A) $\chi T''$ data under 1400 dc field with three different regions highlighted which corresponds to plots (B), (C), and (D).

Er₂K₂COT₄.

A frequency-dependent χ'' signal was observed for **Er₂K₂COT₄** with shifting peak maxima towards lower temperatures confirming **Er₂K₂COT₄** is also an SMM. Using χ'' peak maxima between 32-13 K (Figure 5.6) and the Arrhenius law, an effective energy barrier of 306(1) K (219 cm⁻¹) with a $\tau_0 = 5.0 \times 10^{-9}$ s was obtained. This shows an increase over **ErCOT₂** ($U_{eff} = 286$ K (204 cm⁻¹), $\tau_0 = 3.7 \times 10^{-9}$ s) consistent with hysteresis data. When the Arrhenius data was extrapolated to low temperature, the relaxation time was 100s at 12.9 K.

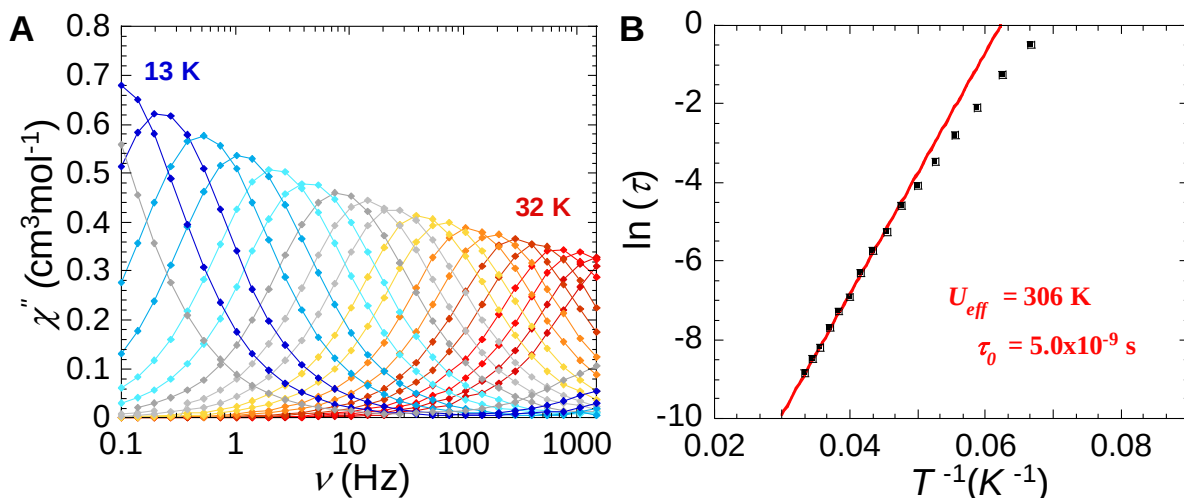


Figure 5.6. Dynamic magnetic data for **Er₂K₂COT₄**. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for **Er₂K₂COT₂** in the temperature range 13-32 K under 0 Oe applied dc field. **(B)** An Arrhenius plot of τ (the natural log of the relaxation time) versus inverse temperature. Relaxation times are extracted from the frequency dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The red line indicates the fit to the data and affords $U_{eff} = 306$ K (219 cm⁻¹) with $\tau_0 = 5.0 \times 10^{-9}$ s, determined via the Arrhenius equation.

The frequency dependent data for **Er₂K₂COT₄** indicates only one relaxation process is occurring between 32-12 K, this is surprising due to the large Er-Er separation. At such a distance we would expect each Er^{III} ion to have a unique magnetic relaxation especially considering they are crystallographically dissimilar. To investigate the ac susceptibility of **Er₂K₂COT₄** over a larger temperature range, temperature dependent studies were conducted between 32-1.8 K (Figure 5.7). The temperature dependent χ'' signal reveals

two relaxation processes occurring at approximately 7-12 K and 19-32 K. The lower temperature relaxation was not observed in the frequency dependent studies due to the frequency limit of the instrument. The two magnetic relaxation processes observed in the temperature dependent studies exhibit spin reversal barriers of 170(2) K (121 cm⁻¹) and 293(7) K (209 cm⁻¹). The difference in energy barrier of the two relaxations most likely arises from the two crystallographically different Er^{III} sites (see structural section above).

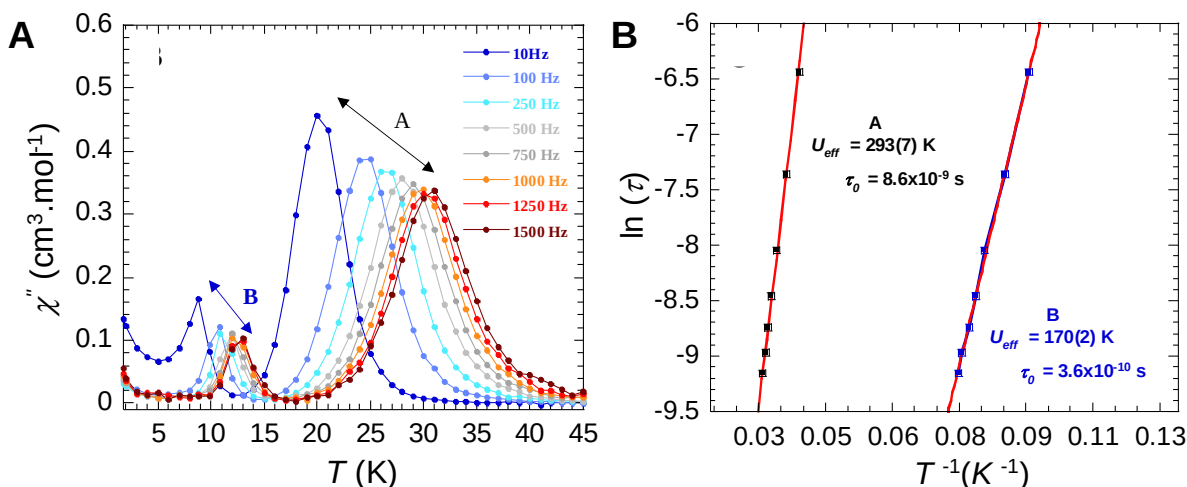


Figure 5.8. Temperature dependent ac susceptibility of **Er₂K₂COT₄**. Solid state variable frequency out-of phase χ'' (A) magnetic susceptibility of **Er₂K₂COT₄** under 0 Oe dc field over the indicated frequency range. (B) Solid-state relaxation time of the magnetization $\ln(\tau)$ vs. T^{-1} for **Er₂K₂COT₄** (Arrhenius plot using ac data) under 0 Oe applied field. Data extracted for the two relaxations, A and B, corresponds to the respective peaks maxima in plot A. The solid lines correspond to the fit of the data.

5.2.4 *Ab initio* Calculations for **Er₂K₂COT₄**⁶

Ab initio calculations of CASSCF/RASSI/SINGLE_ANISO type⁷ reveal that the ground and first excited Kramers doublets on all Er^{III} sites in **Er₂K₂COT₄** are magnetically extremely axial, similar to what was found in the monomer **ErCOT₂** (Chapter 3).⁴ The reason for strong magnetic axiality of Er^{III} ions⁴ is the negative sign of the main crystal field parameters B_2^0 and B_4^0 , which leads to the stabilization of the Kramers doublet $|\pm 15/2\rangle$, with the projection of angular momentum on the symmetry axis of the $[\text{Er}(\text{COT})_2]^-$ unit in the ground state. Moreover, the main magnetic axis of first excited Kramers doublet is almost parallel to the main magnetic axis of the ground state (Tables 5.5).

These axes at different Er^{III} sites are almost parallel to each other (Figure 5.9) which imply a ferromagnetic dipole-dipole interaction between the magnetic moments on these sites (Figure 5.5). To compare these results to $\text{Er}_2\text{COT}''_3$ in Chapter 4, the distance between Er^{III} ions in $\text{Er}_2\text{COT}''_3$ is nearly twice smaller than in $\text{Er}_2\text{K}_2\text{COT}_4$, therefore the dipole-dipole interaction in the latter is nearly eight times weaker. In fact, the reduction is even larger due to an appreciable angle between the magnetic axes on Er^{III} sites in $\text{Er}_2\text{K}_2\text{COT}_4$.

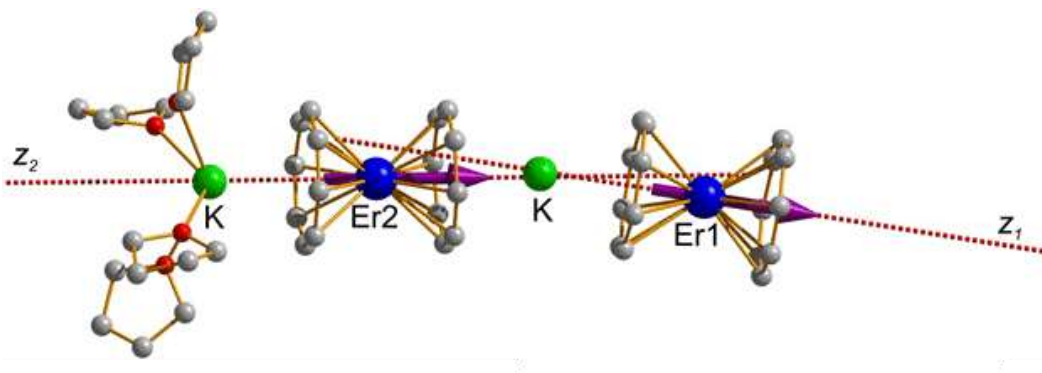


Figure 5. Red dashed lines represent the main magnetic axes of the ground Kramers doublets on Er^{III} ions in $\text{Er}_2\text{K}_2\text{COT}_4$. The large distance between Er^{III} ions significantly lowers the magnetic interaction, making the sites effectively uncoupled at the lowest experimental temperature (Table 5.6). Arrows indicate the orientations of local magnetic moments on both Er^{III} ions in the ground exchange doublet state of $\text{Er}_2\text{K}_2\text{COT}_4$ when only the intramolecular dipole-dipole interaction is considered.¹

Broken Symmetry-DFT calculations confirms a negligible value of the exchange interaction in $\text{Er}_2\text{K}_2\text{COT}_4$. In contrast to $\text{Er}_2\text{COT}''_3$, the significantly larger distance between Er^{III} ions in $\text{Er}_2\text{K}_2\text{COT}_4$ dramatically reduces the magnetic interaction, both exchange and dipolar, leading to much smaller energy splitting between the ground and first excited exchange Ising doublets, of *ca.* 0.20 cm^{-1} (Table 5.6). This means that even at the lowest temperature achieved in experiment (1.8 K) the two $[\text{Er}(\text{COT})_2]^-$ units are magnetically decoupled. In this temperature regime, neighboring magnetic centers act on each other merely as sources of fluctuating magnetic field resulting in the increase of the relaxation rate at each of them.⁸ The same effect of the surrounding molecules are expected to enhance magnetic relaxation in the (undiluted) mononuclear ErCOT_2 compound. The increased magnetic blocking observed in $\text{Er}_2\text{K}_2\text{COT}_4$ can be attributed to the different crystal packing compared to the mononuclear ErCOT_2 compound,

leading to a smaller effect of the random magnetic field created by the crystal environment.

5.3 Conclusions

Three quadruple-decker Ln-COT complexes were isolated and structurally and magnetically investigated in detail. **Er₂K₂COT₄** exhibited a remarkably large T_B and display magnetic hysteresis up to 12 K. In comparison to the mononuclear complex **ErCOT₂** (Chapter 3), the enhancement of SMM properties of **Er₂K₂COT₄** are single-ion in origin. The isotropic Gd^{III} analogue was synthesized and studied to probe the nature and the strength of magnetic interactions between lanthanide ions. This study confirms the exchange interaction in **Er₂K₂COT₄** is negligible compared to the observed interaction in **Er₂COT₂**. Similar results were recently observed in quadruple-decker phthalocyanine (Pc) complexes.⁹ Ishikawa reported the magnetic properties of Pc sandwich complexes with a varying amount of decks including a LnPc₂ (Ln = Dy, Tb) sandwich complex bridged linearly by a Cd ion.⁹ Both the study by Ishikawa and the present results indicate that the alignment of the anisotropy axis is not enough to influence the magnetic properties of dimers. Strong J coupling is essential in order to achieve a single unified ground state in multi-metallic Ln-SMMs.

5.3 Experimental

General Synthetic Considerations. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware was oven dried (120 °C, 6 h) before use. Hexanes, pentane, toluene and tetrahydrofuran (THF) were dried using activated alumina and stored over 3 Å molecular sieves. All chemicals were purchased from Thermofisher Scientific or Strem and used without further purification. IR data were collected on a Varian 640 FT-IR spectrometer. ¹H NMR spectra were recorded on a 300 MHz Bruker Avance spectrometer at room temperature (21-23 °C). THF-d₈ was dried over sodium metal for 24 h, distilled, then stored over 3 Å molecular sieves. Toluene-d₈ was dried using activated alumina and 3 Å molecular sieves.

Synthesis of $\text{Gd}_2\text{K}_2\text{COT}_4$. In a 20 mL scintillation vile, freshly cut K^0 (164 mg, 0.42 mmol) was added to THF (10 mL) and the solution was cooled to $-37\text{ }^\circ\text{C}$ in a dry box freezer. 1,3,5,7-Cyclooctatetraene (0.192 mL, 0.2 mmol) was added and the resulting solution remained at $-37\text{ }^\circ\text{C}$ for 2 days without stirring. GdCl_3 (290 mg, 0.11 mmol) was added and the resulting mixture was slowly warmed to room temperature. The mixture was vigorously stirred for 3 h at room temperature, then filtered through a fine fritted funnel containing celite. The resulting solution was concentrated and single crystals of $\text{Gd}_2\text{K}_2\text{COT}_4$ suitable for X-ray diffraction were grown at $-37\text{ }^\circ\text{C}$ with 10% v/v addition of pentane after 1 week (yield 381 mg, 63%). CCDC 974994. Selected IR data (cm^{-1}): 2969 (w), 2922 (br), 1850 (w) 1457 (m), 1316 (w), 1262 (m), 1099 (w), 1025 (w), 889 (w), 799 (m), 743 (m). ^1H NMR (300 MHz, THF-d_8) δ 3.90 (br s), 1.80 (br s), -0.05 (br s) ppm.

Synthesis of $\text{Dy}_2\text{K}_2\text{COT}_4$. In an analogous manner to $\text{Gd}_2\text{K}_2\text{COT}_4$, freshly cut K^0 (164 mg, 0.42 mmol) was added to THF (10 mL) and the solution was cooled to $-37\text{ }^\circ\text{C}$ in a dry box freezer. 1,3,5,7-Cyclooctatetraene (0.192 mL, 0.2 mmol) was added and the resulting solution remained at $-37\text{ }^\circ\text{C}$ for 2 days without stirring. ErCl_3 (274 mg, 0.11 mmol) was added and the resulting mixture was slowly warmed to room temperature. The mixture was vigorously stirred for 3 h at room temperature, then filtered through a fine fritted funnel containing celite. The resulting solution was concentrated and single crystals of $\text{Dy}_2\text{K}_2\text{COT}_4$, suitable for X-ray diffraction, were grown at $-37\text{ }^\circ\text{C}$ with 10% v/v addition of pentane after 1 week (yield 405 mg, 66%). Selected IR data for **3** (cm^{-1}): 3005 (w), 2925 (br), 1840 (w) 1456 (m), 1319 (w), 1262 (w), 1099 (w), 1058 (w), 893 (s), 799 (m), 743 (m). ^1H NMR (300 MHz, THF-d_8) δ 5.39 (br s), 4.04 (br s), 1.88 (br s) ppm.

Synthesis of $\text{Er}_2\text{K}_2\text{COT}_4$. Synthesis was conducted in an analogous manor to $\text{Gd}_2\text{K}_2\text{COT}_4$ where freshly cut K^0 (164 mg, 0.42 mmol) was added to THF (10 mL) and the solution was cooled to $-37\text{ }^\circ\text{C}$ in a dry box freezer. 1,3,5,7-Cyclooctatetraene (0.192 mL, 0.2 mmol) was added and the resulting solution remained at $-37\text{ }^\circ\text{C}$ for 2 days

without stirring. ErCl_3 (274 mg, 0.11 mmol) was added and the resulting mixture was slowly warmed to room temperature. The mixture was vigorously stirred for 3 h at room temperature, then filtered through a fine fritted funnel containing celite. The resulting solution was concentrated and single crystals of $\text{Er}_2\text{K}_2\text{COT}_4$, suitable for X-ray diffraction, were grown at -37°C with 10% v/v addition of pentane after 1 week (yield 405 mg, 66%). CCDC 974993. Selected IR data (cm^{-1}): 3005 (w), 2925 (br), 1840 (w) 1456 (m), 1319 (w), 1262 (w), 1099 (w), 1058 (w), 893 (s), 799 (m), 743 (m). ^1H NMR (300 MHz, THF-d_8) δ 5.39 (br s), 4.04 (br s), 1.88 (br s) ppm.

X-ray Crystallography. Large single crystals of all complexes were grown from a concentrated THF/pentane solution at -37°C and washed thoroughly with hexanes before use. For each complex a suitable prism shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).¹⁰ The crystal structures were solved and refined using the SHELXTL¹¹ program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

Table 5.3. Unit cell parameters for $\text{Gd}_2\text{K}_2\text{COT}_4$, $\text{Dy}_2\text{K}_2\text{COT}_4$ and $\text{Er}_2\text{K}_2\text{COT}_4$.

	$\text{Gd}_2\text{K}_2\text{COT}_4$	$\text{Dy}_2\text{K}_2\text{COT}_4$	$\text{Er}_2\text{K}_2\text{COT}_4$
CCDC	974992	--	974993
M_r (g/mol)	1097.69	1108.19	1117.710
Formula	$\text{C}_{48}\text{H}_{64}\text{Gd}_2\text{K}_2\text{O}_4$	$\text{C}_{48}\text{H}_{64}\text{Dy}_2\text{K}_2\text{O}_4$	$\text{C}_{48}\text{H}_{64}\text{Er}_2\text{K}_2\text{O}_4$
T(K)	200(2)	200(2)	200(2)
γ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	12.5506(3)	12.5052(4)	12.4865(10)
<i>b</i> (Å)	12.9933(3)	12.9310(4)	12.8999(10)
<i>c</i> (Å)	16.7384(4)	16.7562(6)	16.7853(15)
α (deg)	107.0633(13)	107.209(2)	107.250(2)
β (deg)	98.5557(14)	98.703(2)	98.705(2)
γ (deg)	112.1212(13)	111.593(2)	111.302(2)
<i>V</i> (Å ³)	2311.45(10)	2301.03(13)	2301.4(3)
ρ_{calc} (cm ⁻³)	1.577	1.599	1.613
<i>Z</i>	2	2	2
Reflections collected	13089	18866	19618
Goodness of fit	1.034	1.073	1.046
<i>R</i> 1	0.0409	0.0616	0.0837
<i>wR</i> 2	0.0826	0.1322	0.1559
Reflections with <i>I</i> > 2σ(<i>I</i>)	9370	8526	7065

Magnetic Measurements. Magnetic susceptibility measurements for all complexes were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Dc analyses were performed on polycrystalline samples sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and temperatures between 1.8 and 300 K. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. Magnetization data was collected at 100 K to check for ferromagnetic impurities that were absent in all samples. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

Ab initio calculations.⁶ All calculations were done with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type. The entire molecule was computed *ab initio*, while neighboring Er^{III} ions were computationally modeled by diamagnetic Lu. Two basis set approximations have been employed: 1 – small, 2 – large; Table 5.3 shows the contractions of the employed basis sets for all elements. Active space of the CASSCF method includes the 11 electrons from the last shell spanning the 7 orbitals (4f orbitals of the Er^{III} ion). On the basis of the resulting spin-orbital multiplets the SINGLE_ANISO program computed local magnetic properties (g-tensors, main magnetic axes, local magnetic susceptibility, etc.) Further, the exchange and dipolar interactions between magnetic centers were computed by the POLY_ANISO program.

Table 5.4. Contractions of the employed basis sets for all atoms.

Basis 1	Basis 2
Dy.ANO-RCC...7s6p4d3f1g.	Dy.ANO-RCC...8s7p5d4f2g1h.
Lu.ANO-RCC...7s6p4d3f1g.	Lu.ANO-RCC...7s6p4d3f1g.
Cl.ANO-RCC...4s3p1d. (close)	Cl.ANO-RCC...5s4p2d1f. (close)
Cl.ANO-RCC...4s3p. (distant)	Cl.ANO-RCC...3s2p. (distant)
O.ANO-RCC...3s2p1d. (close)	O.ANO-RCC...4s3p2d1f. (close)
O.ANO-RCC...3s2p. (distant)	O.ANO-RCC...2s1p. (distant)
N.ANO-RCC...3s2p1d. (close)	N.ANO-RCC...4s3p2d1f. (close)
N.ANO-RCC...3s2p. (distant)	N.ANO-RCC...2s1p. (distant)
C.ANO-RCC...3s2p.	C.ANO-RCC...3s2p. (close)
H.ANO-RCC...2s.	C.ANO-RCC...2s1p. (distant)
	H.ANO-RCC...1s.

Table 5.5. Angle between the main magnetic axis of the lowest Kramers doublet and the Er1-Er2 direction (degrees).

conformer 1				conformer 2			
Er1		Er2		Er1		Er2	
Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
4.6770	4.6757	6.0842	6.0713	4.6777	4.6747	5.8214	5.8105

Table 5.6. Magnetic couplings (dipolar and exchange) between Er centers (basis 2) in Er₂K₂COT₄, with respect to the pseudospin $\tilde{S} = 1/2$ of the interacting ground Kramers doublets on Er^{III} ions.

interaction	J_{dip}^*	$J_{\text{exch}}(\text{BS-DFT})$	$J_{\text{total}} = J_{\text{dip}}^* + J_{\text{exch}}$
conformer 1	0.40104	0.00	0.40104
conformer 2	0.40455	0.00	0.40455

* -- contribution coming only from the Ising terms $\sim \hat{S}_{1,z} \hat{S}_{2,z}$ to the dipolar coupling.

5.4 References and Notes

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Chapter 6

Fine Tuning the Magnetic Behaviour of Organouranium Sandwich Complexes through Oxidation State and Ligand Modifications*

**Partial contents of this chapter have been published in: J. J. Le Roy, S. I. Gorelsky, I. Korobkov, M. Murugesu. Organometallics, 2015, Article ASAP, DOI: 10.1021/om501214c.*

As addressed in Chapter 4, one of the main challenges in designing high performance bimetallic lanthanide SMMs is achieving strong exchange coupling between metal centers. This is among the many reasons why trivalent uranium complexes have received increasing attention in recent years. The use of uranium as the spin source in SMMs is attractive due to the large spin ground state of U^{III} as well as the potential covalent interaction with neutral bridging ligands, potentially leading to strong exchange coupling in bimetallic complexes. This chapter explores the magnetic properties of uranium sandwich complexes, and evaluates their potential to be used as magnetic building blocks, as was previously discussed in Chapter 4 and Chapter 5. The synthesis, structure and magnetic properties of a U^{III} -COT²⁻ sandwich complex, $[Li(DME)_3][U^{III}(COT^{2-})_2]$ (COT²⁻ = bis(trimethylsilyl)cyclooctatetraenyl dianion), $U^{III}COT^{2-}_2$, and its coordinatively analogous tetravalent equivalent, $[U^{IV}(COT^{2-})_2]$, $U^{IV}COT^{2-}_2$ are discussed. DFT calculations reveal that $U^{III}COT^{2-}_2$ leads to weaker ligand-to-metal donation as compared with the tetravalent equivalent complex. Additionally, a full structural and magnetic comparison of isostructural and isoelectronic complexes $U^{III}COT^{2-}_2$ and $Nd^{III}COT^{2-}_2$ is provided. Study of the AC magnetic susceptibility reveals slow magnetic relaxation in both $U^{III}COT^{2-}_2$ and $Nd^{III}COT^{2-}_2$ complexes. The enhanced magnetic performance of the U^{III} congener over the Nd^{III} further incites the use of actinides in the design of Single-Molecule Magnets. Lastly this Chapter investigates the magnetic properties of two uranium(IV) sandwich complexes, $[2.2.2.Cryptand][U(\eta-C_7H_7)_2]$ (2.2.2.Cryptand = $K(C_{12}H_{24}O_6)$) ($U^V C7$), and $[18-C-6][U(\eta-C_7H_7)_2]$ (18-C-6 =

1,4,7,10,13,16-hexaoxacyclooctadecane) ($\text{U}^{\text{V}}\text{C7}'$), through utilizing cycloheptatrienyl ligands. Neither complex displays an out-of-phase signal, which is surprising due to the comparatively high symmetry around the spin source.

6.1 Introduction

Tremendous effort has been directed towards improving lanthanide SMMs for their use in magnetic materials.¹ Until now, the best candidates have been single-ion lanthanide complexes such as ErCOT''_2 and ErCOT_2 (Chapter 2-3) which display remarkable magnetic properties due to their unquenched orbital angular momentum.² Unfortunately, the operating temperature of even the best lanthanide SMMs is well below what is required for practical applications. Creating high temperature lanthanide SMMs will require the synthesis of magnetic complexes with strong super-exchange type metal-metal interactions, where metals are strongly coupled through diamagnetic bridging ligands. This requires strong metal-ligand covalency, which is challenging in lanthanide complexes due to the poor radial extension of the 4f orbitals.

Uranium complexes have tremendous potential as SMMs as they possess the key physical properties of large intrinsic total ground state spin (S); and more importantly uniaxial magnetic anisotropy (D), required for magnet-like behavior of slow relaxation of the magnetization.³ Akin to lanthanide ions the heavy element nature of uranium can additionally result in significant spin-orbit coupling constants due to relativistic effects.⁴ However unlike lanthanides, actinides have enhanced 5f radial extension which can lead to substantial metal-ligand covalency, allowing for strong exchange coupling (J) between metals in multi-metallic complexes.

Despite the many obvious advantages, only a handful of actinide SMMs have been reported, none of which have shown enhanced magnetic properties over the best performing lanthanide SMMs.⁵ It is well established that even subtle variations in the ligand field can drastically change the magnetic properties of lanthanide SMMs.⁶

Therefore, in order to isolate new uranium SMMs with large anisotropic barriers it is important to explore how new ligand fields affect the magnetic properties of actinides.

With this in mind we have turned our attention toward uranocene-type sandwich complexes. The influence of a sandwich-type ligand field is unknown on the magnetic properties of uranium. Moreover, strong ligand donation has been well established in uranocene $[\text{U}^{\text{VI}}(\text{COT})_2]$ which is a desirable property in magnetic building blocks (Chapter 4).⁷ However, magnetically speaking U^{III} is preferable to U^{IV} , as U^{III} has been recognized to have inherent SMM character.²⁰

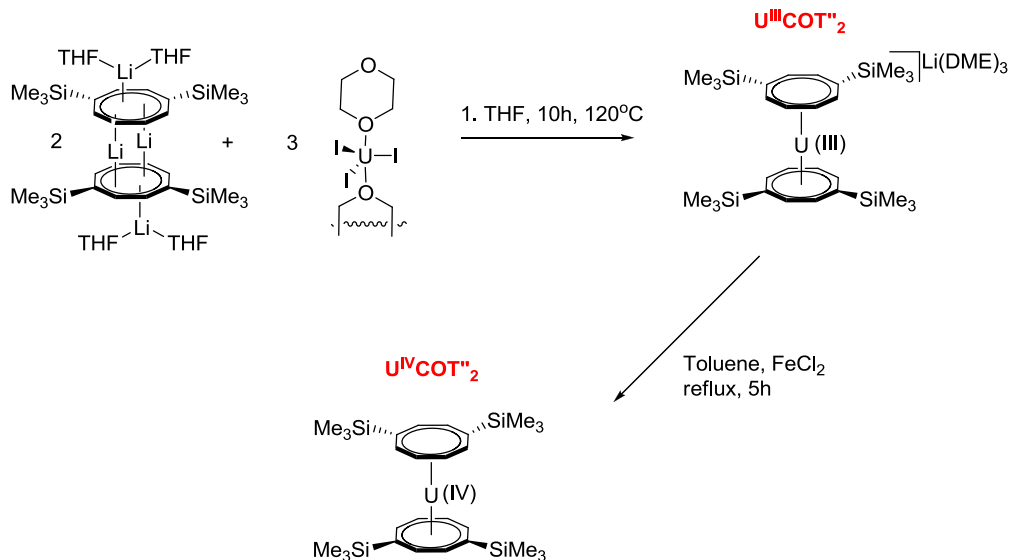
The following discussion is separated into three sections. We first investigate the use of the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT^{2-}) ligand to isolate uranocene-type molecules with unsymmetrical coordination geometries and multiple oxidation states. Here we describe the synthesis, structure and magnetic properties of $\text{U}^{\text{III}}\text{COT}^{2-}_2$, and its coordinatively analogous tetravalent equivalent, $\text{U}^{\text{IV}}\text{COT}^{2-}_2$.

In the next section, we establish the advantage of using high atomic mass metals in the design of SMMs. The magnetic properties of several lanthanide- COT^{2-} complexes have been reported, with the erbium(III) analogue exhibiting a high blocking temperature of 8 K.^{2a,6a,8} Isostructural and isoelectronic complexes in the lanthanide and actinide series provide a unique opportunity to elucidate subtle differences, such as how atomic mass (z) influences magnetic performance. Therefore, the magnetic properties of $\text{U}^{\text{III}}\text{COT}^{2-}_2$ are compared to structural analogue NdCOT^{2-}_2 (Chapter 2).

In the last section, we exploit the availability of the half-integer spin uranium(V) oxidation state to probe the SMM properties of uranium(V) sandwich complexes using cycloheptatrienyl ligands. Here we describe the synthesis, structure and magnetic properties of two bis(cycloheptatrienyl) uranium complexes, $\text{U}^{\text{V}}\text{C7}_2$ and $\text{U}^{\text{V}}\text{C7}'_2$.

6.2 The Magnetic Properties of Uranium-COT” Sandwich Complexes

6.2.1 Synthetic Strategy



Scheme 1. Synthetic route to $\text{U}^{\text{III}}(\text{COT}'')_2$ and $\text{U}^{\text{IV}}(\text{COT}'')_2$ via a U^{III} precursor.

Uranocene is unreactive to lithiation,⁹ and all previous trivalent uranocene type complexes have been prepared via reduction of $[\text{U}^{\text{IV}}(\text{COT}-\text{R})_2]$ ($\text{R} = \text{CH}_3$ ¹⁰) 1,4- $(t\text{BuMe}_2\text{Si})_2$ ¹¹) by potassium. Our synthetic strategy is a direct method where reaction of $[\text{U}^{\text{III}}\text{I}_3(1,4\text{-dioxane})_{1.5}]$ ¹² with $[\text{Li}_4(\text{COT}'')_2(\text{THF})_4]$ ^{8a} in DME (dimethoxyethane) yields $\text{U}^{\text{III}}(\text{COT}'')_2$, the first $[\text{U}^{\text{III}}(\text{COT}'')_2]^-$ lithium salt. Single crystals of $\text{U}^{\text{III}}(\text{COT}'')_2$ suitable for X-ray diffraction are grown from a 50:50 mixture of DME:hexanes. $\text{U}^{\text{IV}}(\text{COT}'')_2$ is produced in a two-step synthesis where $\text{U}^{\text{III}}(\text{COT}'')_2$ is first isolated, following which, the metal is oxidized to U^{IV} using FeCl_2 . Upon concentrating the solution, large green block crystals of $\text{U}^{\text{IV}}(\text{COT}'')_2$ are isolated, suitable for single-crystal X-ray diffraction.

6.2.2 Structure of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$

Solid State Structure

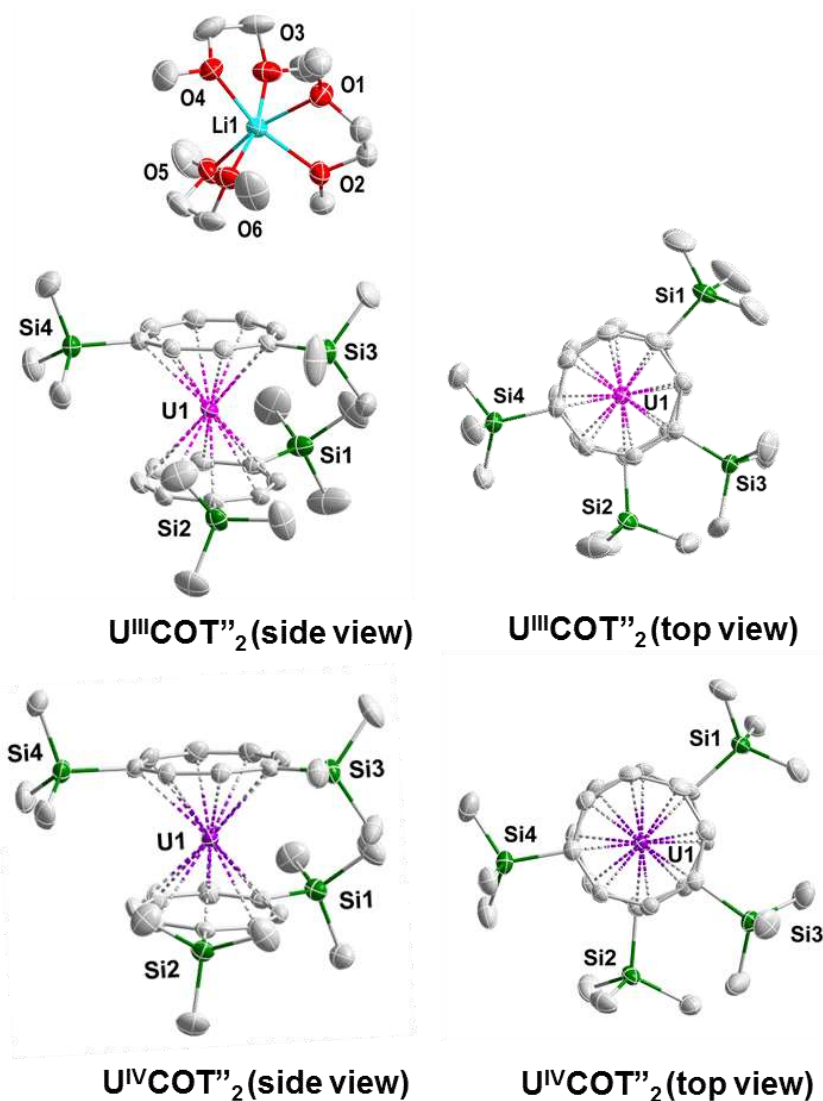


Figure 6.1. Solid state structures of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$. H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), green (Si), red (O), light blue (Li), pink (U^{III}), purple (U^{IV}).

$\text{U}^{\text{III}}\text{COT}''_2$ crystallizes in the triclinic $P-1$ space group where the U^{III} ion is bound to two COT'' ligands in a η^8 -fashion to form a distorted sandwich complex.¹³ The asymmetric η^8 - COT'' coordination is reflected by $\text{U}^{\text{III}}\text{-C}_{\text{COT}''}$ bond distances ranging from 2.726(0)-

2.755(1) Å (Figure 6.1). The lithium counter-ion in the crystal lattice adopts an octahedral coordination environment filled by three DME molecules. $\text{U}^{\text{IV}}\text{COT}''_2$ crystallizes in a monoclinic $P2/c$ space group and the U^{IV} ion is also asymmetrically coordinated by two $\eta^8\text{-COT}''$ ligands with $\text{U}^{\text{IV}}\text{-C}_{\text{COT}''}$ bond distances ranging from 2.646(3)-2.669(3) Å.

Table 6.1. Selected interatomic distances of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$.

	$\text{U}^{\text{III}}\text{COT}''_2$	$\text{U}^{\text{IV}}\text{COT}''_2$
Tilt angle (°)	4.36	6.98
U-COT _{centroid (a)} (Å)	2.027	1.923
U-COT _{centroid (b)} (Å)	2.026	1.922
Centroid-U-Centroid (°)	4.49	6.54
Intermolecular U-U (Å)	10.65	12.17

It is noteworthy, upon oxidation of the U^{III} ion to U^{IV} , metal-COT'' distances become shorter by an average of 0.07 Å as a consequence of the smaller atomic radius and possibly a more covalent interaction between the COT'' and the higher oxidation state U^{IV} ion. When viewing $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ from above, the $\text{C}_{\text{COT}''}$ atoms in each layer are staggered with $\text{C}_{\text{COT}''}$ atoms in other layers, most likely in order to sterically accommodate the bulky TMS groups.¹⁴ Complexes $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ also have distinctly different tilt angles of 4.36° and 6.98°. This difference in tilt angle can be due to several factors such as ionic radii, oxidation state¹⁵ of the metal ion as well as intermolecular interactions. For $\text{U}^{\text{III}}\text{COT}''_2$, the close contact between the sandwich molecule and the DME attached to the Li counter-ion through an unsymmetrical steric interaction (C-H distances between 2.76-2.89 Å ($\text{U}^{\text{III}}\text{COT}''_2$) 2.74-2.88 Å ($\text{U}^{\text{IV}}\text{COT}''_2$)) undoubtedly contributes to the difference in tilt angle.

Also of interest, $\text{U}^{\text{IV}}\text{COT}''_2$ is only the second example of a uranocene with a bent structure where the (ring centroid)-U-(ring centroid) angle deviates from perfect linearity (180°) by 6.5°. ¹⁴ Edelman and Roe recently reported a uranocene with bulky $[\text{C}_8\text{H}_6(\text{SiPh}_3)_2]^{2-}$ ligands leading to a large 11.3° (ring centroid)-U-(ring centroid) linear

deviation.¹⁴ The less sterically bulky TMS groups account for the reduced bend in $\text{U}^{\text{IV}}\text{COT}''_2$ in comparison to SiPh_3 groups. Interestingly $\text{U}^{\text{III}}\text{COT}''_2$ has a (ring centroid)-U-(ring centroid) angle of 172.8° , we can therefore conclude that the oxidation has little effect of the bend angle.

Electronic Structure¹⁶

To fully understand the consequence of oxidation state on Uranium-COT'' bonding the electronic structure of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ was probed using DFT calculations conducted at the spin-unrestricted B3LYP/TZVP level of theory (the SDD basis set and effective core potential for U were conducted using the crystal structure geometries in which COT'' and methyl C-H bond distances were adjusted from the X-ray model values to 1.07 Å and 1.08 Å, respectively). The optimized wavefunctions for the ground states (with $S = 1$ for U^{IV} and $S = 3/2$ for U^{III}) were used to evaluate bonding contributions. Figure 6.2 illustrates the spin density distribution of the ground states.

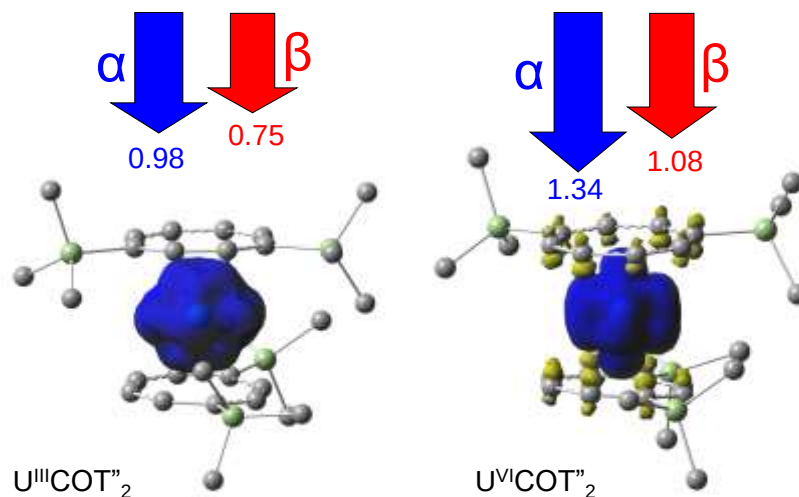


Figure 6.2. Spin density distribution of the ground states of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$. The isosurface values are 0.002 a.u. Blue and yellow regions indicate positive and negative spin density, respectively. Blue and red arrows indicate contributions from α - and β -spin orbitals to the Mayer bond order between a COT'' ligand and the U atom. H atoms are omitted for clarity.

In $\text{U}^{\text{III}}\text{COT}^{2-}_2$, the U^{III} atom carries a spin density of 3.026 a.u. due to three singly-occupied 5f orbitals of the U^{III} ion (α -spin HOMO-2, HOMO-1 and the HOMO of the complex, (Figure 6.3) while the COT^{2-} ligands demonstrate weak spin polarization (a spin density of only -0.013 a.u. per ligand). Overall, each dianionic COT^{2-} ligand donates $\sim 0.92 e^-$ to U^{III} resulting in the +1.16 a.u. charge for the U atom. The Mayer bond order between U^{III} and each COT^{2-} ligand is 1.73; α - and β -spin occupied orbitals contribute 0.98 and 0.75 respectively to the total metal-ligand bond order. The analysis of the wavefunction in terms of contributions from fragment orbitals indicate that only charge donation from the COT^{2-} ligands to the U^{III} contribute to the covalent bonding in $\text{U}^{\text{III}}\text{COT}^{2-}_2$. Five occupied π orbitals of the COT^{2-} ligands (Figure 6.3), namely the highest occupied fragment orbital (HOFO), HOFO-1, HOFO-2, HOFO-3 and HOFO-7, participate significantly (change in orbital population is greater than 3%) in covalent bonding with the U^{III} ion. The changes in the populations of these fragment molecular orbitals are 11.3%, 11.5%, 3.3%, 4.1% and 6.8% for α -spin manifold and 8.0%, 8.2%, 3.0%, 3.7% and 6.2% for β -spin manifold, respectively. The analysis of populations of U^{III} atomic orbitals (Table 6.2) indicates that metal *s*, *p*, *d* and *f* unoccupied orbitals participate in ligand-to-metal donation with the 6*d* orbitals receiving almost half of the total electron density ($1.84 e^-$) transferred from the two ligands.

In $\text{U}^{\text{IV}}\text{COT}^{2-}_2$, the U^{IV} atom carries a spin density of 2.306 a.u. due to two singly-occupied 5f orbitals of the U^{IV} (α -spin HOMO-3 and the HOMO of the complex, Figure S6) while the COT^{2-} ligands demonstrate a more significant spin polarization (a spin density of only -0.153 a.u. per ligand). This is due to a difference in charge donation from the dianionic COT^{2-} ligands to U^{IV} through α - and β -spin orbitals (see below). Overall, each dianionic COT^{2-} ligand donates $\sim 0.99 e^-$ to U^{IV} resulting in the +1.01 a.u. charge for the U^{IV} atom. The Mayer bond order between U^{IV} and each COT^{2-} ligand is 2.42, showing a significant increase in the metal-ligand covalency as compared to the corresponding U^{III} complex. The α - and β -spin occupied orbitals contribute 1.34 and 1.08 respectively to the total metal-ligand bond order. Similar to the U^{III} complex, only charge donation from the COT^{2-} ligands to U^{IV} contribute to the covalent bonding in the U^{IV} complex and five

occupied π orbitals of the COT^{2-} ligands (Figure 6.3) participate in covalent bonding with the U^{IV} ion. The changes in the populations of the HOFO, HOFO-1, HOFO-2, HOFO-3 and HOFO-7 of the COT^{2-} ligand are 22.7%, 22.5%, 6.0%, 5.3% and 7.2% for α -spin manifold and 14.8%, 14.8%, 5.1%, 4.4% and 7.6% for β -spin manifold, respectively. When going from U^{III} to U^{IV} , the energies of the metal orbitals were lowered due to a higher ionic charge and a new 5f orbital became empty and thus opened up for donation. Thus, ligand-to-metal donation became stronger (Table 6.2) with the 5f and 6d orbitals receiving most of the total electron density ($1.99 e^-$) transferred from the two ligands.

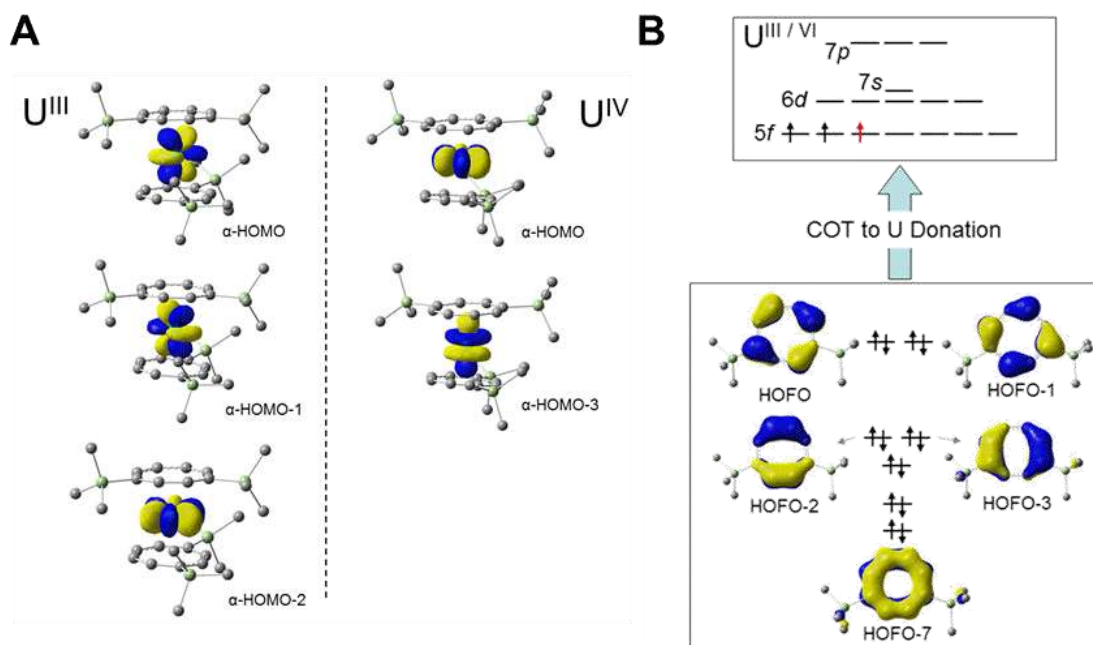


Figure 6.3. (A) Singly-occupied molecular orbitals of $[\text{U}^{\text{III}}(\text{COT}'')_2]^-$ (left) and $[\text{U}^{\text{IV}}(\text{COT}'')_2]$ (right). H atoms are omitted for simplicity. (B) Fragment orbitals of the COT^{2-} ligand and the metal ion that participate in ligand-to-metal donation in $[\text{U}(\text{COT}'')_2]^{0/-1}$ complexes. H atoms are omitted for simplicity.

As can be seen from the electronic structure descriptors such as bond orders, atomic charges and changes in populations of fragment orbitals, the U-C bonds in the U^{IV} complex are more covalent than the U-C bonds in the U^{III} complex. The observation of shorter U^{IV} -C bonds (average value of 2.66 Å) in the X-ray structure of $\text{U}^{\text{IV}}\text{COT}''_2$

relative to the $\text{U}^{\text{III}}\text{-C}$ bonds (average value of 2.74 Å) in the X-ray structure of $\text{U}^{\text{III}}\text{COT}''_2$ is consistent with a stronger, more covalent metal-ligand interaction in $\text{U}^{\text{III}}\text{COT}''_2$.

Table 6.2. Changes of orbital populations of the $\text{U}^{\text{III/IV}}$ ions upon the formation of the $[\text{U}(\text{COT})_2]^{0/-1}$ complexes.

	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
U^{III}	0.35	0.20	0.85	0.44
U^{IV}	0.47	0.28	1.11	1.14

6.2.3 Slow Magnetic Relaxation

The magnetic properties of $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ were probed using a SQUID magnetometer. Dc magnetic susceptibility measurements were performed in the temperature range of 1.8-300 K. Under a 1000 Oe applied dc field the room temperature χT value of $1.13 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ for $\text{U}^{\text{III}}\text{COT}''_2$ and $1.50 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ for $\text{U}^{\text{IV}}\text{COT}''_2$ is within the range typically reported for U^{III} and U^{IV} monomers respectively.^{5, 17}

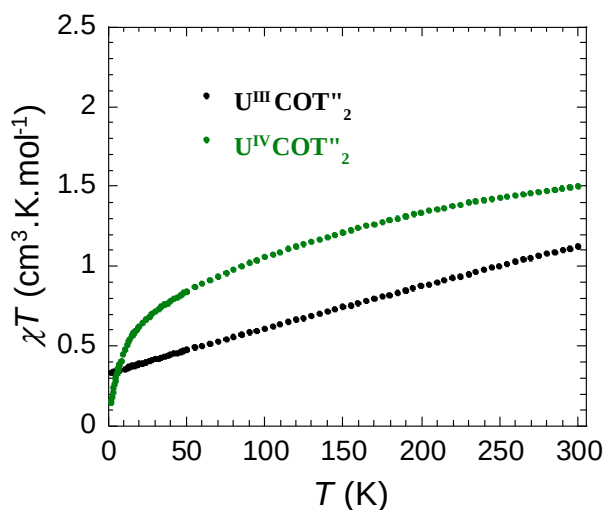


Table 6.3 Select magnetic data for $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$

	$\text{U}^{\text{III}}\text{COT}''_2$	$\text{U}^{\text{IV}}\text{COT}''_2$
χT product 300 K $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$	1.13	1.50
χT product 1.8 K* $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$	0.333	0.145

Figure 6.4. Left: Temperature dependence of the χT product under 0.1 T for $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ with χ being the molar susceptibility per complex defined as M/H . **Right:** Table 6.3 Select magnetic data for $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$.

The temperature dependence of the χT product for $\text{U}^{\text{III}}\text{COT}''_2$ shows near linear behavior which decreases slightly with decreasing temperature to reach a minimum value of $0.66 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ at 1.8 K. The final decrease at low temperature is most likely due to significant anisotropy as often encountered in U^{III} compounds rather than intermolecular interactions (closest $\text{U}^{\text{III}}\text{-U}^{\text{III}}$ distance is $11.51 \text{ \AA}$). $\text{U}^{\text{IV}}\text{COT}''_2$ exhibits radically different magnetic susceptibility. From room temperature, the χT product decreases gradually with decreasing temperature, below 50 K there is a sharp decrease to a minimum value of $0.14 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ at 1.8 K (Figure 6.4). The sharp decrease in the χT product is due to the thermal depopulation of higher excited states leading to a non-magnetic ground state at very low temperature as expected for a U^{IV} ion (ground term 3H_4).

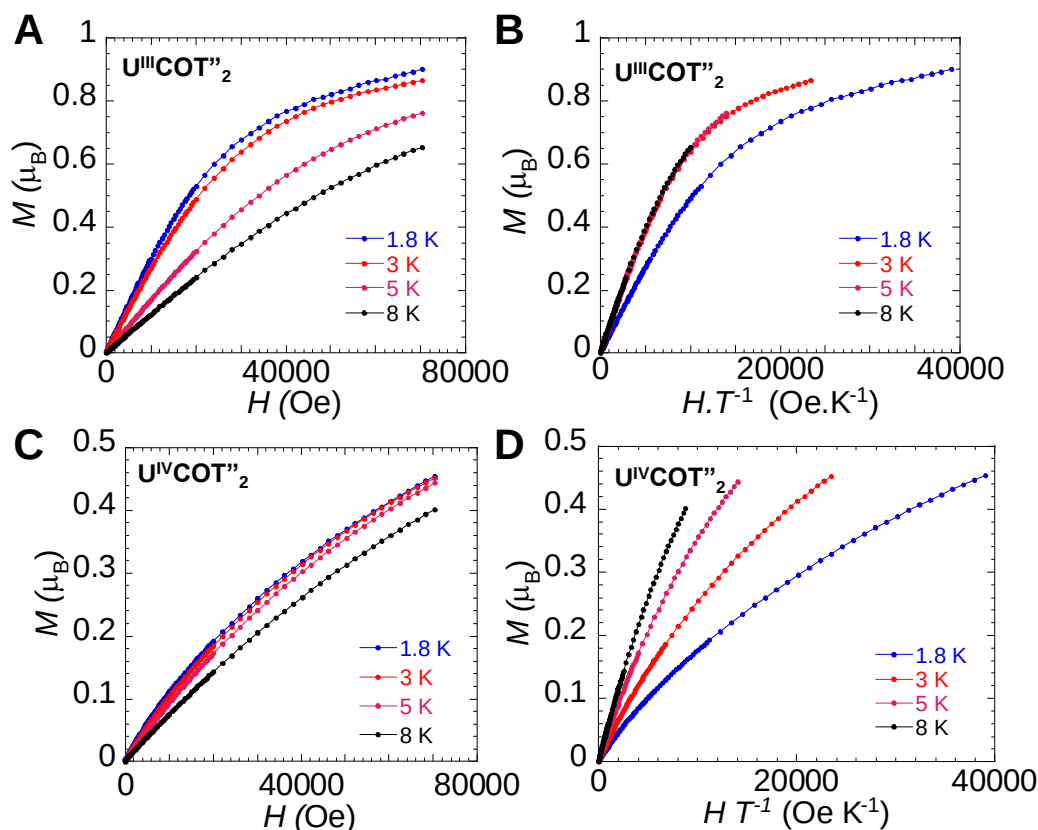


Figure 6.5. Field dependence of the magnetization (**right**) and reduced magnetization (**left**) for $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$ at the indicated temperatures.

The magnetization as a function of field in $\text{U}^{\text{III}}\text{COT}''_2$ (Figure 6.5) shows no saturation even at low temperature and high fields. The reduced magnetization plot shows non-superimposition of iso-temperature lines indicating significant magnetic anisotropy in $\text{U}^{\text{III}}\text{COT}''_2$. In the case of $\text{U}^{\text{IV}}\text{COT}''_2$, the vanishingly small values are most likely arising from the low-lying excited states which can be easily populated even at 1.8 K (Figure 6.5).

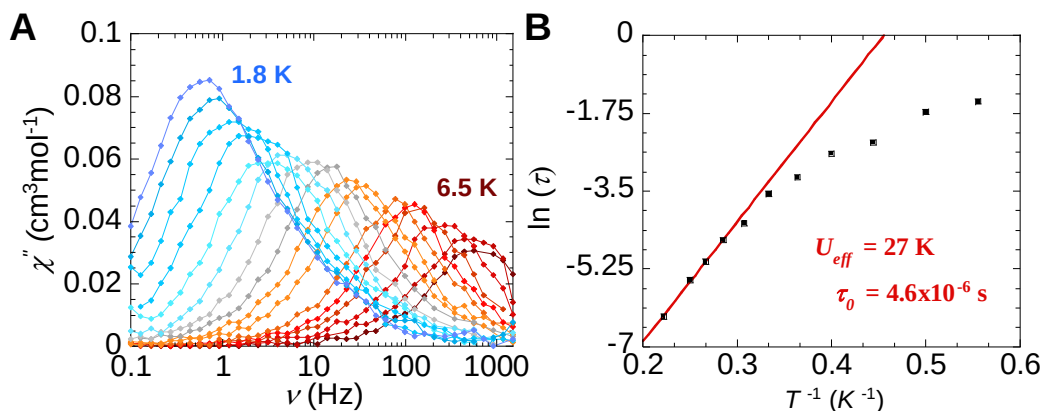


Figure 6.6. Dynamic magnetic data for $\text{U}^{\text{III}}\text{COT}''_2$. **(A)** Out-of-phase susceptibility (χ'') versus frequency (ν) for $\text{U}^{\text{III}}\text{COT}''_2$ in the temperature range 1.8-6.5 K under 1000 Oe applied dc field. **(B)** An Arrhenius plot of τ (the natural log of the relaxation time) versus inverse temperature. Relaxation times are extracted from the frequency-dependent peak maxima (χ'' data) using a Gaussian fit for each peak. The red line indicates the fit to the data and affords $U_{\text{eff}} = 27 \text{ K}$ (19 cm^{-1}) with $\tau_0 = 4.6 \times 10^{-6} \text{ s}$, determined via the Arrhenius equation.

To probe slow magnetic relaxation dynamics, ac susceptibility measurements were performed on $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$. Under a zero dc field, no ac signal was observed for $\text{U}^{\text{III}}\text{COT}''_2$ nor $\text{U}^{\text{IV}}\text{COT}''_2$. Under a 1000 Oe applied dc field frequency-dependent studies reveal a strong frequency-dependent in-phase (χ') and out-of-phase magnetic susceptibility (χ'') below 6.5 K (Figure 6.6) indicative of field-induced SIM behavior of $\text{U}^{\text{III}}\text{COT}''_2$. An effective energy barrier of 27 K (19 cm^{-1}) with a pre-exponential factor (τ_0) of $4.6 \times 10^{-6} \text{ s}$ was extracted from the ac data (Figure 6.6). This obtained value is within the range with other recently reported U^{III} field-induced SIMs ($U_{\text{eff}} = 4\text{-}31 \text{ K}$).⁵ In the case of $\text{U}^{\text{IV}}\text{COT}''_2$ no SIM behavior was observed once more

confirming the non-magnetic ground state of U^{IV} ions.¹⁷ The observed barrier for $U^{III}COT''_2$ is smaller than the one observed in our analogous $DyCOT''_2$ (Chapter 2) compound however it is important to emphasize that the inherent spin value for the Dy^{III} ion is much higher than for U^{III} compound. Thus it is reasonable to conclude that in the same ligand field environment the inherent magnetic anisotropy of the U^{III} ion may be significantly larger.

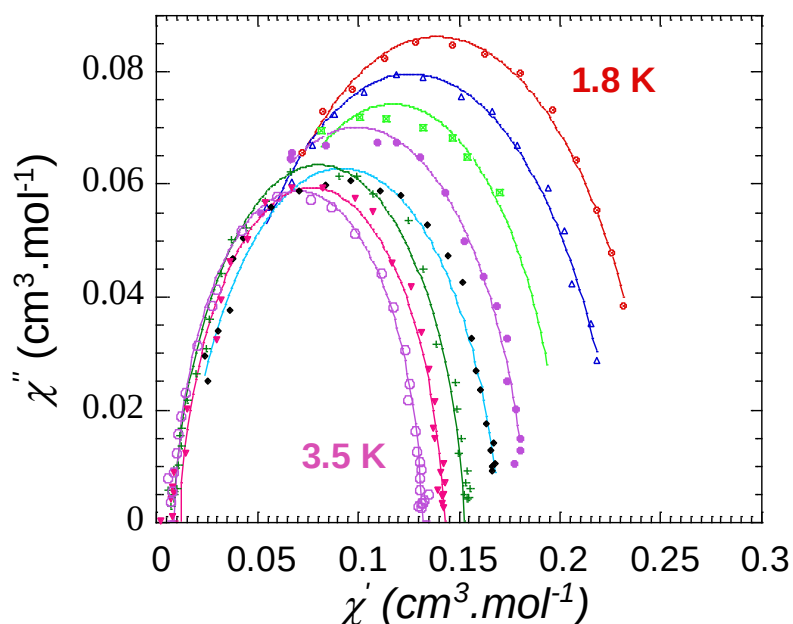


Figure. 6.7. Cole-Cole plot for ac susceptibility of $U^{III}COT''_2$. Experimental data points are represented by symbols and the solid line represents a fit to the data.

The frequency dependent ac susceptibility data was used to confirm only a single magnetic relaxation process was occurring in $U^{III}COT''_2$. The graphical representation of χ' vs. χ'' (Cole-Cole¹⁸ plot) between 1.8-3.5 K is given in Figure 6.7. Under 3.5 K large semicircles are obtained and the data is in good agreement with the generalized Debye model.¹⁹ Small α^2 values with a narrow distribution (0.033 to 0.22) confirm the magnetic susceptibility of $U^{III}COT''_2$ is unique to a single relaxation process.

6.3 Slow Magnetic Relaxation in Uranium and Neodymium Cyclooctatetraenyl Complexes

One potential advantage of utilizing actinides as molecular magnets is that spin orbit coupling increases with atomic mass (z), which may subsequently increase anisotropy.⁴ However, in order to understand the extent higher z has on the magnetic properties of SMMs, valence isoelectronic complexes need to be carefully examined. Only one direct comparison between isostructural and isoelectronic 4f/5f molecular magnets has been presented, where U^{III} and Nd^{III} trispyrazolylborate (Tp) complexes exhibited slow magnetic relaxation with $U_{\text{eff}} = 3.8$ and 2.8 cm^{-1} respectively under a 100 Oe applied dc field.^{5h} UTp_3 exhibited nearly twice the spin-orbit coupling interaction as NdTp_3 , however very little difference in magnetic performance, possibly due the mixing of low-lying excited states in both complexes.^{5h} Isostructural and valence isoelectronic NdCOT''_2 and $\text{U}^{\text{III}}\text{COT}''_2$ complexes provide the perfect opportunity to further probe the influence of atomic mass on SMM behavior.

6.3.1 Structural and Magnetic Comparison of NdCOT''_2 and $\text{U}^{\text{III}}\text{COT}''_2$

NdCOT''_2 is isostructural to $\text{U}^{\text{III}}\text{COT}''_2$, where both complexes crystalize in a triclinic $P-1$ space group. As expected, complexes NdCOT''_2 and $\text{U}^{\text{III}}\text{COT}''_2$ have very similar average metal-carbon distances of 2.74 Å and 2.73 Å respectively. A table containing the structural details of both NdCOT''_2 and $\text{U}^{\text{III}}\text{COT}''_2$, is provided in Table 6.5. Single crystal X-ray diffraction confirms that the complexes are essentially isomorphous.

As described above and in Chapter 2 (NdCOT''_2), no hysteresis was observed for $\text{U}^{\text{III}}\text{COT}''_2$ or NdCOT''_2 . To compare the slow relaxation of complexes $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 , all ac susceptibility measurements were performed under a small dc field (1000 Oe). Frequency dependent studies reveal a strong frequency dependent in-phase (χ') and out-of-phase magnetic susceptibility (χ'') in both $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 indicative of field induced SMM behaviour. Effective energy barriers of 27 K and 21 K

with pre-exponential factors of (τ_0) of 4.6×10^{-6} s and 5.5×10^{-5} s for $\text{U}^{\text{III}}\text{COT}''_2$ or NdCOT''_2 respectively were extracted from the ac data (Figure 6.8).

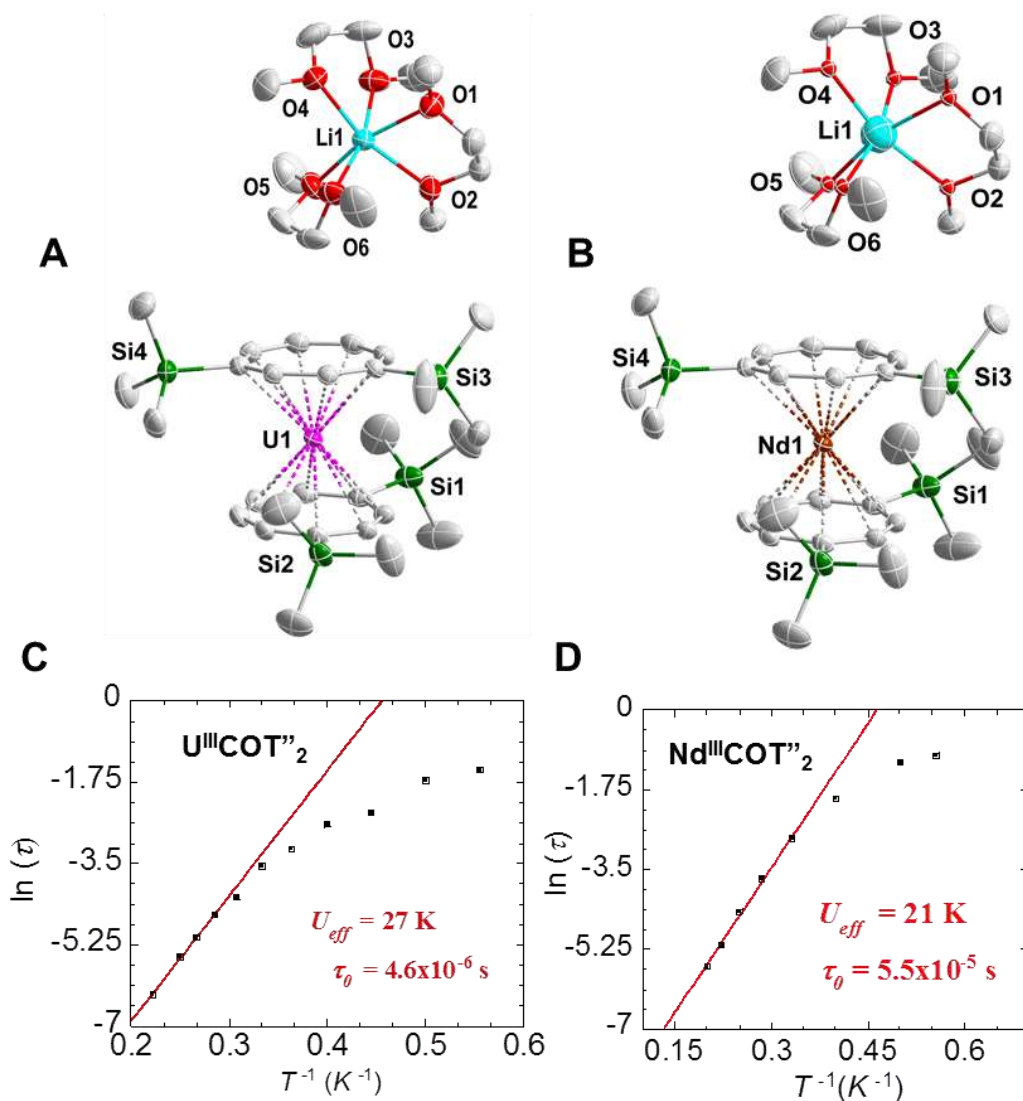


Figure 6.8. Solid state structures of $\text{U}^{\text{III}}\text{COT}''_2$ (A) and NdCOT''_2 (B). H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), green (Si), red (O), light blue (Li), pink (U^{III}), brown (Nd^{III}). C and D are the Arrhenius plots of τ versus inverse temperature for $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 respectively.

The observed relaxation barriers for both $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 are smaller than the one observed in our analogous DyCOT''_2 compound however it is important to

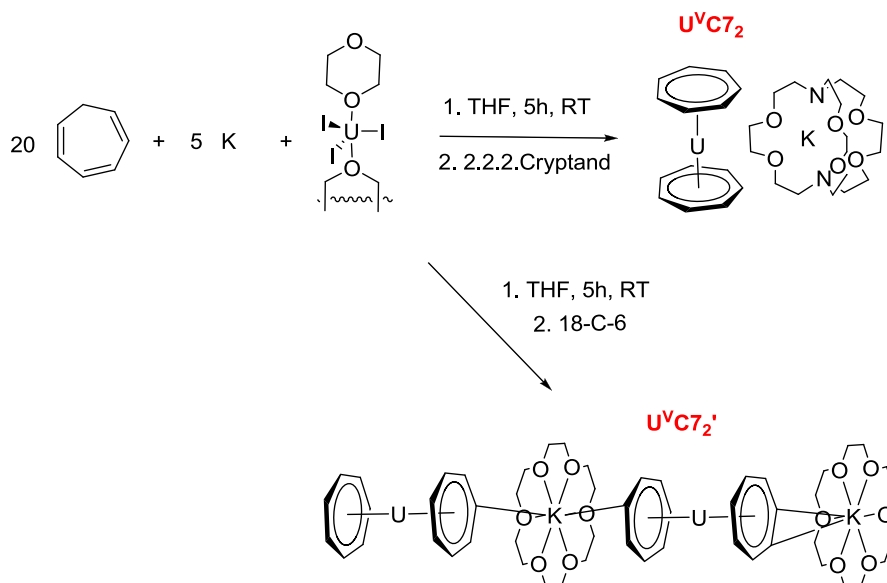
emphasize that the inherent spin value for the **DyCOT**"₂ ion is much higher than for the **U^{III}COT**"₂ and **NdCOT**"₂ compounds.^{2a} Thus from the direct comparison of isostructural and isoelectronic complexes of **U^{III}COT**"₂ and **NdCOT**"₂, it is reasonable to conclude that in the same ligand field environment the inherent magnetic anisotropy of the U^{III} ion is moderately larger. The enhanced magnetic properties of **U^{III}COT**"₂ compared to **NdCOT**"₂ further motivates the exploration of 5f SMMs.

6.4 Tailoring the Magnetic Properties of Uranium Sandwich Complexes through Oxidation State and Ring Modifications

One of the unique attributes of uranium magnetism is the synthetic availability to explore multiple oxidation states where complexes of U(II) through U(VI) are synthetically accessible. Liddle and Slagereen recently reported the first U(V) SMM where the complex [U(O)-(Tren^{TIPS})] (Tren^{TIPS} = (N(CH₂CH₂NSiPr₃)₃)³⁻), exhibited magnetic hysteresis at 1.8 K.²⁰ This report inspired us to explore the magnetic properties of U(V) sandwich complexes. We chose the aromatic cycloheptatrienyl ligand because of its high symmetry and potential 3⁻ charge which allows for easy access to U(V) sandwich-type complexes.²¹

6.4.1 Synthesis and Structure of Cycloheptatrienyl Sandwich Complexes

The synthetic strategy of **U^VC7₂** was **U^VC7₂'** was inspired by Ephritikhine²¹ where potassium metal is first used to reduce cycloheptatriene in THF followed by the in-situ addition of UI₃(dioxane)_{1.5}. **U^VC7₂** and **U^VC7₂'** were next crystallized following the addition of 2.2.2.Cryptand and 18-C-6 respectively. Single crystals of both complexes were crystallized in a concentrated THF/pentane solution. Structural details and refinement parameters are located in Table 6.4 and 6.5 respectively.



Scheme 6.2. Synthetic route to $\text{U}^{\text{V}}\text{C}_7_2$ and $\text{U}^{\text{V}}\text{C}_7'_2$ starting from a U(III) precursor.

Table 6.4. Selected interatomic distances of UC_7 and UC_7' obtained from single crystal X-ray analysis.

	UC_7	UC_7'
Tilt angle ($^\circ$)	5.33	2.46
U- $\text{C}_{7\text{centroid}}$ (a) ($\text{\AA}$)	1.995	2.003
U- $\text{C}_{7\text{centroid}}$ (b) ($\text{\AA}$)	1.998	2.002
Nearest K- C_{C_7} ($\text{\AA}$)	4.947	3.09(2)
Intermolecular U-U ($\text{\AA}$)	6.0365(6)	9.065
Intramolecular U-U ($\text{\AA}$)	--	11.057

$\text{U}^{\text{V}}\text{C}_7_2$ and $\text{U}^{\text{V}}\text{C}_7'_2$ crystallize in monoclinic P2/n and C2/m space groups respectively. Both structures consist of a uranium(V) ion bound η^7 to two cycloheptatrienyl rings where each ring has a formal -3 charge. Both complexes adopt a fairly symmetrical sandwich architecture with both uranium-COT(centroid) distances being almost identical (Table 6.4). $\text{U}^{\text{V}}\text{C}_7_2$ and $\text{U}^{\text{V}}\text{C}_7'_2$ differ by chelating agent used, 2.2.2 Cryptand or 18-C-6. In $\text{U}^{\text{V}}\text{C}_7_2$ the potassium counter ion is well separated from the sandwich structure thanks to the cage-like arrangement of 2.2.2 Cryptand. In contrast, the one dimensional arrangement of 18-C-6 allows for a K- C_{COT} interaction with the closest bond distance of 3.09 Å. This interaction allows for the chain-like arrangement in $\text{U}^{\text{V}}\text{C}_7'_2$ and most likely contributes to the difference in tilt angle of cycloheptatrienyl rings compared to $\text{U}^{\text{V}}\text{C}_7_2$.

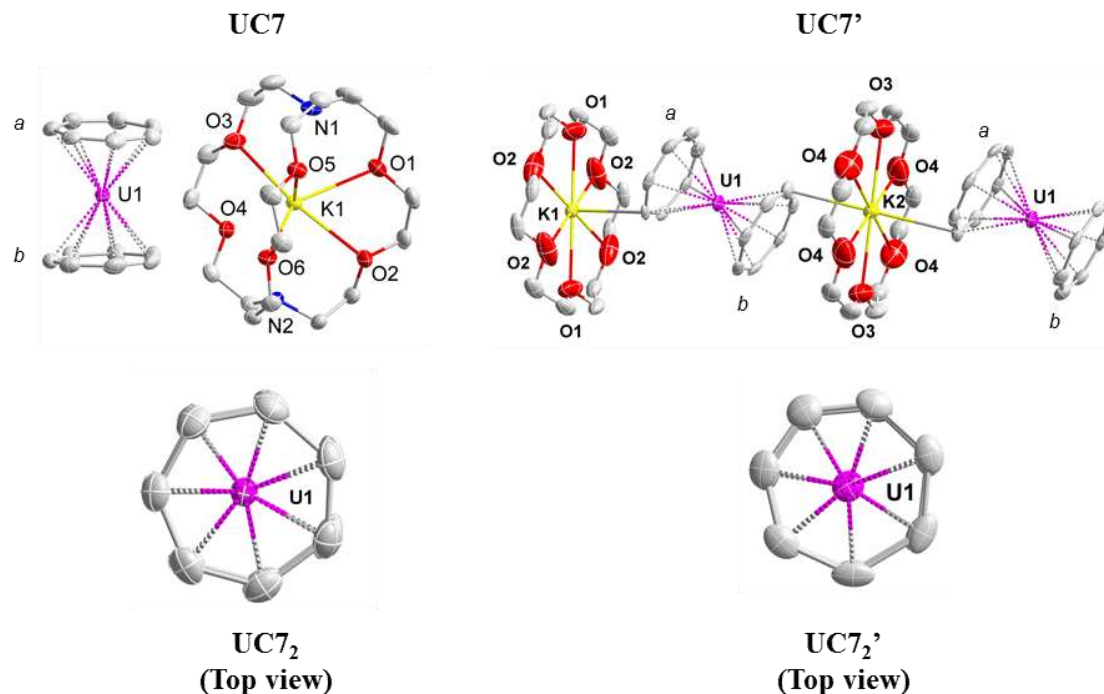


Figure 6.8. Solid state structures of $\text{U}^{\text{V}}\text{C}_7_2$ (left) and $\text{U}^{\text{V}}\text{C}_7_2'$ (right). The bottom images depict the eclipsed arrangement of Carbon atoms in both complexes. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Colour code: grey (C), red (O), yellow (K), pink (U^{V}).

6.4.2 Magnetic Properties of UC_7_2 and UC_7_2'

The magnetic susceptibility of UC_7_2 and UC_7_2' was investigated using both dc and ac SQUID measurements. The χT data for complexes UC_7_2 and UC_7_2' showed similar behavior, which is not surprising due to the close structural similarities. The room temperature χT values of $0.38 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for UC_7_2 , is within the range typically reported for uranium(V) mononuclear complexes.^{17e} The room temperature χT value for UC_7_2' ($0.98 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) is close to double that of UC_7_2 which is expected for a uranium(V) dimer. Both complexes show decreasing susceptibility with decreasing temperature with an additional low temperature deviation. Such behavior is similar to that observed with $\text{U}^{\text{III}}\text{COT}''_2$ and is indicative of significant anisotropy and/or antiferromagnetic U-U interactions.

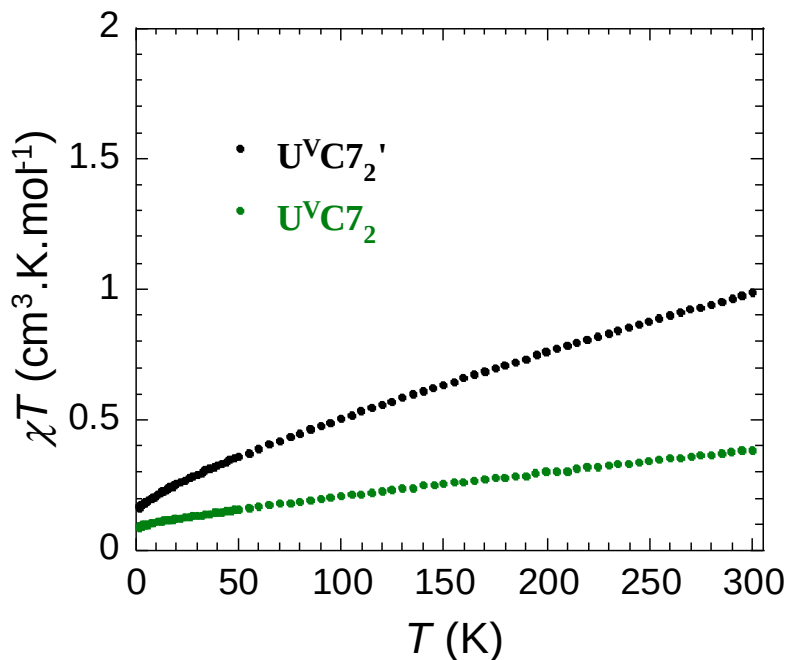


Figure 6.9. Left: Temperature dependence of the χT product under 0.1 T for UC7_2 and $\text{UC7}_2'$ with χ being the molar susceptibility per complex defined as M/H .

Ac susceptibility studies were performed on both UC7_2 and $\text{UC7}_2'$. Neither complex displayed an out-of-phase signal even under an applied dc field of 1000 Oe. The lack of slow relaxation in both UC7_2 and $\text{UC7}_2'$ is surprising considering they have a half-integer spin ground state, and are structurally similar to $\text{U}^{\text{III}}\text{COT}''_2$ which had an anisotropy barrier of 27 K.

6.5 Conclusions

This Chapter began with a discussion of two structurally similar sandwich complexes, $\text{U}^{\text{III}}\text{COT}''_2$ and $\text{U}^{\text{IV}}\text{COT}''_2$. Contrary to previous understanding, the comparative structural study reveals that the oxidation state of the metal ion has little effect on the (ring centroid)-U-(ring centroid) bend angle. Detailed DFT calculations reveal ligand-to-metal donation is stronger for the U^{IV} ion compared to U^{III} due to the additional vacant metal orbital. The observed difference in low temperature magnetic behavior is due to the presence of significant spin-orbit coupling in the U^{III} . The latter effect not only enhances the anisotropy of the system but also contributes towards the magnet-like behavior seen

in $\text{U}^{\text{III}}\text{COT}''_2$. Although this first U^{III} sandwich SIM has a smaller U_{eff} barrier than the structurally analogous $\text{Er}^{\text{III}}\text{COT}''_2$ complex (Chapter 2), the inherently larger anisotropy and covalent bonding of the U^{III} ion with the COT'' ligand suggests these mononuclear units may be ideal for the preparation of multinuclear SMMs. Multinuclear sandwich complexes, such as those discussed in Chapter 4, incorporating U^{III} instead, have the potential to lead to large energy barriers.

Next, we took advantage of the isostructurality of $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 , to determine if higher spin-orbit coupling found in heavy elements directly influences SMM properties. $\text{U}^{\text{III}}\text{COT}''_2$ and NdCOT''_2 have very similar SMM properties where $\text{U}^{\text{III}}\text{COT}''_2$ demonstrated a slightly higher energy barrier of $U_{\text{eff}} = 27 \text{ K}$ (19 cm^{-1}) ($U_{\text{eff}} = 21 \text{ K}$ (15 cm^{-1}) for NdCOT''_2). These results are in line with those presented by Long (UTp_3 and NdTp_3)^{5h} to show an emerging trend where isoelectronic heavier elements harvest slightly larger energy barriers. Even more interesting is that apart from a higher energy barrier, both studies showed valence isoelectronic complexes to have very similar magnetic behaviour. These results complement a recent approach by Long,^{5l} who speculate that an effective design strategy for actinide SMMs may be to first look at valence isoelectronic lanthanide complexes under the same ligand field.

A major challenge in the rational design of U^{III} SMMs is the limited predictability of how different ligand field environments will affect SMM properties. Coronado and Gait-Arino recently suggested complexes with ligand electron density along the symmetry axis as well as a trigonal prismatic geometry may provide ideal conditions to harness U^{III} SMM behavior.²² With this in mind we explored the low temperature magnetic properties of two highly symmetric U^{V} complexes, UC7_2 and $\text{UC7}_2'$. Neither complex displayed slow magnetic relaxation which is surprising both due to their high symmetry and sandwich-type arrangement. These results pinpoint one of the current challenges in uranium magnetism which is the limited predictability as discussed in detail in Chapter 1.

6.6 Experimental

General Considerations. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven dried before use (3h, 200°C). Hexanes, toluene, 1,4-dioxane, diethyl ether and dimethoxyethane (DME) were dried using activated alumina and stored over 3Å molecular sieves. Cycloheptatriene was purchased from Sigma Aldrich and was degassed prior to use. All other chemicals were purchased from Thermofisher Scientific or Strem and used without further purification. The $[\text{Li}_4(\text{COT})_2(\text{THF})_4]$ was synthesized using a previously published procedure.²³

Oxide-Free Uranium Metal Turnings. Similar to previously published procedures^{24,25} oxide-coated depleted uranium turnings (5 g) were immersed and swirled in 10 mL of concentrated HNO_3 to remove the oxide coating. The nitric acid was carefully decanted off [*Caution!* this reaction was very exothermic and produced NO_2 gas, this manipulation should be carried out in a well-ventilated fume hood]. The nitric acid washing was repeated two more times until the U turnings presented a shiny metallic surface. Turnings were next rinsed with de-ionized water (3 x 20 mL), after each washing the water was decanted off. Turnings were next rinsed with acetone (3 x 20 mL), dried on a Schlenk line under reduced pressure (0.03 Torr, 3 h) and were used immediately.

$\text{UI}_3(1,4\text{-dioxane})_{1.5}$. $\text{UI}_3(1,4\text{-dioxane})_{1.5}$ was prepared in a similar manner to that described by Kiplinger¹² by adding U^0 (1.25 g, 5.25 mmol) to a 20 mL scintillation vial containing freshly sublimed I_2 (1.8 g, 7.1 mmol) in 10 mL 1,4-dioxane. The reaction mixture was stirred at room temperature for 24 h during which time a dark purple suspension formed. The solution was decanted from the unreacted U^0 turnings and filtered through a medium-porosity fritted filter which collected a dark purple solid. The solid was washed thoroughly with diethyl ether (30 mL) and dried under vacuum to yield

$\text{UI}_3(1,4\text{-dioxane})_{1.5}$ in 95% yield. Selected IR data (cm^{-1}): 2992 (w) 2955 (br), 2899 (w), 1247 (s), 1063 (w) 1042 (w), 835 (s), 749 (w), 718 (w), 668 (w), 650 (w).

$\text{U}^{\text{III}}\text{COT}''_2$. $\text{UI}_3(1,4\text{-dioxane})_{1.5}$ (0.132 g, 0.17 mmol) was added to $[\text{Li}_4(\text{COT}'')_2(\text{THF})_4]$ (0.200 g, 0.25 mmol) in 5 mL of DME. The solution was stirred at room temperature and after 36 h the precipitate (LiCl) was immediately filtered off after the addition of 1 mL hexanes through a fine fritted funnel. Large purple block crystals were grown from a concentrated solution (1:1 DME:hexanes) providing $\text{U}^{\text{III}}\text{COT}''_2$ in 70% yield. Isolated crystals are extremely air and moisture sensitive. Selected IR data (cm^{-1}): 3006 (m), 2949 (br), 2829 (m), 1553 (w), 1472 (m), 1452 (m), 1407 (m), 1365 (w), 1246 (br), 1194 (m), 1161 (w), 1122 (m), 1085 (s), 1059 (m) 1036 (m), 980 (s), 931 (s), 902 (w), 834 (br), 791 (w), 743 (s), 719 (w), 675 (m), 635 (s).

$\text{U}^{\text{IV}}\text{COT}''_2$. To a 20 mL scintillation vial $\text{U}^{\text{III}}\text{COT}''_2$ (0.100 g, 0.091 mmol) was added to FeCl_2 (0.006 g, 0.045 mmol) in 10 mL toluene. The resulting solution was refluxed for 8 h, filtered through a fine fritted funnel to remove Fe^0 and then concentrated to yield crystals of $\text{U}^{\text{IV}}\text{COT}''_2$ (40% yield) suitable for X-ray diffraction. Selected IR data(cm^{-1}): 2993 (m), 2954 (br), 2896 (m), 1598 (m), 1494 (w), 1446 (m), 1405 (s), 1317 (m), 1247 (s), 1221 (w), 1064 (m), 1038 (s), 979 (m), 939 (m), 902 (w), 834 (br), 790 (w), 739 (m), 719 (w), 689 (w), 651 (w), 637 (m). Anal. Calc. for $\text{C}_{40}\text{H}_{78}\text{LiO}_6\text{Si}_4\text{U}$ ($M_r = 781.12$): C, 48.43; H, 6.71. Found: C, 48.01; H, 7.52.

UC7_2 . Excess cycloheptatriene (0.732 g, 7.8 mmol) was added to a cold (-37°) solution of $\text{UI}_3(\text{dioxane})_{1.5}$ (300mg, 0.40 mmol), freshly cut potassium (78mg, 2.0 mmol) and THF (15mL) in a 20 mL scintillation vial. The reaction mixture was stirred for 4 h at room temperature, and then filtered to give a dark purple solution. UC7_2 was crystallized from the addition of 2.2.2.cryptand (150mg, 0.39 mmol) to the concentrated THF solution and slow diffusion with pentane. (70% yield). ^1H NMR, 300 MHz THF- d_8 (-40 , bs).

UC7₂'. **Similar to UC7₂**, Excess cycloheptatriene (0.732 g, 7.8 mmol) was added to a cold (-37°) solution of UI₃(dioxane)_{1.5} (300mg, 0.40 mmol), freshly cut potassium (78mg, 2.0 mmol) and THF (15mL) in a 20 mL scintillation vial. The reaction mixture was stirred for 4 h at room temperature, and then filtered to give a dark purple solution. **UC7₂'** was crystallized from the addition of 18-C-6 (105mg, 0.39 mmol) to the concentrated THF solution and slow diffusion with pentane. (55% yield).

X-ray Crystallography. Single crystals of **U^{III}COT''₂** were grown from a concentrated solution of 1:1 DME:hexanes at room temperature, crystals were thoroughly washed with hexanes before use. Single crystals of **U^{IV}COT''₂** were grown from a concentrated toluene solution and the resulting large green block crystals were thoroughly washed with cold cyclopentane. Single crystals of both **UC7₂** and **UC7₂'** were grown by slow diffusion with THF/hexanes. For all complexes, a suitable prism shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).²⁶ The crystal structure was solved and refined using the SHELXTL²⁷ program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. The published crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 939534 (**U^{III}COT''₂**), and 992620 (**U^{IV}COT''₂**).

Table 6.5. Refinement details.

	$\text{U}^{\text{III}}\text{COT}''_2$	NdCOT''_2	$\text{U}^{\text{IV}}\text{COT}''_2$	UC7_2	$\text{UC7}_2'$
CCDC	939534	992620	939701	--	--
M_r (g/mol)	1012.35	918.56	781.12	1002.08	1510.54
Formula	$\text{C}_{40}\text{H}_{78}\text{LiO}_6\text{Si}_4\text{U}$	$\text{C}_{40}\text{H}_{78}\text{LiO}_6\text{Si}_4\text{Nd}$	$\text{C}_{31.50}\text{H}_{52}\text{Si}_4\text{U}$	$\text{C}_{45}\text{H}_{60}\text{KN}_2\text{O}_6\text{U}$	$\text{U}_2\text{K}_3\text{O}_{12}\text{C}_{54}\text{H}_{76}$
T(K)	200(2)	200(2)	200(2)	200(2)	200(2)
γ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P -1	P -1	P2/c	P2/n	C2/m
a (Å)	11.6442(6)	11.6313(2)	18.7988(3)	15.3273(5)	11.9933(5)
b (Å)	12.3067(6)	12.3221(3)	10.5392(2)	11.2000(4)	13.5975(5)
c (Å)	18.4598(9)	18.4994(4)	18.3902(3)	19.7382(7)	16.8729(7)
α (deg)	99.136(3)	99.1930(10)	90.00	90.00	90.00
β (deg)	102.301(2)	102.2920(10)	100.0160(10)	95.4650(19)	98.2717(15)
γ (deg)	98.987(2)	99.0690(10)	90.00	90.00	90.00
V (Å³)	2501.8(2)	2506.33(9)	3588.01(11)	3373.0(2)	2722.99
ρ_{calc} (cm⁻³)	1.344	1.217	1.446	1.973	1.765
Z	2	2	4	4	5
Reflections collected	45273	39940	32285	39709	21436
Goodness of fit	1.035	1.082	1.012	1.001	1.007
$R1$	0.0202	0.0260	0.0366	0.0220	0.0505
$wR2$	0.0516	0.0631	0.0634	0.0494	0.1085
Reflections with $I > 2\sigma(I)$	11446	11279	8352	7137	2964

Computational Details.¹⁶ Density functional theory (DFT) calculations were carried out with the Gaussian '09 software (revision A.02)²⁸ using the spin-unrestricted molecular orbital formalism. The triple-zeta TZVP basis set²⁹ for C and H atoms and the SDD basis set and effective core potential³⁰ for U were used. The calculations employed the B3LYP exchange-correlation functional.³¹ The wavefunction stability checks were performed to make sure that the calculated wavefunction corresponds to the electronic ground state (the *stable* keyword in Gaussian). Atomic spin densities, charges, Mayer bond orders,³² orbital compositions and changes in fragment orbital populations³³ were calculated using the AOMix software³⁴ and the Mulliken population analysis (MPA).³⁵

Magnetism. The magnetic susceptibility measurements for all complexes were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Dc analyses were performed on polycrystalline samples sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and temperatures between 1.8 and 300 K. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz and dc fields ranging from 0 to 1600 Oe. Magnetization data was collected at 100 K to check for ferromagnetic impurities that were absent in all samples. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

6.7 References and Notes

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Chapter 7

Perspectives and Future Directions

The greatest challenge facing the research field of SMMs is increasing the T_B of these molecular systems so that they can be realistically utilized in applications. In recent years, the majority of contributions have focused on trying to understand what dictates the origin of slow magnetic relaxation in different complexes.¹ Despite the vast progression in this area, there has been very little advancement in the observed maximum T_B . The goal of this graduate work was to exploit the most recent design principles and synthesize new SMMs with predictably high T_B utilizing a sophisticated synthetic approach.

When this project began, the only method employed in synthesizing SMMs was the use of coordination chemistry. We saw organometallic chemistry as an unexplored opportunity to create new SMMs with a high degree of synthetic control. The idea behind utilizing sandwich complexes was inspired by Naoto Ishikawa's collection of lanthanide-phthalocyaninate (Pc) SMMs.² Motivated by the use of a triple-decker sandwich-type architecture, we speculated that replacing the nitrogen-based bridging ligand (used in Pc SMMs) with an aromatic carbon ligand such as a COT ring could result in a strong J interaction (and potentially high T_B). Our approach was methodical, where we first examined the SIM behaviour of a series of isostructural complexes with the same COT'' ligand but with a wide range of metal ions, including Ce^{III}, Nd^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III} and Yb^{III} (Chapter 2).³ Next, we took the metals exhibiting the strongest SMM properties with the COT'' ligand (Er and Dy) and fine-tuned the ligand to maximize the T_B of these monomers by increasing the symmetry (Chapter 3).⁴ In Chapters 4 and 5 we investigated different coupling strategies to try and enhance the SMM properties of the double-decker monomers by increasing the total spin of the complex (through increasing the number of metal centers).^{3a,5} Overall, one of our strategies was successful where we demonstrated an unparalleled 4 K increase between the T_B of **ErCOT''**₂ (Chapter 2) and

the triple decker $\text{Er}_2\text{COT}''_3$ complex (Chapter 4).⁶ Lastly, we investigated the SMM properties of numerous uranium sandwich complexes. Our results suggest that this is not the appropriate ligand environment to harness SMM behaviour in uranium.⁷ The research area surrounding uranium SMMs is still in its infancy, and more ligands with different symmetry environments need to be explored before determining the viability of high T_B uranium SMMs.

In Chapters 2 and 3, the high T_B observed in ErCOT''_2 and ErCOT_2 was quite surprising considering the vast majority of reported Er^{III} complexes either show very weak SMM behaviour or no SMM behaviour at all. Only one other Er^{III} complex has displayed a T_B higher than a few kelvin, and it is a heteroleptic sandwich-type complex with mixed Cp^* (pentamethylcyclopentadienyl) and COT ligands.⁸ A detailed *ab initio* study by Rajaraman⁹ recently shed light on this vast discrepancy by carefully investigating 4 complexes; three high T_B Er^{III} sandwich complexes $(\text{Cp}^*)\text{Er}(\text{COT})$,⁸ $[\text{Er}(\text{COT}''_2)]^-$,^{3b} $[\text{Er}(\text{COT})_2]^-$,⁴ and a coordination complex $[\text{Er}(\text{thd})_3(\text{bath})]$ (thd = (2,2,6,6-tetramethyl-3,5-heptanedionate) and bath = bathophenanthroline)¹⁰ (Figure 7.1).

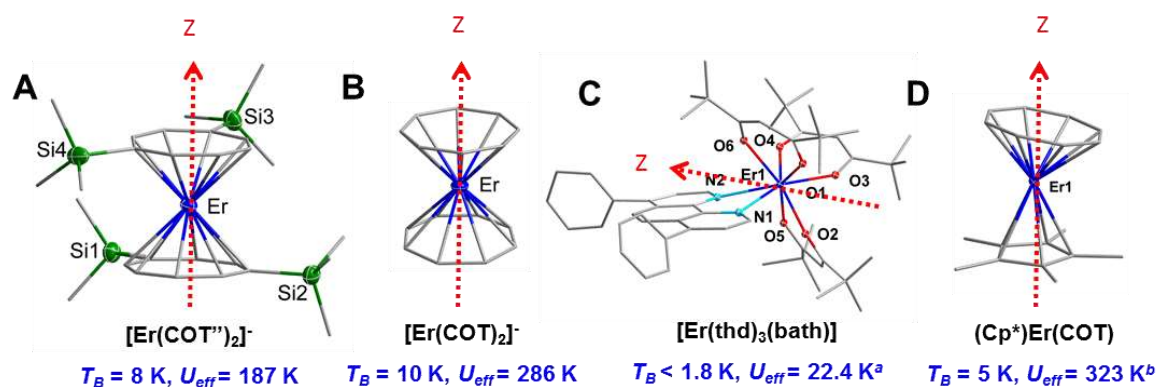
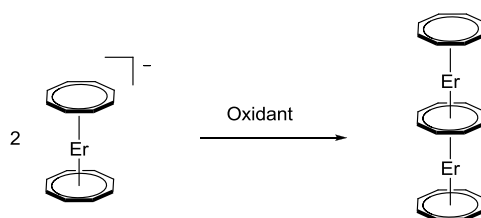


Figure 7.1. Solid state structures of $(\text{Cp}^*)\text{Er}(\text{COT})$, $[\text{Er}(\text{COT}''_2)]^-$, $[\text{Er}(\text{COT})_2]^-$ and $[\text{Er}(\text{thd})_3(\text{bath})]$, with the approximate orientation of the g-tensor of the ground Kramers doublet graphically illustrated (red arrow). H atoms are omitted for clarity. Colour code: blue (Er), grey (C), green (Si), red (O), light blue (N). *a* = The U_{eff} was obtained under a 0.05 T dc applied field, *b* = a second relaxation barrier was also observed with $U_{\text{eff}} = 197 \text{ K}$ due to a second conformer in the packing structure. Adapted from ref 9.

In complexes **A**, **B** and **D** the ground state anisotropy axis is in line with the principal symmetry axis, where in **C**, the main anisotropy axis is directed towards one of the nitrogen donors. The high U_{eff} values observed in **A** and **B** are due to the high symmetry environment around the metal which causes magnetic relaxation via the 2nd excited state in these complexes.⁹ This is a desirable but unusual property and not the case in the lower symmetry **C** and **D** complexes. In **D**, the large bend angle between Cp* and COT rings lowers the symmetry environment and results in electron repulsion along the anisotropy axis. **D** is a low symmetry complex with transverse anisotropy resulting in ground state QTM which is consistent with the observed field-induced SMM behaviour reported for this complex.¹⁰ To fully maximize the SMM behaviour of a discrete molecule, it is essential to both suppress QTM, and obtain magnetic relaxation beyond just the first excited state. This study clearly illustrates that two factors are extremely important in achieving this goal. First, high point symmetry is essential as it causes co-linearity between the anisotropy axes of Kramers doublets which facilitates magnetic relaxation beyond the first excited state. Equally as important is minimizing electron repulsion along the main magnetic axis of a complex. In context to this thesis, these principles can be applied to explain the high T_B observed in **ErCOT₂** ($T_B = 10$ K, Chapter 3). In addition to the high symmetry, the breadth of the COT ring allowed for minimal electrostatic repulsion along the symmetry axis, which is particularly optimal for a prolate-type metal ion such as Er^{III} .¹¹



Scheme 7.1. Proposed synthetic scheme to a high symmetry lanthanide linear triple decker sandwich complex.

The Er^{III} complexes in this thesis highlight both the importance of symmetry as well as the need for strong Ln-Ln interactions in order to achieve a substantial T_B . Chapters 2-5 provide the groundwork for Er^{III} -COT magnetism, as well as identify some potential areas for future expansion of this work. For example, the T_B of **Er₂COT''₃** in solution is

14 K and *ab initio* calculations of the Dy^{III} analog suggest this can be enhanced by removing the TMS groups from the ligand.^{3a} Synthetically this is quite challenging due to the predictably low solubility of this neutral complex. However, one plausible synthetic route is to use a similar building block approach as was used to obtain **Er₂COT''₃**, except start with **ErCOT₂** as the precursor (Scheme 7.1). The next obvious route to further improve the T_B of Er^{III}-COT complexes is simply to add more decks to the triple decker **Er₂COT''₃**. A 4 K increase in T_B was observed between **Er₂COT''₃** and **Er₂COT'''₃**, therefore it is plausible that increasing the number of decks in this complex could have a strong impact on T_B .

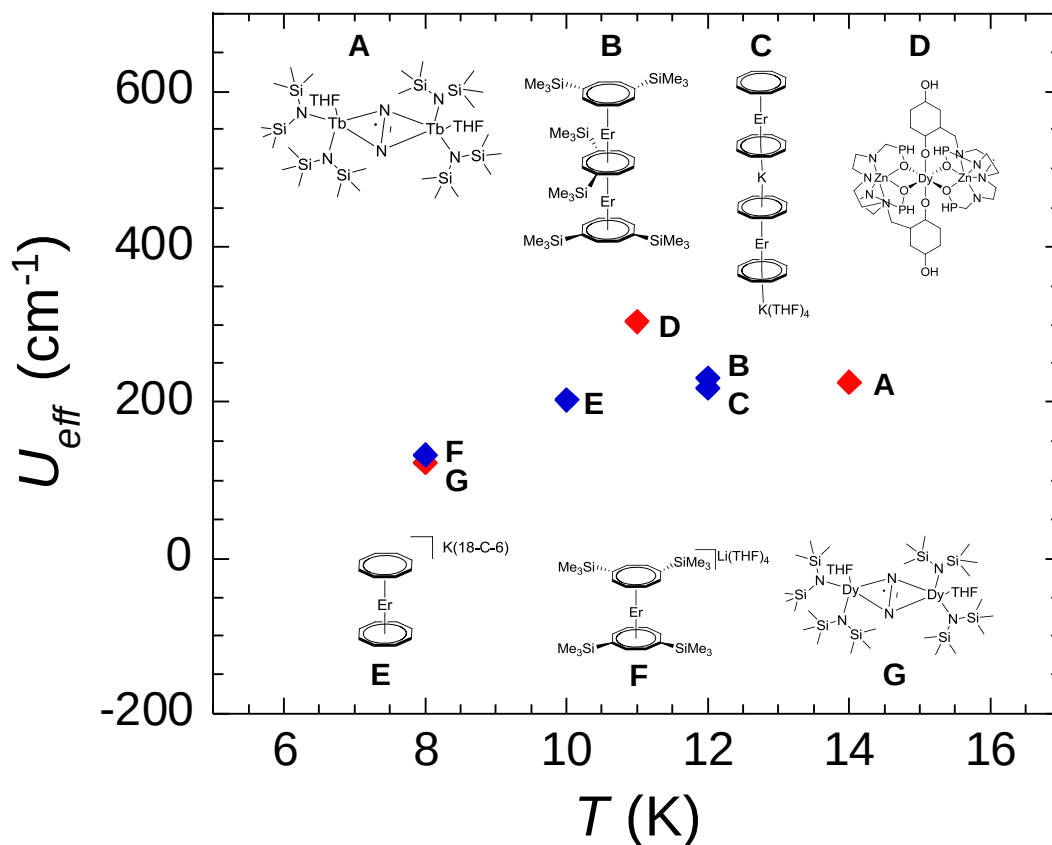


Figure 7.2. Highest recorded hysteresis temperature vs. anisotropy barrier of reported SMMs. Hysteresis is defined by a measurable coercive field. Blue diamonds indicate complexes in this thesis,³⁻⁵ and red diamonds indicate other reported SMMs.¹²⁻¹⁴ Note: complex E was simultaneously reported by the Ref. 15.

The fate of utilizing SMMs in real applications is dependent on a significant jump in T_B . No current strategy appears to provide an obvious solution, therefore it is essential to introduce new strategies into SMM design. There is much to be learned from analysing

the complexes which exhibit the highest reported T_B 's (figure 7.2). The most striking observation is the number of single-ion complexes that are among the highest performing SMMs. The next notable trend is the strong benefit of radical bridging ligands. In such complexes, placing a radical in between two metals forces a (usually strong) ferromagnetic interaction between the metals. However, it is evident that not all radical-bridged Ln^{III} complexes exhibit high T_B , which means ligand field is equally as important as a strong Ln-Ln interaction. Figure 7.2 also illustrates both the strength and the limitation of utilizing lanthanide ions. Firstly, the only metals that compose the highest T_B complexes are lanthanides. The majority of such complexes, however, exhibit a high T_B due to single ion effects. This thesis clearly demonstrates that high T_B single-ion complexes can be enhanced using a building block strategy as long as the change in symmetry is minimized. $\text{Er}_2\text{COT}''_3$ is the first neutral complexes to rival the high blocking temperature of the best radical bridged SMMs, and this is due to the aromatic super-exchange pathway. The logical progression is the unexplored avenue of combining the two best coupling strategies. Developing highly symmetric multi-deck sandwich complexes containing a bridging radical may be the unexplored solution this field requires to achieving more functional T_B values.

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