Synthesis and Characterisation of Lanthanide Complexes as Possible Single-Molecule Magnets

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Synthesis and Characterisation of Lanthanide Complexes as Possible Single-Molecule

Magnets

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List of Abbreviations and Physical Constants

μ-	a bridging ligand
μ _n -	a ligand bridging <i>n</i> number of metal centres
η _n	a ligand coordinating via <i>n</i> donor atoms
τ	lifetime
τ ₀	attempt time
V	frequency
Хм	magnetic susceptibility
X	in-field magnetic susceptibility
Χ"	out-of-field magnetic susceptibility
a.c.	alternating current
Bu	<i>n</i> -butyl
COSY	correlation spectroscopy (in NMR)
СОТ	cyclooctatetraene
Ср	cyclopentadienyl
Cp'	methylcyclopentadiene
Cp*	pentamethylcyclopentadiene
Су	cyclohexyl

d	doublet NMR peak
d.c.	direct current
dipp	2,6-diisopropylphenyl
dmpe	1,2-bis(dimethylphosphino)ethane
DOSY	diffusion ordered NMR spectroscopy
Elem. Anal.	elemental analysis
EPR	electron paramagnetic resonance
Et	ethyl
g	Landé g-factor
н	magnetic field
НМВС	heteronuclear multiple bond correlation NMR spectroscopy
HSQC	heteronuclear single quantum coherence NMR spectroscopy
ⁱ Pr	isopropoxide
J	coupling constant
k _B	Boltzmann constant
Ln	a rare earth element (yttrium, scandium, lanthanum and the lanthanides)
М	a metal
Me	methyl

Mes	mesityl
mյ	magnetic sub-state
n%Ln@YR	a magnetically dilute species where n% of Y sites are replaced by Ln
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
OAc	acetonate
OEt ₂	diethyl ether
Рс	phthalocyaninate
Ph	phenyl
ру	pyridine
quad	quadruplet NMR peak
R	a generic substituent
r.t.	room temperature
S	singlet NMR peak
S	spin
SCF	Self-Consistent Field
SMM	single molecule magnet
t	triplet NMR peak

Т	temperature
Τ _Β	magnetic blocking temperature
^t Bu	tert-butoxide
THF	tetrahydrofuran
tmeda	tetramethylethylenediamine
tmmeH₃	tris(mercaptomethyl)ethane
U _{eff}	effective energy barrier to reversal of magnetisation
UV-vis	ultraviolet to visible
VT	variable temperature
х	a halide

List of Compounds

1.1 $[Tb_{2}{N(SiMe_{3})_{2}}_{4}(thf)_{2}(N_{2})]^{-}$ $[Dy_4K_2O(O^tBu)_{12}]$ 1.2 $[Dy_5O(O^iPr)_{13}]$ 1.3 1.4 [(Cp'₂Dy)(µ-PHMes)]₃ 1.5 [(Cp'₂Dy)(µ-AsHMes)]₃ 1.6 $[(Cp'_2Dy)(\mu-SSiPh_3)]_2$ 1.7 $[Li(Cp'_2Dy)_3(\mu-PMes)_3][Li(THF)_4]_2$ 1.8 [Cp'₃Dy(H₂PMes)] 1.9 [(Cp'₂Dy)₃(µ-AsMes)₃Li][Li(THF)₄]₂ 1.10 [(Cp'₂Dy)(µ-SeMes)]₃ 2.1 $[Cp'_{3}Gd(H_{2}PMes)]$ 2.2 $[Cp'_3Er(H_2PMes)]$ 2.3 [(Cp'₂Gd)(µ-PHMes)]₃ 2.4 [(Cp'₂Er)(µ-PHMes)]₃ 3.1 [(Cp'₂Y)₃({µ-SCH2}₃CMe)]₄ 3.2 $[(Cp'_{2}Gd)_{3}({\mu-SCH_{2}}_{3}CMe)]_{4}$ 3.3 [(Cp'₂Dy)₃({µ-SCH₂}₃CMe)]₄

- **4.1** $[(Cp'_2Y)(\mu$ -SCH₂{C₄H₇S₂})]₂
- **4.2** $[(Cp'_2Gd)(\mu-SCH_2\{C_4H_7S_2\})]_2$
- **4.3** $[(Cp'_2Dy)(\mu-SCH_2\{C_4H_7S_2\})]_2$
- **4.4** 10%Dy@[(Cp'₂Y)(µ-SCH₂{C₄H₇S₂})]₂
- 5.1 [Dy₂K₃(OSiMe₃)₉]
- 5.2 [Dy₂K₄(OSiMe₃)₁₀]
- 5.3 [Y₄K₆O₆(OSiMe₃)₁₂]⁶⁻
- 5.4 [Dy₃K₈O₃(OSiMe₃)₁₂]⁻

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ABSTRACT OF THESIS, submitted by: Sara R. King to **THE UNIVERSITY OF MANCHESTER** for the degree of **DOCTOR OF PHILOSOPHY** and entitled: **Synthesis and Characterisation of Lanthanide Complexes as Possible Single-Molecule Magnets**. Month and Year of Submission: March 2016.

A range of lanthanide compounds incorporating soft bridging ligands or alkoxide ligands have been synthesised and their magnetic properties investigated. These two classes of compound have shown promise as single molecule magnets but have not been widely studied; this thesis aims to expand on this area of research. Softer bridging ligands are found to slightly increase superexchange interactions between metal centres compared to harder bridging ligands.

The introduction to this thesis covers the basic properties of the lanthanides, paying special attention to their chemistry with soft donor ligands and alkoxide ligands. Also included is an introduction to the field of single-molecule magnetism and the role of lanthanide complexes in the study of this behaviour.

In Chapter 2, four complexes are reported: the phosphine adducts $[Cp'_{3}Ln(H_{2}PMes)]$ and the phosphide-bridged trimers $[(Cp'_{2})Ln(\mu-PHMes)]_{3}$ (Ln = Er, Gd). Their structures and magnetic properties are characterised.

In Chapter 3, the novel dodecametallic thiolate-bridged lanthanide macrocycles $[(Cp'_{2}Ln)_{3}({\mu-SCH_{2}}_{3}CMe)]_{4}$ (Ln = Dy, Y, Gd) are reported and characterised by X-ray crystallography, NMR spectroscopy and magnetometry. $[(Cp'_{2}Dy)_{3}({\mu-SCH_{2}}_{3}CMe)]_{4}$ is shown to be a single-molecule magnet with $U_{eff} = 69 \text{ cm}^{-1}$.

In Chapter 4, the novel thiolate-bridged lanthanide dimers $[Cp'_{2}Ln(\mu-SCH_{2}\{C_{4}H_{7}S_{2}\})]_{2}$ (Ln = Dy, Y, Gd) are reported, showing sulfur-sulfur bonding leading to ring cyclisation of the bridging ligand $[MeC(CH_{2}S)_{3}]^{3^{-}}$. These complexes are characterised by X-ray crystallography, NMR spectroscopy and magnetometry. Extra NMR spectroscopic studies were performed to investigate the mechanism of ring closure on the bridging ligand. $[Cp'_{2}Dy(\mu-SCH_{2}\{C_{4}H_{7}S_{2}\})]_{2}$ is shown to be a single-molecule magnet with $U_{eff} = 87 \text{ cm}^{-1}$.

In Chapter 5, four new lanthanide siloxide clusters incorporating alkali metals are reported: the trigonal bipyramidal $[Dy_2K_3(OSiMe_3)_9]$; the octahedral $[Dy_2K_4(OSiMe_3)_{10}]$; the bi-capped cuboid $[Y_4K_6O_6(OSiMe_3)_{12}]^{6-}$; and the $[Dy_3K_8O_3(OSiMe_3)_{12}]^{-}$ 'burger' cluster. All clusters are structurally characterised by X-ray crystallography and $[Dy_2K_4(OSiMe_3)_{10}]$ is magnetically characterised. The synthetic rationalisation for formation of these diverse structures is investigated.

Declaration

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1. Introduction to Lanthanides and Single Molecule Magnetism

1.1. Chemistry of the Lanthanides

The lanthanides consist of the elements numbered 57 to 70 in the periodic table, which make up the first row of the *f* block elements. [1] Lanthanides generally have very similar chemistry to one another because of the behaviour of the 4*f* orbitals, so they can easily be considered as a group. Outside of the pure metal, lanthanides occur almost solely in the +3 oxidation state. While all lanthanides have now been reported in the +2 oxidation state, only Yb^{II}, Sm^{II} and Eu^{II} are particularly stable. Tm^{II}, Dy^{II} and Nd^{II} can be isolated as Lnl₂, but they are extremely reducing. Other Ln^{II} species are extremely unstable and have only recently been reported as [Cp(SiMe₃)]⁻ derivatives. [2] Likewise, Ce^{IV} is the only commonly encountered Ln^{IV} ion, in compounds such as CeO₂ or Ce(COT)₂. [3]



Figure 1.1: Ionisation energies of the lanthanides, taken from [5].

The stability of Ln oxidation states is neatly explained by the ionisation energies of the lanthanides (Figure 1.1). The relative stability of Sm^{II}, Eu^{II} and Yb^{II} are due to the high value of the third ionisation energy compared to other lanthanides, and cerium has a much lower fourth ionisation energy than any of the other lanthanides, explaining why it is the only one to adopt the +4 oxidation state. These trends can in turn be explained by the electronic structures of the lanthanides. Lanthanide metals commonly adopt the [Xe]4 $f^{n}6s^{2}$ electronic structure, with a few (Ce, Gd, Lu) taking the form [Xe]4 $f^{n}5d^{1}6s^{2}$ in order to keep the *f* electron count favourable; empty (La⁰; [Xe]5 $d^{1}6s^{2}$), and half-filled (Gd⁰; [Xe]4 $f^{7}5d^{1}6s^{2}$) orbitals are especially stable, and Lu has no choice ([Xe]4 $f^{14}5d^{1}6s^{2}$). [3] When ionising, the lanthanides will lose the *d* and *s* electrons first, as they sit further from the nucleus than the core-like *f* electrons (Figure 1.2), and take the [Xe]4 f^{m} electronic structure. Again, the relative stability of empty and half-filled shells can explain why certain lanthanides are more likely to adopt the +2 or +4 oxidation states: Ce^{IV}, [Xe], [3] removing the fourth electron gives an especially stable full shell configuration; Eu^{III}, [Xe]4 f^{7} , removing the third electron will disrupt the favourable half-filled orbital and is therefore more difficult; Yb^{III}, [Xe]4 f^{14} , again, removing a third electron will disrupt the filled *f* orbitals and is energetically unfavourable. Due to relativistic effects [4] and the effect of increasing nuclear charge on the poorly-shielded outer electron shells, the ionic radius of the lanthanides decreases across the series, and this is called the 'lanthanide contraction'. [5]



Figure 1.2: Electron probability distribution of the 4*f*, 5*d* and 6*s* orbitals as a function of distance from the nucleus. [7]

The transition metals yttrium and scandium are also rare earth elements, as their chemistry and physical properties are extremely similar to the lanthanides. This has some interesting uses, which will become apparent throughout this work. Y^{III} and Dy^{III} in particular tend to be very alike in their reactivity and in the geometry adopted by comparable complexes, due to the similarity of the ionic radii of the two metals (9-coordinate Dy^{III} , 108 pm; Y^{III} 107 pm). [6]

The 4*f* orbitals are held closely to the core of the lanthanides (Figure 1.2), [7] and so their bonding has very little covalent character. The 6*s* and 5*d* orbitals extend further, but are pulled closer into the nucleus with increasing atomic number as the 4*f* orbitals are poorly shielding, giving a smaller ionic radius and higher charge density. Lanthanides are therefore very hard metals and prefer to bond with hard Lewis bases. [5] They are extremely oxophilic, and will prefer to coordinate to water than to many of the more structurally or chemically interesting ligands explored within this work. Anhydrous anaerobic conditions are therefore essential for lanthanide organometallic chemistry. They are also prone to form insoluble hydroxides in the presence of water. The oxides are easily formed by thermal decomposition of coordination compounds (the temperature at which this happens depends upon the stability of the complex), and can react further with CO₂ or water in air to form carbonates and hydroxides. [8]

Bonds to lanthanides are highly ionic and so, unlike for transition metals and main group elements, the bonding geometry is not constrained by the need for orbital overlap. Ligand geometry is therefore controlled mainly by steric effects, and lanthanides often have a large number of coordinating groups; eight- and nine-coordinate lanthanide complexes are by far the most common, [3] and complexes with up to twelve coordinating groups are known. $[Ln(H_2O)_9]^{3+}$ (Ln = La - Eu) is the classic examples of a nine-coordinate lanthanide complex with a tricapped trigonal prismatic geometry in crystalline salt form, [9] and in the absence of ligand bulk, this type of configuration is extremely common. For the higher coordination numbers, very small multi-dentate ligands with a tight bite angle are required; $[Ln(NO_2)_6]^{3-}$ is the classic case of a lanthanide compound with dodecahedral geometry.

One-coordinate lanthanides are nonexistent, and two-coordinate lanthanides are extremely rare; they exist only in the Ln^{II} oxidation state and require bulky ligands such as $[C(SiMe_3)_3]^{-}$ [10] or $[N(Si^{I}Pr_3)_2]^{-}$ [11] in order to prevent further coordination of e.g. solvent. The compounds can be further stabilised by agostic



Figure 1.3: Crystal structure of $[Sm(N{SiⁱPr_3}_2)_2]$ showing agostic interactions between Sm^{II} and ⁱPr groups. [11] Sm, teal; N, blue; Si, orange; C, grey.

interactions between the metal and pendant groups on the ligand (Figure 1.3).

$$[Sml_{2}(THF)_{2}] + 2KN(Si^{i}Pr_{3})_{2} \xrightarrow{toluene} -2KI \xrightarrow{iPr_{3}Si} N - Sm - N Si^{i}Pr_{3}$$

Figure 1.4: Synthesis of $[Sm(N{Si}^{i}Pr_{3})_{2}]$. [11]

Ligand geometry tends to be more disordered and less symmetrical when compared to transition metal compounds, and so it is much more difficult to rationally design the ligand environment to enhance certain properties such as the SMM behaviour this work is based upon.

1.2. Synthesis of Lanthanide Organometallic Complexes

Due to the ionic nature of the lanthanides, salt metathesis is the most common way of forming compounds (Figure 1.6). Reaction between the lanthanide halide and an alkali metal-ligand salt forms the desired product with an energetically favourable side product of alkali metal halide salt, which can easily be filtered away for purification.



Figure 1.5: Reaction scheme for synthesis of lanthanide cyclopentadienyls. [12]

However, it is not uncommon for an alkali metal to be incorporated into the structure, forming an 'ate' complex which may not be desired. This work includes many reactions involving lanthanide cyclopentadienes, which are formed in exactly this way from lanthanide chloride and sodium cyclopentadiene (Figure 1.5). [12]

 $LnX_3 + 3MR \longrightarrow LnR_3 + 3MX$ $LnR'_3 + HR" \longrightarrow LnR'_2R" + HR'$

Figure 1.6: General reaction schemes for the two most common types of lanthanide complex formation. Top: salt metathesis. Bottom: ligand deprotonation. M = alkali metal, R = ligand, X = halogen

 $LnCl_3 + 3LiN(SiMe_3) \longrightarrow Ln\{N(SiMe_3)_2\}_3 + 3LiCl$

Figure 1.7: Synthesis of [Ln{N(SiMe₃)₂}₃]. [13]

Other common and important classes of lanthanide complexes formed by salt metathesis of lanthanide halides are the amides and the alkoxides. As mentioned, bulky amides are very useful for stabilising low-coordinate lanthanide compounds, and the first reported 3-coordinate lanthanide complex $[Ln(N{SiMe_3}_2)_3]$ is easily made by reaction of $LnCl_3$ with the potassium or lithium amide in anhydrous anaerobic conditions (Figure 1.7). [13] This can then be used to perform the other common type of lanthanide reaction, ligand deprotonation (Figure 1.6, e.g. R = N(SiMe_3)_2). Due to the oxophilic nature of the lanthanides, alkoxides and other oxygen-donor ligands such as β -diketonates are extremely common in lanthanide chemistry, and a large number of complexes with a huge variety of structures, ligands and behaviour have been reported. [14] Lanthanide alkoxide complexes in particular are covered in detail later in the chapter.

$$[Cp_{2}LnCI]_{2} + 2LiAIMe_{4} \xrightarrow{toluene} 2 Cp_{2}Ln \xrightarrow{Me} AIMe_{2} + 2LiCI$$

$$Cp_{2}Ln \xrightarrow{Me} AIMe_{2} + \underbrace{N} \xrightarrow{toluene} [Cp_{2}LnMe]_{2} + Me_{3}AI(py)$$

Figure 1.8: An early reported synthesis for [Cp₂LnMe]₂. [16]

Alkyl complexes are another type of widespread and important lanthanide compound, and like the silylamides, these are also often synthesised using salt metathesis and then used for ligand deprotonation, of which several examples are given in later sections. These compounds tend to be highly unstable to air and moisture and must often be stored at low temperature to avoid thermal decomposition. The first of these reported was $[Cp_2Ln(\mu-Me)]_2$, [15] although it was initially proposed as a monomeric species and not confirmed to

be a dimer until crystallographic characterisation was carried out. [16] Many more alkyl and aryl complexes of the lanthanides have been synthesised since. [17]

The ionic nature of lanthanide bonding is only one factor in their chemistry; the other major driver of compound formation is the need for the metal ion to be sterically saturated. Neutral ligands will therefore coordinate to the metal centre if there is space. Adducts to LnCp₃ are common; each cyclopentadienyl ligand is formally considered to take up three coordination sites, but there is still space around the metal centre for another ligand to coordinate. This tendency of LnCp₃ to complex neutral ligands is why it is necessary to purify by sublimation, as one molecule of solvent is coordinated to the metal centre after synthesis in THF (Figure 1.5). Using a pure hydrocarbon solvent such as toluene or hexane, if solubility allows, is therefore usually a sensible choice. This tendency to bond to oxygen is also what causes many organometallic complexes of the lanthanides to be air and moisture sensitive. If any water is present, it will bond to the metal and may then donate a proton to another ligand, resulting in the formation of an insoluble lanthanide hydroxide and the decomposition of the original compound. [5]

1.3. Origins and Measurement of Single Molecule Magnetism

A single molecule magnet (SMM) is a molecule which can become magnetised by application of a magnetic field and retain that magnetisation after the field is removed (Figure 1.9). [18] This is a quantum property of a single molecule, rather than a property of interaction between many different units within a bulk material, as seen in conventional magnets such as SmCo₅.



Figure 1.9: Magnetisation of a sample by application of an external magnetic field.

Single molecule magnetism has possible applications in the fields of data storage and spintronics. The hard disk drive is based on encoding data into domains within a magnetic material; grains within the material



Figure 1.10: Many magnetic grains make up a single domain in bulk magnetic data storage. [19]

can hold a different magnetisation than their neighbours, and so binary data can be recorded. Due to the size of the read / write head, and due to magnetic interactions



Figure 1.11: Use of an SMM as a spin valve. Electrons with opposing spin to the molecule are impeded; electrons with the same spin as the molecule pass unaffected. [18]

between grains, several grains compose a single bit (Figure 1.10) and developments in storage density tend to focus on reducing the number of grains within each bit. [19] New technologies such as bit-patterned media, which consists of fabricated isolated magnetic islands less than 10 x 10 nm in size, can lead to further increases in storage density in the near future to 1.3 Tbit inch⁻². [20] However, there is a theoretical limit to the storage density which can be achieved with hard disk technology, currently considered to be 20 Tbit inch⁻². [21] If storage density and efficiency must be increased further, it will be necessary to work on the scale of single molecules. This is where SMM materials can be useful.

Where conventional electronic computing is based on electron charge, spintronics uses the electron spin to encode and transmit data. [22] Spin-encoded electrons can then interact with magnetised materials in a variety of ways. There have already been several demonstrations of the use of SMM materials in constructing spintronic devices such as spin valves (Figure 1.11) or spin transistors. [18]



Figure 1.10: Common mechanisms to relaxation of spin in an SMM. Red arrows, electron spin; blue lines, energy levels; green arrows, state transitions.

Single molecule magnetism occurs in molecules with a bistable magnetic ground state in which opposing the spins on the unpaired electron cannot interconvert due to a high energy barrier to reversal of spin (Figure 1.12). In the early days of the field, it was thought that the most important factor in SMM

behaviour was making a molecule with a very high total spin, using interaction between metal centres in a multimetallic compound. The very first reported SMM, $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$ (Figure 1.13), does in fact attain its then-unique magnetic properties in such a way. [23] Ferromagnetic interaction forces the spins on the metal centres to align with one another, whereas antiferromagnetic interactions



force opposite spins. Making a compound with a [23] (from [27]). Mn, purple; O, red; C, grey.

large number of aligned metals would therefore induce a very large molecular spin; $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$ has a ground state S = 10. Transition metal complexes were the most obvious choice for building SMMs in this fashion, as interactions between the dorbitals of these metals and the ligand p or s orbitals can be quite strong, allowing for a large superexchange effect (metal-metal interaction via the electron density of bridging ligands), and it is not uncommon for the coupling constant J to be larger than 100 cm⁻¹. [24] Lanthanides do not interact in the same way, as their valence 4f orbitals are buried deep within the electron density, so strong orbital overlap cannot be achieved. Superexchange can occur, and can be calculated from magnetic susceptibility measurements of gadolinium compounds, but the effect is much smaller; typically, the exchange interaction J is usually less than 1 cm⁻¹ in lanthanide complexes, [25] although it has been reported to be as high as cm⁻¹ strongly-coupled 27 in complexes such as the radical-bridged $[Tb_2{N(SiMe_3)_2}_4(thf)_2(N_2)]^{-}$ (1.1). [26] Dipolar magnetic exchange is usually more important in lanthanide compounds; this is a through-space interaction, where the magnetic fields of each metal centre act upon one another, and if the easy axes of magnetisation are not parallel, this can be detrimental to the SMM properties of the compound.

However, in recent years, it has been discovered that anisotropy is actually a much more important property for SMM behaviour, and lanthanides have become more widely used. As discussed in Section 1.3, anisotropy is the deviation of the electron density from a spherical configuration. In an anisotropic magnetic centre, one axis of the electron distribution will be either longer or shorter than the others, and this is the direction in which the magnetisation will prefer to align itself. This is referred to as the 'easy axis of magnetisation'. Alignment of the magnetisation perpendicular to the easy axis is much less favourable, and so interconversion between the two possible magnetic states ('up' and 'down') is blocked.

Both of these deductions (the importance of spin, and later, anisotropy) arose from the same equation which governs the energy barrier to reversal of magnetisation: $U = |D|S^2$ or $U = |D|(S^2 - 0.25)$ for integer and non-integer spins respectively, where U is the energy barrier, S is the total spin, and D is the axial zero-field splitting parameter. This equation makes spin appear to be the most important variable, but a mathematical exploration of the origin of the D term shows that D is also inversely proportional to S², which results in the final energy barrier U being effectively independent of the spin of the molecule. [27]

In order to measure SMM behaviour, it is necessary to use SQUID (superconducting quantum interference device) magnetometry. This involves exposing the sample to an alternating (a.c.) magnetic field at various frequencies and temperatures and recording the in-field and out-of-field magnetisations; that is, the components of



Figure 1.12: Out of field a.c. magnetic susceptibility of **1.4**. [35] Note how the peak moves to higher frequency as the temperature increases.

the magnetisation vector of the sample parallel and perpendicular, respectively, to the oscillating field. If the sample is an SMM, a temperature dependent peak in the out of field measurement will be observed (Figure 1.14). At low frequencies, the magnetisation of the sample follows the magnetisation of the external field exactly, as the lifetime of the magnetisation is short enough that the spin can invert before the external field returns. However, as the frequency of the external field increases, a delay will be observed between the field switching and the sample inversion. A peak in the out of field measurement is observed when this delay is at its maximum, and the magnetisation of the sample is held perpendicular to the external magnetic field.

The temperature dependence of the out of field a.c. measurement is important, as the lifetime of the magnetisation is directly linked to the energy barrier to reversal of the magnetisation. At higher temperatures, it is easier for the sample to have enough energy to cross the barrier, and so the frequency at which the maximum delay is observed is higher. At lower temperatures, there is not as much available energy in the system and the sample magnetisation is delayed even at low frequencies. It follows that if there is no temperature dependence, there is no energy barrier to be overcome and so the sample is not an SMM. The energy barrier to thermal relaxation is calculated using the Arrhenius equation $\tau = \tau_0 e(U_{eff}/k_BT)$, where $\tau = 1/2\pi v$; τ is the lifetime of magnetisation, k_B is the Boltzmann constant, T is the temperature, and v is the frequency at which a maximum is observed in the Cole-Cole plot of χ' against χ'' (the in-field and out-of-field magnetisation).

Most SMM work focuses on this thermal relaxation mechanism, as it is the one most active at the relatively higher temperatures which are of interest for applications of these materials. However, there are also several other relaxation processes which may be active in

different temperature regimes, the importance of which varies between compounds. Quantum tunnelling is very important at low temperatures in lanthanide complexes and as such has already been mentioned in this work, but Raman and direct processes may also play a role, as has been explored in some recent reports. [28] For a full description of the magnetic behaviour of a material, these processes must also be accounted for, and a detailed spectroscopic analysis of the sample must be carried out. However, in a good SMM, the thermal process will overwhelm all others and a simple model accounting only for thermal and quantum processes is sufficient.

Another important property of an SMM is the blocking temperature T_B . This is sometimes defined as the highest temperature at which the material holds magnetisation over 100 s, [29] but there is no agreed standard within the field. Other commonly used metrics are the highest temperature at which magnetic hysteresis is observed (which is the measurement used within this work) (Figure 1.15) – although it depends on the scan rate of the experiment – and the highest temperature at which a peak is observed in the out-of-phase

a.c. measurement (χ "). Until recently, the highest observed blocking temperature for any SMM was 14 K for the radical-bridged terbium compound [Tb₂{N(SiMe₃)₂}₄(thf)₂(N₂)]⁻ (**1.1**), [26] which means it is still necessary to cool the material with liquid helium. This is currently one of the main obstacles to practical application of SMM



technology. If devices are to be produced and used outside of a specialist academic setting, this parameter is a crucial target for improvement. Hysteresis can also show whether quantum tunnelling relaxation processes are active; lanthanide SMMs in particular often show so-called 'butterfly' or 'closed-waist' hysteresis, where the loop closes at zero field due to efficient magnetic relaxation by quantum tunnelling between ground states. Uncommonly for a lanthanide complex, there is no waist restriction of hysteresis in **1.1**; the strong coupling of the radical ligand to the metal induces an exchange bias, which suppresses quantum tunnelling of the magnetisation.

1.4. Lanthanide Complexes as Single Molecule Magnets

Lanthanide complexes have the potential to be extremely good SMM materials. Depending on the lanthanide, there can be many unpaired electrons within a single metal centre, giving the potential for high spin values. The most commonly used lanthanide in SMM work is Dy^{III} , which has the ground state term symbol ${}^{6}H_{15/2}$ and therefore the maximum m_J value of the magnetic ground state is ±15/2. Most important however is the single-ion anisotropy of the lanthanides, which allows this high spin value to be exploited.

Each separate m_J value of the ground state of an Ln^{III} ion has its own angular dependence and therefore its own preferred electron density distribution (Figure 1.16). [30] While the crystal field does not itself have a substantial effect on the splitting of lanthanide electronic states, it can interact with the ground state to cause separation of these otherwise degenerate m_J energy levels. This is extremely useful to keep in mind when designing or analysing lanthanide SMMs. SMM behaviour is strongly influenced by the interaction between the magnetic ground state electron distribution of the lanthanide and the ligands surrounding it. Correct ligand placement can greatly enhance SMM properties by stabilising
only one orientation of the magnetic ground state, locking the easy axis of magnetisation in place and preventing inversion or relaxation via an alternative m, state.

A good example of this is [TbPc₂], [31] which was the first reported lanthanide SMM and is still the SMM with the highest known U_{eff} value (a derivative

> of this compound with {OPh-p-^tBu} groups added to one phthalocyanine ligand has U_{eff} = 652 cm^{-1}). [32] As shown (Figure 1.16), the m_J = ± 6 Tb^{III} ground state has an extremely oblate (disc-shaped) angular dependence, which places its magnetisation along the shortest

Figure 1.16: Approximate calculated angular dependence of every lanthanide magnetic state. [30]

4

т,

5

6

Ce(III

m(III зн

Yb(III

0

1

2

3

axis, through the centre of the disc. The large planar ligands above and below the metal

7

8

(Figure 1.17) hold this electron distribution in place, making sure that the easy axis of magnetisation is unable to position itself in any other direction, which holds the ground magnetic states far apart from each other and prevents tunnelling. All other m_J states of Tb^{III} are quite green; N, blue; C, grey. Ln = Tb, Ho



Figure 1.17: Crystal structure of [Ln(Pc)₂]⁻ [31] Ln,

prolate, which interacts unfavourably with the ligand environment and causes these states to lie at much higher energy levels: the calculated first excited state $m_J = \pm 5$ is approximately 430 cm⁻¹ above the ground state [33] which accounts for the very high energy barriers to relaxation observed in this molecule.

However, this is not the only way to encourage stable magnetic alignment. Another good way to capitalise on anisotropy is to induce asymmetry within the coordination environment of the metal. One example of this is $[Dy_4K_2O(O^tBu)_{12}]$ (**1.2**), which at the time of its report had the highest U_{eff} for any dysprosium SMM at 585 cm⁻¹ for the magnetically diluted



species $[DyY_{3}K_{2}]$. [34] The highly charged $[12]^{2}$ ligand in the centre of the cage is the main driver of anisotropy within this system; the easy axis of magnetisation corresponds to the axis pointing directly toward this central oxide. The ligand environment on each Dy^{III} centre involves four

Figure 1.14: Structure of **1.2** with calculated easy axes of magnetisation. [34] Dy, purple; K, green; O, red; C, grey.

evenly-spaced approximately equatorial $[\mu-O^tBu]^$ ligands, with one terminal $[O^tBu]^-$ and the central

 $[12]^{2-}$ in the axial positions. This arrangement concentrates more negative charge in the axial sites, leading to a pure and completely axial $m_J = \pm 15/2$ ground state. The first excited state $m_J = \pm 13/2$ is also stabilised by this ligand environment, and is also calculated to be pure and highly axial; the second excited state contains a mixture of m_J states, and this is the energy level at which magnetic relaxation must occur.

There are several ways in which SMM behaviour in lanthanides can be reduced, despite the presence of a favourable ligand field. One of the usual problems is dipolar magnetic

exchange between metal centres; metal centres with easy axes of magnetisation in different directions such as those in **1.2** (Figure 1.18) can apply their magnetic fields to one another, introducing local transverse fields and allowing for magnetic relaxation at lower energies. These interactions must be quenched for the SMM properties of the compound to return.

Magnetic dilution is an effective way of eliminating exchange. Instead of co-crystallising already formed molecules, which is the classic experiment used to show the single-molecule origin of the magnetism, the dilution is incorporated during synthesis. The monometallic precursor is mixed with a large proportion of a diamagnetic precursor before the reaction takes place (often 1:20 para- to diamagnetic), substituting sites within the molecule with non-magnetic metals which will not interfere with the magnetism. Applying this 5% dilution level to 1.2 gives species in approximate proportion: Dy₄K₂, 0.0006%; Dy₃YK₂, 0.048%; Dy₂Y₂K₂, 1.38%; DyY₃K₂, 17.1%; Y₄K₂, 81.5%. DyY₃K₂ is therefore the dominant magnetic species in the sample, and so the magnetic behaviour observed arises from a single Dy^{III} ion with no intra- or intermolecular magnetic interaction. In lanthanide studies, the most commonly used diamagnetic metal is yttrium, as its chemistry is similar to that of the lanthanides, and it has an ionic radius close to those seen in the 4f block – the ionic radius of Y^{III} is close to Dy^{III}, the most commonly used lanthanide for SMM studies. This process was used in the studies of $[Dy_5O(O^{i}Pr)_{13}]$ (1.3) and 1.2, and greatly improved their U_{eff} values (Table 1.1). [34] It can also improve magnetic hysteresis by eliminating competing relaxation pathways, as observed for $[Cp'_2Dy(\mu-PHMes)]_3$ (**1.4**) and $[Cp'_2Dy(\mu-AsHMes)]_3$ (**1.5**). [35] [36]

Hyperfine interactions between the magnetic spin of the electrons and the nuclear magnetic spin of the metal are also a concern. While the effect is usually smaller than that of intramolecular electronic interactions, it is almost ubiquitous. This tunnelling pathway has

been demonstrated in an experiment with $[HoPc_2]^7$, [37] the structure of which is given in Figure 1.17. The hysteresis observed for the $\frac{1}{2}$ 0 holmium compound contained multiple steps (Figure 1.19), the energies of which were matched to hyperfine coupling between nuclear magnetic states and the ground



Figure 1.15: Hysteresis loops for [HoPc2]. The 'steps' in the loop indicate energies at which opposite states can mix and quantum tunnelling can occur. [37]

electronic state, showing this effect definitively for the first time.

It may be possible to eliminate this hyperfine coupling by enriching the metal with a different isotope. Isotopic enrichment of a sample of [Dy(tta)₃(L)] (Figure 1.20) in this



Figure 1.16: Crystal structure of [Dy(tta)₃(L)] [38] Dy, pink; O, red; N, blue; S, yellow; F, green; C, grey.

gave a significant improvement in manner relaxation times; relaxation at 2 K in the enriched and magnetically diluted 164 Dy version (I = 0) is slower than in the pure, non-enriched compound by a factor of 10,000. [38] Unfortunately, the SMM behaviour of the original compound ($U_{eff} = 28 \text{ cm}^{-1}$) was not impressive; for a molecule that is already a good SMM, such an effect could be enormous.

However, isotopic enrichment would be an extremely expensive procedure to perform regularly.

As well as having the largest U_{eff} values in the SMM field, lanthanides also show SMM properties to the highest temperatures. To date, this phenomenon is a purely low temperature behaviour, requiring cooling the sample with liquid helium. This is the single largest problem preventing application of SMM materials for technological advances. There are two lanthanide compounds which are far superior to any others in this measurement. **1.1** (Figure 1.21) is a terbium dimer bridged by a radical N_2^{3-} ligand and shows hysteresis with coercivity to 14 K, [26] which for



Figure 1.17: Crystal structure of **1.1** [26] Tb, brown; N, blue; O, red; Si, green; C, grey.

a long while was by far the highest temperature at which any SMM was active. It was demonstrated for the Gd^{III} version that the bridging radical ligand facilitates extremely strong magnetic superexchange ($J = 27 \text{ cm}^{-1}$, two orders of magnitude higher than in most lanthanide complexes). [39] This strong superexchange is also theorised to stabilise the orientation of the magnetism, leading to the high temperature SMM behaviour observed.

Recently, the monomeric Dy species $[Dy(Cy_3PO)_2(H_2O)_5]^{3+}$ (Figure 1.22) was reported. [40]



Figure 1.18: Crystal structure of $[Dy(Cy_3PO)_2(H_2O)_5]^{3+}$ [40] Dy, green; O, red; P, purple; C, grey.

With Cl⁻ counter-ions, this complex shows magnetic hysteresis to 11 K with $U_{eff} = 328 \text{ cm}^{-1}$; with Br⁻ counter-ions, this temperature increases to 20 K with $U_{eff} = 377 \text{ cm}^{-1}$, setting a new record for the highest temperature at which SMM behaviour can be observed. Hysteresis was observable at scan rates ranging from 200 Oe s⁻¹ to 10 Oe s⁻¹. The [Cy₃PO] ligands are bonded much more strongly than the H₂O ligands, with Dy-O bonds shorter by 0.106 – 0.165 Å to [Cy₃PO]. This creates a strongly axial ligand environment and suppresses low-lying relaxation processes.

Compound	Pure U _{eff}	Diluted U _{eff}	T _B	Reference
[Cp' ₂ Dy(PHMes)] ₃	210	256	4.4	[35]
[(Cp' ₂ Dy) ₃ (PMes) ₃ Li][Li(THF) ₄] ₂	13	N/A	< 1.8	[35]
[Cp' ₂ Dy(AsHMes)] ₃	256	301	5.4	[36]
[(Cp' ₂ Dy) ₃ (AsMes) ₃ Li][Li(THF) ₄] ₂	23	35	< 1.8	[36]
[Cp' ₂ Dy(SeMes)] ₃	285	301	4.7	[36]
[Cp' ₂ Dy(SSiPh ₃)] ₂	135	N/A	1.8	[47]
[Dy ₅ O(O ⁱ Pr) ₁₃]	367	559	N/A	[74]
[Dy ₄ K ₂ O(O ^t Bu) ₁₂]	220, 481	585	5	[34]
[Tb(Pc) ₂][Bu ₄ N]	230	N/A	N/A	[31]
[Tb(Pc)(Pc{OPh- <i>p</i> - ^t Bu} ₈)]	652	N/A	N/A	[32]
$[({Me_3Si}_2N)_2(THF)Tb_2N_2]$	227	N/A	14	[26]
[Dy(Cy ₃ PO) ₂ (H ₂ O) ₅]Cl ₃	328	N/A	11	[40]
$[Dy(Cy_3PO)_2(H_2O)_5]Br_3$	377	N/A	20	[40]

Table 1.1: SMM properties for a selection of lanthanide complexes. T_B in this case refers to the maximum temperature at which magnetic hysteresis is observed. Units: U_{eff}, cm⁻¹; T_B, K.

1.5. Lanthanide Complexes with Soft Donor Ligands

The majority of lanthanide SMM work involves oxygen or nitrogen donor ligands. [41] As lanthanides have a strong affinity for these ligands, the synthesis of these compounds tends to be easier than for complexes containing soft donor ligands. However, it is worthwhile to work with these more difficult materials, as they may possess unique behaviour and properties not found in more easily accessible compounds. For SMMs in particular, when lanthanide centres are linked by soft ligands, the bridge has a more diffuse electron distribution than if an oxygen or nitrogen donor was used. This was hypothesised to increase exchange between the metals. Whereas oxygen or nitrogen donors give highly ionic bonds, soft bridges can introduce more covalency, and this is not an area that has been widely explored in lanthanide SMM studies.

As mentioned, the majority of lanthanide organometallic and soft ligand chemistry involves [Cp]⁻ ligands and their derivatives. These ligands allow a single negative charge to cover up to three coordination sites, which help with formation of a neutral sterically-saturated compound, and can be made quite bulky to allow for stabilisation of weak bonds to other ligands, while being weakly bonded enough to the metal that ligand substitution can still occur.

$$2Cp_3Ln + 2MSR \longrightarrow [Cp_2Ln(SR)]_2 + 2MCp$$

 $2Cp_3Ln + 2HSR \longrightarrow [Cp_2Ln(SR)]_2 + 2CpH$

Figure 1.19: General synthetic routes to sulfur-bridged lanthanide Cp dimers. [42] M = K, Li

Formation of sulfur-bridged lanthanide $[Cp]^{-}$ dimers is well known in the literature, and there are many examples of this $[(Cp_2Ln)(\mu-SR)]_2$ structure. [42] There are two common routes for this reaction (Figure 1.23): salt metathesis of an alkali metal thiolate, and deprotonation of a thiol by the $[Cp]^{-}$ ligand. Which route is most suitable is dependent on the acidity of the thiol proton and therefore its ability to protonate $[Cp]^{-}$. Metathesis reactions of $[Cp_2Ln(\mu-CH_3)]_2$ with RSSR leading to elimination of MeSR are also well represented in the literature, as is reduction of RSSR by a Ln^{II} compound such as $[Cp*_2Ln]$. [42] [43] Despite these compounds being somewhat common, characterisation of their magnetic properties was overlooked for some time.

The first structurally characterised thiolatebridged lanthanide complex was the amide dimer $[{(SiMe_3)_2N}_2Ln(\mu-S^tBu)]_2$ synthesised by reaction of $[N(SiMe_3)_2)_2Ln(\mu-Cl)]_2$ with LiS^tBu and elimination of LiCl, where complexes with Gd^{III}, Y^{III} and Eu^{III} were synthesised and the crystal structure of the Gd compound reported. [44] The



Figure 1.20: Crystal structure of [Cp*₂Lu(S^tBu)₂Li(THF)₂]. [45] Lu, green; Li, blue; S, yellow; O, red; C, grey.

first fully-characterised organometallic sulfur-ligated compounds were bridged ate complexes formed by reaction of $[Cp*_2Ln(\mu-CH_3)_2Li(THF)_2]$ with ^tBuSH; two thiolate ligands bridge the lanthanide and lithium centres (Figure 1.24), and methane is eliminated. [45] The first synthesis of an Ln₂ organometallic sulfur-bridged dimer was reported for $[(^tBuCp)_2Ce(\mu-S^iPr)]_2$ as a deprotonation reaction between the metallocene and thiol. It was also shown by NMR spectroscopy that a mixture of different thiolate-bridged lanthanide complexes will undergo ligand exchange in solution (Figure 1.25), indicating that the ligands are somewhat labile. [46]

$$[Cp_2Ln(SR^1)]_2 + [Cp_2Ln(SR^2)]_2 \longrightarrow 2[Cp_4Ln_2(SR^1)(SR^2)]$$

Figure 1.21: A mixture of thiolate-bridged lanthanide complexes undergo ligand exchange in solution.

An early example of the study of soft ligands specifically for SMM use is the sulfur-bridged Dy dimer $[(Cp'_2Dy)(\mu$ -SSiPh_3)]_2 (**1.6**) (Figure 1.26), which has an energy barrier of 135 cm⁻¹ in



Figure 1.22: Crystal structure of 1.6. [47] Dy,

green; S, yellow; Si, grey; C, black.

zero applied field. At the time of publication, this was the highest U_{eff} value observed for a polymetallic Dy^{III} SMM, and **1.6** is also notable as the first sulfur-bridged lanthanide compound studied as an SMM. Analysis of the magnetic behaviour showed that the easy axis of magnetisation was directed by the position of the [Cp']⁻ groups. [47]

Although less common and often much less stable, selenium- and tellurium-ligated lanthanide complexes can be synthesised in similar ways to their sulfur-bridged analogues (Figure 1.23). [42] The first structurally-characterised selenium-ligated organometallic lanthanide complex was $[Cp_2Lu(\mu-SePh)_2Li(THF)_2]$, which was synthesised by reaction of $[Cp_2Lu(\mu-CH_3)_2Li(THF)_2]$ and HSePh. [48] Most other early reports of these compounds, including tellurium species, involved synthesis from Ln^{II} precursors, [49] until the reaction of $[Cp_2Ln(\mu-CH_3)]_2$ and RSeSeR was shown to produce a selenium-bridged homometallic dimer. [43]

Lanthanide complexes containing neutral phosphine adducts are surprisingly common, [42] [50] although until recently only compounds containing secondary or tertiary phosphines were known. However, rare earth complexes containing anionic phosphide or phosphinidene species are much rarer; [51] for phosphinidenes in particular, only a handful of compounds have been reported.



Figure 1.23: General reaction schemes for synthesis of lanthanide phosphides. M = alkali metal, X = halide.



Figure 1.24: Synthesis and crystal structure of [(N{SiMe₃}₂)₂Yb(dmpe)] [53] Yb, green; P, purple; N, blue; Si, orange; C, grey.

The phosphine adduct Cp₃Yb(PPh₃) was reported as early as 1965, [52] based on comparison of the UV-vis spectra of Cp₃Yb and PPh₃ alone with the spectrum of the final product, and by elemental analysis. Due to the technical limitations of the time and problems with the materials – extreme air and moisture sensitivity and a tendency to form small, flat crystals which make it difficult to obtain high quality X-ray diffraction data – it was not until 1982 that full structural characterisation of a lanthanide phosphine adduct was confirmed. [53] [Ln(N{SiMe₃}₂)₂](OEt₂)₂ (where Ln = Yb, Eu) reacts with both dmpe and P^tBu₃ to give the respective phosphine adducts (Figure 1.28) by displacement of diethyl ether. Similar reactions of phosphines and solvent-ligated lanthanides in non-polar solvent form the phosphine adduct, although if the ligating solvent is reintroduced in higher concentration it will displace the phosphine to give the starting material. Not all phosphine ligands are so labile; it was reported that PEt₃ will bind to lanthanides strongly enough to displace THF. [54] There are also several reports of multidentate phosphine ligands incorporating other donor groups such as alkoxides or amides, which bind well to lanthanides. [42] [50]



Figure 1.25: Synthesis of $[Cp_2Lu(\mu-PPh_2)_2Li(tmeda)]$. [56]

Phosphide complexes of the lanthanides are generally formed in two ways (Figure 1.27), the common synthetic routes for lanthanide compounds covered several times already: salt metathesis and ligand deprotonation reactions. [51] Again, complexes involving secondary phosphines dominate the literature. The first lanthanide phosphide complexes were reported in 1976, [55] but as with



by air and moisture sensitivity and problems with crystallisation. The first fully structurally characterised lanthanide phosphide compound $[Cp_2Lu(\mu-PPh_2)_2Li(tmeda)]$ was reported in 1986 (Figures 1.29 and 1.30). [56] Lanthanide phosphide complexes occur most commonly with μ -phosphide ligands, either between two lanthanides or an 'ate' complex of a lanthanide and an alkali metal, but monometallic lanthanide phosphides are also known.

There are also several reports of multidentate ligands incorporating one or more phosphide groups. [51]



Figure 1.27: Synthesis of [(PNP^{iPr})Lu(µ-PMes)]₂. [57]

Phosphinidene complexes of the lanthanides are extremely rare. They are generally synthesised in a similar manner to the phosphides, by salt metathesis or ligand deprotonation of a primary phosphine (Figure 1.27).

[51] The first lanthanide phosphinidene complex,



complex, Figure 1.28: Crystal structure of $[(PNP^{iPr})Lu(\mu-PMes)]_2$. [57] Lu, green; P, purple; N, blue; C, grey.

 $[(PNP^{iPr})Lu(\mu-PMes)]_2$, was reported in 2008. This phosphorus-bridged lutetium dimer acts as a phosphinidene transfer reagent when exposed to an aldehyde or ketone. [57] Later that year, the neodymium complex $[(THF)_3(I)Nd(\mu-Pdipp)]_2$ was also reported, [58] which can be reacted with KCp* or KTp (where Tp = hydro(trispyrazolyl)borate); these ligands displace THF rather than the phosphinidene ligands, to give two further phosphinidene-bridged lanthanide dimers. [59] The phosphinidene-bridged trimer [{(PhC{Ndipp}₂)Ln(μ_2 -Me)}₃(μ_3 -Me)(μ_3 -PPh)] (where Ln = Y, Lu) was reported recently, and was also found to act as a phosphinidene transfer reagent. [60] Other than a small handful of scandium complexes and P³⁻-bridged species, [51] this summary represents all but one of the lanthanide phosphinidene reports in the literature.



Figure 1.29: Crystal structures of 1.4 (left) and 1.7 (right). In 1.7, the lithium sits out of the plane formed by the three Dy atoms. [35] Dy, green; Li, pink; P, orange; C, white.



Figure 1.30: Synthesis of 1.8, 1.4 and 1.7. [35]

A recent example of lanthanide phosphorus chemistry is the family of phosphorus-bridged lanthanide trimers, which are the first SMMs containing lanthanide-phosphorus bonds. This work also gives another example of a lanthanide phosphinidene complex, and the first reported example of a lanthanide compound containing a primary phosphine. The phosphine adduct $Cp'_{3}Dy(H_{2}PMes)$ (**1.8**) and the phosphide and phosphinidene trimers $[(Cp'_{2}Dy)(\mu-PHMes)]_{3}$ (**1.4**) and $[Li(Cp'_{2}Dy)_{3}(\mu-PMes)_{3}][Li(THF)_{4}]_{2}$ (**1.7**) are all single molecule magnets. Compounds **1.8** and **1.7** are poor SMMs, with such poor SMM properties in **1.8** that it was not possible to calculate the energy barrier to reversal of magnetisation, and U_{eff}

= 13 cm⁻¹ for **1.7**. Compound **1.4** is much more impressive at U_{eff} = 210 cm⁻¹ in the pure sample and U_{eff} = 256 cm⁻¹ in the magnetically diluted 5%Dy@Y₃P₃ compound, which also shows good hysteresis up to 4.4 K.

The difference between the SMM properties of **1.4** and **1.7** were attributed to the differing charge on the bridging phosphorus atoms. In **1.4** as in the sulfur-bridged **1.6**, the easy axis of magnetisation was related strongly to the position of the [Cp']⁻ ligands as they are much more closely bonded to the metal centre than the [HPMes]⁻ ligands. In **1.7**, the more highly charged phosphorus ligands are more strongly bonded to the metal centre, breaking the [Cp']-directed axial ligand environment and allowing for easier magnetic relaxation. [35] These effects are described in more detail in Section 2.1.



Figure 1.31: Synthesis of [Cp₂Lu(µ-AsPh₂)₂Li(tmeda)]. [62]

Lanthanide chemistry with the heavier *p*-block elements is rare. A series of arsenic-ligated lanthanide complexes was reported in 1982, [61] but as with early reports of other unusual compounds, they were only characterised by spectroscopy. The first fully structurally characterised organometallic compound with a lanthanide-arsenic bond was reported in 1988 for the lutetium compound $[Cp_2Lu(\mu-AsPh_2)_2Li(tmeda)]$ (Figure 1.35) which was synthesised in a similar way to the analogous phosphide-bridged compound (Figure 1.29). [62] The first rare earth arsinidene complex $[(Cp'_2Y)_3(\mu-AsMes)_3Li][Li(THF)_2]_2$ was reported in

2015. [63] The dysprosium analogues of this arsinidene (Ln = Dy, **1.9**) and the arsenide trimer $[(Cp'_{2}Ln)(\mu$ -AsHMes)]_{3} (Ln = Dy, **1.5**) reported in the same work have since been magnetically characterised, giving the first report of an arsenic-ligated SMM. [36] That work also includes the first report of a selenium-ligated SMM, $[(Cp'_{2}Dy)(\mu$ -SeMes)]_{3} (**1.10**). **1.5** and **1.10** have structures similar to **1.4**, and **1.9** is analogous to **1.7** (Figure 1.33). The arsenic and selenium versions of each structure show slightly improved SMM properties compared to the phosphorus complexes (Table 1.1).

1.6. Lanthanide Alkoxide Compounds

As mentioned, reactions of lanthanide compounds with oxide donors such as alkoxides are nominally facile compared to reactions involving organometallic or soft donor ligands, although it will be demonstrated that this chemistry is not necessarily simple. The use of oxide donors as ligands in lanthanide complexes is much more common than the other classes of compounds discussed here and lanthanide SMMs incorporating oxygen donors are the most numerous. [41] There is an enormous range of structural variety within lanthanide alkoxide complexes specifically, ranging from single-ion compounds to large multi-metallic clusters. [64] The structural diversity that can be attained through this type of work is extremely valuable for studying the effect of the ligand environment on lanthanide SMMs.



Figure 1.32: Some general synthetic routes to lanthanide alkoxides (M = alkali metal). [5] [65]

Lanthanide alkoxide complexes can be made in a variety of ways. Common routes include salt metathesis from the lanthanide trichloride and alkali metal alkoxide, and the deprotonation of an alcohol by lanthanide tris(amide). [5] Reaction of metal shavings or powder with alcohol, catalysed by mercuric chloride, was also a popular early method of forming these compounds, but has mostly been replaced due to long reaction times and poor yields. [65] Alkoxide-ligated [Cp₂Ln(μ -OR)] can also be formed from a similar reaction

to that used to synthesise some sulfur-bridged complexes covered in the previous section, by reaction of $[Cp_2Ln(\mu-CH_3)Li(THF)_2]$ with an alcohol. [45] The main reason for interest in rare earth alkoxide chemistry is as a precursor for controlled formation of metal oxides. [66] At the time of the earliest reports of lanthanide alkoxides, crystallographic characterisation of compounds was difficult and therefore uncommon. These complexes [72] (From [64]) Y, green; O, red; C, white.



Figure 1.33: Crystal structure of [Y(OC₂H₄OMe)₃]₁₀.

were only characterised by spectroscopy and physical analytical methods such as elemental analysis, and were generally assumed to take the form Ln(OR)₃. [65]

It was not until 1989 that the crystal structure of the pyramidal cluster $[Y_5O(O^iPr)_{13}]$ was obtained, [67] and rare earth alkoxides were shown to not necessarily form the assumed three-coordinate monomer structure. Since then, many more studies have investigated the structure of lanthanide alkoxide compounds, and these complexes are shown to adopt a wide range of structures. Some do indeed form simple monomers, such as $[Y(OSi^tBu_2(CH_2)_3NMe_2)_3]$ [68] or $[Ln(OC^tBu_2CH_2PMe_2)_3]$ (Ln = Y, Nd), [69] which require chelating ligands incorporating an alkoxide and an alternative donating group (an amine and a phosphine respectively), as well as bulky organic substituents to stabilise the lanthanide



Figure 1.34: Crystal structures of $[Y_3(OC_2H_4OMe)_5(OAc)_4]$, (top) [70] and $[Nd_5(O)(O^iPr)_{13}(HO^iPr)_2]$ (bottom) [71]. Y, navy; Nd, green; O, red; C, grey.

coordination sphere. Dimers can also be formed, such as $[Cp^{tBu}_{2}Ce(\mu-O^{i}Pr)]_{2}$. [46]

However, many clusters take more complicated structures as demonstrated in the Y₅ study, such as the triangular [Y₃(OC₂H₄OMe)₅(OAc)₄], [70] the trigonal bipyramidal [Nd₅(O)(OⁱPr)₁₃(HOⁱPr)₂], [71] and the decametallic ring [Y(OC₂H₄OMe)₃]₁₀. [72] Other metals (such as alkali metals or transition metals) can also be incorporated into the structure to form a mixed-metal cluster. [73] As usual, bulky or chelating ligands incorporating different donor atoms are more likely to form mono- or bimetallic compounds. It is much more difficult to predict the outcome of reactions with smaller alkoxide ligands such as [OⁱPr]⁻, although ligand substitution of lanthanide precursors of $\{R_2Ln\}$ units (where R denotes a $[Cp]^-$ or

 $[N(SiMe_3)_2]^-$ ligand or derivative thereof) gives greater control over the final product. It is in the reaction of smaller monodentate alkoxide ligands with simple lanthanide salts that a rich structural variety can be obtained.



As was the case with the soft ligand-bridged

lanthanide compounds already discussed, the Figure 1.35: Crystal structure of 1.2. [34] Dy, magnetic properties of these materials were not

purple; K, green; O, red; C, black; H omitted for clarity.

investigated until recently when $[Dy_5O(O'Pr)_{13}]$ (**1.3**) [74] and, later, $[Dy_4K_2O(O^tBu)_{12}]$ (**1.2**) [34] were reported. At the time of their reports, each of these complexes broke records for the highest U_{eff} of not only multimetallic SMMs, but also dysprosium SMMs in general. These compounds were formed by reaction of LnCl₃ with alcohols or alkali metal alkoxides, or a mixture of the two. However, the ease of the chemistry itself is misleading in this case, as the cage formation can be incredibly sensitive to the conditions of the reaction, as will be explored in much greater detail later in this thesis.

In **1.2**, the metals form an octahedron with one $[O^tBu]^-$ ligand bridging each face and one terminal ligand situated on each dysprosium. A single [O]²⁻ anion sits in the centre of the cluster. The two potassium centres are next to each other. The easy axis of magnetisation on each dysprosium was calculated to point directly towards the central oxide. 1.2 has an extremely high energy barrier to reversal of magnetisation with the pure compound having $U_{eff} = 220 \text{ cm}^{-1}$ and 481 cm⁻¹ (two relaxation processes were observed), and magnetic dilution to form 5%Dy@Y₄K₂ giving U_{eff} = 585 cm⁻¹. [34]

1.3 is a square-based pyramid of metals, with one [O'Pr]⁻ ligand bridging each triangular face, each edge of the base, and one terminal ligand on each metal. Again, **1.3** contains a single [O]²⁻ anion, which in this case bridges the square base. As mentioned, this structure was reported for yttrium in 1989 [67] and several other rare earth



Figure 1.36: Crystal structure of 1.3. Dy, isopropoxides since, [75] but magnetic characterisation green; O, red; C, black. [74]

was neglected until recently. The easy axis of magnetisation on each dysprosium again points directly towards the oxide. **1.3** has $U_{eff} = 367 \text{ cm}^{-1}$ in its pure form, and with magnetic dilution $U_{eff} = 559 \text{ cm}^{-1}$. [74] As these two lanthanide alkoxide clusters possess such good SMM properties, it would be worthwhile to explore the wide variety of compounds in this class that have not yet been magnetically characterised.

1.7. Research Aims

The aim of this thesis is to synthesise new lanthanide complexes which may display SMM properties. In particular, lanthanide complexes with soft bridging ligands or alkoxide ligands have not been given much attention in the SMM field, but have shown promise in the few reports available; compounds **1.6** ($[Cp'_2Dy(\mu-SSiPh_3)]_2$, first sulphur-bridged SMM), **1.4** ($[Cp'_2Dy(\mu-PHMes)]_3$, first phosphorus-bridged SMM), **1.5** ($[Cp'_2Dy(\mu-AsHMes)]_3$, first arsenic-containing SMM), **1.10** ($[Cp'_2Dy(\mu-SeMes)]_3$, first selenium-containing SMM), **1.3** and **1.2** ($[Dy_5O(O^{i}Pr)_{13}]$ and $[Dy_4K_2O(O^{t}Bu)_{12}]$, each broke the record for U_{eff} of dysprosium compounds at the time of their reports) are all notable. The focus of this thesis is to expand the range of soft ligand bridged organometallic lanthanide complexes and lanthanide alkoxide complexes which have been magnetically characterised.

2. Phosphorus Bridged Lanthanide Compounds

2.1. Introduction

Ln^{III} cations are classified as hard Lewis acids, and so the chemistry of the rare earth metals with soft ligands such as phosphines is challenging. Due to this hard-soft mismatch, phosphorus ligands tend to bind weakly to lanthanides and are easily displaced by other ligands, including polar solvents such as THF.

The first potential phosphine adduct of a lanthanide was reported in 1965 as Cp₃Yb(PPh₃), based on comparison of the UV-vis spectra of the reagents and the product. [52] However, it was not until 1982 that a lanthanide phosphine complex was fully characterised, when

dmpe and PBu₃ complexes of europium (II) and ytterbium (II) were reported. [53] Since then, many more complexes of lanthanides with secondary or tertiary phosphines have been reported, [42] although several of these are based on chelating ligands where the phosphine moiety contains another coordinating group with a hard donor group such as Figure 2.1: Crystal structure of an amido or alkoxy.



 $[Yb(N{SiMe_3}_2)_2(dmpe)]$. [53] Yb, green; P, purple; N, blue; Si, orange; C, grey.

Lanthanide complexes with anionic phosphorus ligands are most commonly formed by either deprotonation of the phosphine by the lanthanide precursor (for example, $[Ln(N{SiMe_3}_2)_3])$, or a salt metathesis reaction between the lanthanide precursor and an alkali metal phosphide. [51] Deprotonation of a phosphine already coordinated to a lanthanide centre, as described in this and other related work, is uncommon. Due to the air sensitivity of this type of compound, the first lanthanide phosphide complex was not structurally characterised until 1986, [56] and the first lanthanide phosphinidene complex was reported in 2008 [57] (see Section 1.5). Lanthanide phosphinidenes remain rare in the literature.

The first phosphorus-bridged lanthanide SMM was reported in 2015. [35] A family of compounds has been synthesised using H₂PMes as the phosphorus-containing ligand. Three structures were synthesised: first, the adduct of the phosphine to LnCp'₃ (where Cp' refers to methylcyclopentadiene), which is notable as the first reported instance of a lanthanide coordinated to a primary phosphine; a cyclic phosphide-bridged trimer formed by deprotonation of the adduct; the triple deprotonation of this trimer gives the third compound, a phosphinidene-bridged trimer with a Li⁺ cation positioned in the centre of the ring to stabilise the high negative charge on the ligands. These have been reported with Dy and Y, and we aim to expand the range of lanthanides studied within this family, for reasons which will be covered shortly.



Figure 2.2: Crystal structures of (left to right) 1.8, 1.4, and 1.7. [35]

The monomer Cp'₃Dy(H₂PMes) (**1.8**) is an extremely weak SMM; temperature-dependent relaxation of magnetisation was observed, but the measurements that could be obtained for this compound were not sufficient to calculate U_{eff} . The phosphide trimer $[(Cp'_2Dy)(HPMes)]_3$ (**1.4**) is a much better SMM, with $U_{eff} = 210 \text{ cm}^{-1}$ in zero field, increasing to 256 cm⁻¹ with magnetic dilution (5%Dy@Y₃). Magnetic hysteresis greatly improves with dilution, from a very narrow opening at 1.8 K and below for the pure compound to a much wider butterfly loop at 4.4 K and below for the dilute sample (Figure 2.3). The phosphinidene $[(Cp'_2Dy)_3(PMes)_3Li][Li(thf)]_2$ (**1.7**) is again a weak SMM, with $U_{eff} = 13 \text{ cm}^{-1}$ and slow relaxation occurring only below 3.6 K in the out-of-field a.c. susceptibility

measurements. Its SMM properties are not improved by dilution, suggesting that this low barrier is not due to interaction between metal centres but is intrinsic to the molecule. This supposition is supported by *ab initio* calculations, which show that the



greater charge on the bridging ligands increases the electron density in the equatorial plane; this disrupts the axial environment provided by the $[Cp']^{-}$ ligands and destabilises the magnetic ground state. The ground and first excited magnetic states in **1.4** are almost entirely ±15/2 and ±13/2 respectively, closely aligned and both strongly axial and so the magnetisation must relax via the second excited state, the energy of which corresponds well to the energy barrier to reversal of magnetisation observed for this compound. The difference in the charge distribution of the ligand environment in **1.7** reduces the axial character of the first excited state and causes state mixing, allowing for relaxation to occur at lower energy in this complex and giving a lower U_{eff} value. Expanding this family of complexes by using different metals can give more information on the system. Er was chosen due to its magnetic differences from Dy; where the Dy magnetic ground state has an approximately oblate electron distribution and benefits from axial ligand placements, the Er magnetic ground state has a prolate electron distribution and is stabilised by an equatorial ligand arrangement. [30] This means that the easy axis of magnetisation is likely to be different within the same structure, resulting in different magnetic behaviour. As the target compound is a cyclic trimer, we are hoping to form a compound with a toroidal magnetic moment, which is an unusual and interesting property only observed in a few other SMMs. [76] In such a system, the magnetisation axes of three metal centres sit at 120° from one another and the magnetic moment of the complex as a whole forms a ring.

Gd was chosen, as in other studies, in order to give insight into the exchange interactions between metal sites within the compound. This should give a greater understanding of the SMM properties of the other complexes within this family.

2.2. Synthesis

For experimental details, see Section 7.2. All syntheses were performed as reported for the equivalent Dy and Y compounds. [35] Synthesis and isolation of **2.1**, **2.2**, **2.3** and **2.4** are fairly simple, but the phosphinidenes are much more challenging due to their greater instability and problems with solubility. Compounds **2.1** – **2.4** crystallise easily in good yield from toluene (**2.1**, 26%; **2.2**, 66%; **2.3**, 41%; **2.4**, 71%) and survive in solution for a long time. The phosphinidenes, however, are insoluble in toluene but extremely soluble in THF, which poses a problem for crystallisation. Rather than crystallisation by slow evaporation and cooling, as is used for isolation of **2.1** – **2.4**, the THF solution of the phosphinidenes may be

layered with Et_2O , but this still does not guarantee the formation of crystals; formation of amorphous precipitate can occur instead, whereas crystalline material is necessary for the analytical methods used to characterise these compounds. Additionally, the phosphinidenes are much less stable in solution than 2.1 - 2.4 and even within a sealed Schlenk tube, decomposition can occur before crystals form. This also makes it difficult to obtain a crystal structure, as the crystals can degrade before they can be safely mounted on the diffractometer. Because of these problems, neither the Er nor Gd phosphinidene could be isolated or analysed by the time of writing.



Figure 2.4: Reaction schemes for 2.1/2.2 (top), 2.3/2.4 (middle) and 1.7 (bottom). Ln = Dy, Y (1.8, 1.4, 1.7); Gd (2.1, 2.3); Er (2.2, 2.4).

2.3. Description of Crystal and Molecular Structures

For crystal data, see SI.1.1 for **2.1** and **2.3** compounds and SI.1.2 for **2.2** and **2.4**. **2.1** and **2.2** are simple phosphine adducts of LnCp'₃. Three η^5 [Cp']⁻ ligands and an H₂PMes ligand are coordinated to the metal, with the Ln-P bond and the Ln-Cp' centroid bonds forming a pseudo-tetrahedral geometry at the metal centre. **2.3** and **2.4** are cyclic trimers consisting of three [LnCp'₂] units bridged by μ_2 -[PHMes]⁻ units; three [Cp']⁻ ligands are arranged on one face of the ring, while all the Mes groups are arranged on the opposite side, with the remaining [Cp']⁻ rings equatorial. This gives a non-centrosymmetric structure in the *Cc* space group. The {Ln₃P₃} ring adopts a chair conformation as shown in Figures 2.6 and 2.8. The [Cp']⁻ ligands on one face of the ring are almost coplanar. The metal environment in **2.3** and **2.4** is also pseudo-tetrahedral, with bonds to two η_5 -[Cp']⁻ centroids and two [μ -PHMes]⁻ ligands.

	2.1	2.2	2.3	2.4
LnLn	8.644(10)	8.354(9)	5.303(9)-5.424(4)	5.275(4)-5.362(5)
Ln-P	3.042(5)	2.979(5)	2.905(8)-2.973(3)	2.901(3)-2.917(3)
Ln-Cp _{cent}	2.444(4)-2.472(4)	2.399(4)-2.426(5)	2.374(8)-2.402(9)	2.319(11)-2.345(9)
Ln-P-Ln	N/A	N/A	126.41(9)-134.5(3)	129.91(11)-134.33(12)
P-Ln-P	N/A	N/A	93.7(2)-101.68(9)	87.49(11)-95.94(11)

Table 2.1: Selected distances (Å) and angles (°) for 2.1, 2.2, 2.3, and 2.4.

2.1 crystallises in the monoclinic space group $P2_1/c$, with 8 molecules in the unit cell and 2 in each asymmetric unit, and no solvent of crystallisation. The two molecules in the asymmetric unit vary in the positioning of the methyl group of one $[Cp']^-$ ligand, with one

pointing towards the H₂PMes ligand and one pointing away, the latter of which is shown in Figure 2.5. The Gd-P bond length is 3.042(5) Å and Gd-Cp' centroid distances are 2.444(4) - 2.472(4) Å.

2.3 crystallises in the monoclinic space group *Cc*, with one molecule of **2.3** and one molecule of toluene in the asymmetric unit and four of each in the full unit cell. The [μ -PHMes]⁻ ligand at P3 in Figure 2.6 is disordered over two sites, which vary in respect to rotation around the GdP plane. There is slightly more variance in Gd-P bond distances (2.905(8) – 2.973(3) Å) than in Er-P (2.901(3) – 2.917(3) Å, Table 2.1), but otherwise the structures are similar. Variance in metal-Cp' centroid distances are similar, with a difference of 0.028 Å between the longest and shortest bond for both **2.1** (0.028(4) Å; 2.444(4) – 2.472(4) Å) and **2.3** (0.028(8) Å; 2.374(8) – 2.402(9) Å). Bond angles are a little more variable in **2.3** than in **2.4**, with the Gd-P-Gd (126.41(9) – 134.5(3)°) and P-Gd-P (93.7(2) – 101.68(9)°) angles having variations of 8.09(9)° and 7.98(9)° respectively. Metal-ligand bonds are shorter in **2.3** than in **2.1**, by 0.069(5) – 0.137(8) Å for Gd-P and 0.042(9) – 0.098(8) Å for Gd-Cp' centroid distances, again due a combination of electrostatic and steric factors.



Figure 2.5: Molecular structure of 2.1. Thermal ellipsoids are set at 50%. Gd, green; P, purple; C, grey; H, white (on the phosphine) or omitted for clarity (elsewhere). See Table 2.1 for bond lengths and angles.



Figure 2.6: Molecular structure of 2.3. Gd, green; P, purple; C, grey; H omitted for clarity. Thermal ellipsoids are set at 50%. See Table 2.1 for bond lengths and angles.

2.2 crystallises in the monoclinic space group $P2_1/n$. There are four molecules in the unit cell with one molecule in each asymmetric unit and no solvent of crystallisation. One $[Cp']^-$ ligand is rotationally disordered, with the methyl disordered over two sites (one pointing towards the H₂PMes ligand and one pointing away) with equal population. This corresponds well to the Cp' methyl positions observed in the structure of **2.1**. The Er-P bond length is 2.979(5) Å and the Ln-Cp' centroid distance is 2.399(4) – 2.426(5) Å.

2.4 crystallises in the monoclinic space group *Cc*, with an asymmetric unit consisting of one molecule of **2.4** and one molecule of toluene; there are four of each in the unit cell. Geometrical differences between Er sites in **2.4** are minor: the greatest bond length variation is in Er-C bonds, with a difference of approximately 0.077(12) Å (2.588(12) – 2.665(10) Å). Distances to ring centroids vary by less than 0.026(11) Å (2.319(11) – 2.345(9), Table 2.1). The greatest bond angle variation is in P-Er-P angles, with a difference of 8.45(11)° (87.49(11) – 95.94(11)°). Er-Cp' centroid distances in **2.4** are 0.054(9) - 0.107(11) Å shorter than in **2.2**, and the Er-P bonds are also shorter by 0.062(5) - 0.078(5) Å in **2.4** (2.901(3) – 2.917(3) Å) than in **2.2** (2.979(5) Å) due to a combination of steric and electrostatic factors.



Figure 2.7: Molecular structure of 2.2. Thermal ellipsoids are set at 50%. Er, green; P, purple; C, grey; H, white (on the phosphine) or omitted for clarity (elsewhere). For bond lengths and angles, see Table 2.1.



Figure 2.8: Molecular structure of **2.4**, with hydrogen omitted for clarity and thermal ellipsoids at 50%. Er, green; P, purple; C, grey. Top: Side view showing chair configuration of the {Er₃P₃} ring and facial arrangement of ligands. For bond lengths and angles, see Table 2.1.

Structural differences between **2.1** and **2.2** are minor. The Gd-P bond (3.042(5) Å) is longer than the Er-P bond (2.979(5) Å) by 0.063(5) Å, and bonds between Gd and Cp' ring centroids (2.444(4) – 2.472(4) Å) are 0.018(5) – 0.073(4) Å longer than the corresponding Er-Cp' bonds (2.399(4) – 2.426(5) Å). This can be attributed to the slightly larger ionic radius of Gd due to the lanthanide contraction (as each Cp'' ligand takes up three coordination sites, metal centres in **2.1** and **2.2** are formally 8-coordinate: Gd^{III}, 105 pm; Er^{III}, 100 pm). [6] The C-P-Ln angle is identical in each, within error (123.54(10)° in **2.1**; 123.64(14)° in **2.2**). Even the arrangement of Cp' ligands matches well. Where the positional differences in Cp' are modelled by disorder in **2.2**, they are more ordered in **2.1**, showing as different molecules in the asymmetric unit; however, the actual positions of the Me groups match well (Figures 2.5 and 2.7). The Ln-P bond distance in **1.8** falls between those of **2.1** and **2.2** at 3.009(1) Å [35] as do the Ln-C distances (averages of: 2.671 Å for **2.2**, 2.710 Å for **1.8**, 2.766 Å for **2.1**). This is expected behaviour due to the lanthanide contraction.

Structural differences between **2.3** and **2.4** are again minor. Metal-ligand bond distances are longer overall in **2.3** than in **2.4** – LnP distances range from 0.012(8) Å longer in **2.4** (2.901(3) – 2.917(3) Å) to 0.072(3) Å longer in **2.3** (2.905(8) – 2.973(3) Å), while Ln-Cp' centroid distances are 0.029(9) - 0.083(11) Å longer in **2.3** (2.374(8) – 2.402(9) Å) than **2.4** (2.319(11) – 2.345(9) Å), for the same reason as the monomers. Ln-P-Ln bond angles are almost identical, being 129.91(11) – 134.33(12)° in **2.4** and 126.41(9) – 134.5(3)° in **2.3**, but P-Gd-P bond angles (93.7(2) – 101.68(9)°) are larger than P-Er-P (87.49(11) – 95.94(11)°) by 2.24(20) – 14.19(11)°. Ln---Ln distances are longer overall in **2.3** (5.303(9) – 5.424(4) Å) than **2.4** (5.275(4) – 5.362(5) Å), ranging from 0.059(4) Å longer in **2.4** to 0.149(9) Å longer in **2.3**. While there is no significant disorder observed in **2.4**, one [μ -PHMes]⁻ ligand in **2.3** is disordered with respect to rotation around the Gd-P plane. Bond lengths in **1.4** again tend to fall in between those observed in **2.3** and **2.4**: Ln-P bonds are smallest in **2.4** at 2.901(3) – 2.917(3) Å, slightly larger in **1.4** at 2.926(6) – 2.951(6) Å, and largest on average in **2.3** at 2.905(8) – 3.973(3) Å, with the larger variance in bond lengths attributed to the disorder on one [HPMes]⁻ moiety. Average Ln-C bonds are smallest in **2.4** at 2.636 Å followed by **1.4** at 2.640 Å and finally **2.3** at 2.752 Å. Infra-red spectra of **2.2** and **2.4** confirm the presence of P-H bonds in these complexes, with diagnostic stretches observed at 2354 cm⁻¹ in **2.2** and 2314 cm⁻¹ in **2.4**; the P-H stretch generally occurs as a sharp peak in the 2280-2440 cm⁻¹ region of the spectrum, which is usually otherwise empty. [77]

2.4. Magnetic Property Measurements

All magnetic measurements were performed on polycrystalline samples suspended in eicosane by Dr. Thomas Pugh (a postdoctoral researcher in the Layfield group).

Direct current magnetic susceptibility measurements of **2.3** were performed in static applied fields of 0.1 T and 1 T; the 1 T data is shown. The $\chi_M T$ value at 300 K is 23.5 cm³ K mol⁻¹ in a 1 kG field, and 22.9 cm³ K mol⁻¹ in a 0.1 T field. These values agree well with each other and with the calculated value of 23.64 cm³ K mol⁻¹ for three independent Gd^{III} ions in the ${}^8S_{7/2}$ ground state. [78]



Figure 2.9: Direct current magnetic susceptibility data for **2.3** in a 1 T static field. X_M blue; $\chi_M T$ red.

The magnetic susceptibility data was fitted to extract the *J* coupling and *g* values for **2.3**, using the PHI fitting program. [79] Values of $J = -0.138 \text{ cm}^{-1}$ and g = 1.998 give a good fit for the 1 kG susceptibility data (Figure 2.10). This indicates weak antiferromagnetic exchange between the Gd^{III} ions, mediated by the phosphide ligands; these are consistent with the range of literature values for Gd^{III} superexchange in other magnetic complexes. [47] [80] This result is also consistent with the calculated antiferromagnetic exchange interactions reported for **1.4**. [35] A similar quality of fit could not be replicated by simulating simple crystal field splitting of an isolated Gd^{III} ion, and therefore exchange is the only possible explanation. Simulating the energy levels for this system using the derived parameters gives a degenerate ground state spin ½ doublet, with a quadruply degenerate spin 3/2 first excited state very close in energy (+0.414 cm⁻¹).



Figure 2.10: Data fitting for **2.3**. Blue squares and green triangles are experimental magnetic susceptibility data in 1 kG and 0.1 kG static field respectively. The blue line is the calculated fit given by the parameters J = -0.138 cm⁻¹ and g = 1.998; this is a good fit for the 1 kG experimental data.

Antiferromagnetic exchange in a triangular Ising spin system is a classic case of spin frustration, [81] where the spins are unable to attain an energetically favourable configuration due to interactions between neighbouring spins. Neighbouring sites would prefer to have opposing spins, but in a triangular system this is not possible, and so there are six degenerate configurations as shown in Figure 2.11. This type of spin system has previously been reported for a Gd^{III} triangle. [82]


Figure 2.11: Spin frustration in 2.3. All six spin configurations are degenerate.

Direct current (d.c.) magnetic susceptibility measurements were performed in an applied field of 1 kG. The magnetic susceptibility $\chi_M T$ for **2.2** of 11.28 cm³ K mol⁻¹ at 300 K agrees well with the calculated value for a single Er^{III} ion of 11.5 cm³ K mol⁻¹ for the ground state ${}^4I_{15/2}$. The $\chi_M T$ value for **2.4** of 32.9 cm³ K mol⁻¹ at 300 K agrees with the calculated value of 34.5 cm³ K mol⁻¹ for three independent Er^{III} ions. [78]



Figure 2.12: Direct current magnetic susceptibility measurements of 2.2 (top) and 2.4 (bottom) in a static field of 1 kG. χ_M blue; $\chi_M T$ red.

Neither **2.2** nor **2.4** show any slow relaxation of magnetisation. Complete Active Space Self-Consistent Field (CASSCF) calculations were performed using MOLCAS 8.0 [83] on the crystal structure of **2.4** by Dr. Nick Chilton of The University of Manchester. As the positions of the phosphide H atoms could not be determined using X-ray crystallography, they were optimised using ORCA 3.0.2 [84] employing the BP86 functional with the RI approximation, [85] Grimme's D3BJ dispersion corrections [86] and the def2-TZVP basis set for all atoms; [87] the Er atoms were substituted for Y atoms in order to facilitate solution of the SCF. Each Er^{III} centre was studied independently, with the others replaced by the closed-shell Lu^{III}. The basis sets were chosen from the ANO-RCC library, [88] where the Er^{III} centre of interest had VTZP quality, the first coordination sphere had VDZP quality and all other atoms had VDZ quality. The active space consisted of the seven 4*f* orbitals, with 11 active electrons. 35 quartets and 112 doublets were considered in both the orbital optimisation and mixed by spin-orbit coupling. The results of these calculations are given in Table 2.2.



Figure 2.13: Top-down view of 2.4. Metal centre labels correspond to those used in Table 2.2.

Table 2.2: Calculated values for ground and excited magnetic states in 2.4: energy above the ground state an	۱d
anisotropic g-values. Values are given for individual Er ^{III} centres: Er1 (Er2) [Er3].	

State	Energy (cm ⁻¹)	<i>g_x</i> Er1 (Er2) [Er3]	<i>g_y</i> Er1 (Er2) [Er3]	<i>g</i> _z Er1 (Er2) [Er3]
Ground	0	3.42 (3.37) [2.82]	5.53 (5.86) [6.01]	9.23 (10.10) [7.00]
1 st excited	36 (43) [36]	1.56 (1.59) [2.69]	4.21 (4.99) [2.99]	8.55 (8.29) [7.67]
2 nd excited	58 (75) [45]	0.54 (0.99) [2.26]	3.72 (1.52) [4.03]	9.63 (11.15) [4.51]
3 rd excited	118 (117) [121]	3.01 (2.13) [1.82]	5.68 (6.28) [4.64]	9.13 (8.68) [9.59]
4 th excited	142 (139) [129]	0.02 (0.23) [0.08]	0.51 (0.51) [1.08]	14.83 (14.47) [14.85]
5 th excited	210 (224) [196]	0.81 (1.67) [0.63]	2.49 (3.79) [2.67]	10.42 (10.22) [8.73]
6 th excited	251 (269) [232]	0.75 (1.17) [0.36]	2.30 (3.61) [1.27]	9.65 (9.35) [8.62]
7 th excited	349 (357) [334]	0.11 (0.27) [0.06]	0.20 (0.59) [0.09]	15.75 (15.46) [15.82]

The energies of the first and second excited states are low, but the real problem is the calculated anisotropic *g* values for the system, which indicate the degree of anisotropy at each metal centre. For a lanthanide complex to show SMM properties, the ground state needs to have $g_z \approx 20$ and $g_x \approx g_y \approx 0$, which shows an environment in which the easy axis of magnetisation strongly prefers to lay in one direction (defined as the z axis) and not in a direction perpendicular (defined as the x and y axes). However, the calculated *g* values in Table 2.2 are far from ideal; g_z values much lower than 20, and g_x and g_y values much higher than 0, indicate that the easy axis of magnetisation can deviate from the z axis, and therefore the magnetisation can readily invert and the compound is not an SMM. These results confirm the hypothesis that the ligand environment is unsuitable to stabilise the prolate ${}^4l_{15/2}$ magnetic ground state of Er^{III}. Even a magnetically dilute sample in a strong static d.c. field would not show SMM properties. However, it was suggested that magnetically dilute 5%Er@Y₃ may give interesting EPR spectra

2.5. Conclusions and Further Work

Erbium phosphine $[Cp'_{3}Er(PH_{2}Mes)]$ and phosphide $[Cp'_{2}Er(\mu-PHMes)]_{3}$ complexes were synthesised and characterised; neither of these showed SMM properties. This was anticipated due to simple models of magnetic anisotropy, and rationalised using calculations which showed that the ligand environment in **2.4** is poorly suited to stabilisation of the magnetic ground state ±15/2. The gadolinium versions of these complexes were also synthesised, and magnetic characterisation of **2.3** showed that there is a weak antiferromagnetic interaction between metal sites within this trimer, which can be used to further analyse other complexes of this type. The phosphinidene trimers $[(Cp'_{2}Ln)_{3}(\mu-PMes)_{3}Li]^{2-}$ of erbium and gadolinium are more difficult to isolate, and this is necessary to complete the study of these two series. Given the comparison between the magnetic behaviours of the dysprosium and erbium compounds, the erbium phosphinidene is of great interest; it may show interesting SMM properties. The gadolinium phosphinidene is, again, useful to give insight into the magnetic exchange between metal sites in these systems. Due to the higher negative charge on the bridging ligand, there is likely to be stronger interaction between sites than in the phosphide, so it is important to determine the nature of the interaction.

It would be rational to synthesise similar complexes using different phosphorus ligands RPH₂, as changing the R group may lead to formation of different structures (e.g. a phosphide dimer rather than a trimer) due to steric effects. This could also have a subtle effect on the metal site geometry, which can allow for a study of how this affects the magnetism of the complex. Other unusual bridging atoms (including As, Se and Sb) are also being studied in similar compounds within the group. [63] [36]

3. Sulfur-Bridged Lanthanide Macrocycles

3.1. Introduction

Thiolate-bridged lanthanide complexes are well represented in the literature. As mentioned in Section 1.5, there are two common routes to lanthanide thiolate complexes: salt metathesis and deprotonation (Figure 3.1). $[Cp]^-$ ligands are not always necessary; other basic ligands will also work, and $[CH_3]^-$ and $[N(SiMe_3)_2]^-$ are also commonly encountered in the literature. [42]



Figure 3.1: Common syntheses of [Cp]⁻-ligated sulfur-bridged lanthanide complexes. [42]



Figure 3.2: Crystal structure of **1.6**. [47] Dy, green; S, yellow; Si, grey; C, black.

Despite the wide range of reported sulfur-bridged lanthanide complexes, their magnetic properties were not explored until recently. The synthesis of [(Cp'₂Ln)₂(Ph₃SiS)₂] (**1.6**) involves addition of LiSSiPh₃ to a solution of LnCp'₃ in toluene to form the dimer and a side product of LiCp' which can be filtered away. The magnetic behaviour of **1.6** was investigated and it was

found to be the first sulfur-bridged lanthanide SMM, with an energy barrier of 135 cm⁻¹, [47] which at the time was the largest U_{eff} value found for a polymetallic complex.

Since **1.6** was reported, there have been few other reports of soft ligand-bridged lanthanide SMMs, [35] [36] [89] and so it may be worthwhile to investigate similar systems to increase

understanding of the effect of soft donor atoms on the magnetic behaviour of lanthanide complexes. The tripodal sulfur ligand tris(mercaptomethyl)ethane (Figure 3.3) was chosen in order to potentially incorporate more metal centres into the system;

forming a trimer would be ideal, as some of these have been shown to have unusual magnetic properties such as a toroidal SH SH

Figure 3.3: Tris(mercaptomethyl)ethane.

magnetic moment, [76] and it would be interesting to observe the effect of soft bridging ligands on such a system.

The metals used in this work were chosen to ensure a full analysis of the structure. Dy^{III} is the most common lanthanide used to study SMM behaviour, [41] so this was essential. Y^{III} is also very commonly used in SMM work, as its ionic radius and chemistry is almost identical to that of dysprosium but it is diamagnetic, so it makes performing NMR studies much easier and the results more useful. It is also used for magnetic dilution studies. Gd^{III} is also commonly used for probing magnetic exchange between metal sites in lanthanide compounds as it is a spin-only system; modelling its magnetic behaviour is easier than it is for the other lanthanides, because spin-orbit coupling does not need to be taken into account.

3.2. Synthesis

Tris(mercaptomethyl)ethane (tmmeH₃) was prepared according to literature procedure. [90] The lithiated salt MeC(CH₂SLi)₃ can be formed as a white powder by addition of 3 equivalents of ⁿBuLi to tmmeH₃; however, the salt is highly insoluble in toluene and THF and therefore difficult to characterise by NMR spectroscopy. When mixed with a solution of LnCp'₃, no reaction occurs, most likely because of the low solubility of the salt. All further reactions were therefore attempted with the pure trithiol. For experimental details, see Section 7.3.



Figure 3.4: Reaction scheme for synthesis of **3.1** – **3.3**. The structure of part of the macrocycle is shown below. Ln = Y (**3.1**), Gd (**3.2**), Dy (**3.3**).

Instead of the anticipated trimer of metals around a single ligand unit, this reaction forms a dodecametallic macrocycle bridged by four $[tmme]^{3-}$ ligand units, $[(Cp'_{2}Ln)_{3}({\mu-SCH_{2}}_{3}CMe)]_{4}$ (3.1 – 3.3). This may be due to steric hindrance around the relatively small $[tmme]^{3-}$ ligand. The binding mode of $[tmme]^{3-}$ may be described using Harris notation as 4.2.2.2; the ligand binds 4 metals in total, with each arm coordinated to two. [91] The only by-product of the reaction is Cp'H, which is removed by decanting the mother liquor (if crystallising) or by washing with hexane. Compared to **1.6**, [47] **3.1** – **3.3** are relatively air stable. The small colourless plate-like crystals can be left in Fomblin[®] but otherwise exposed to air for up to an hour before any noticeable deterioration occurs, in the form of conversion to a yellow powder. However, air stability still proved a problem for obtaining good elemental analysis results. The acquisition of good crystal data was hindered more by the large unit cell and small crystal dimensions than by the air sensitivity of the complex.

3.3. Description of Crystal and Molecular Structures

For crystal data, see SI.2.1. **3.1**, **3.2**, and **3.3** all crystallise in the same space group, P-1 triclinic. Each asymmetric unit contains one molecule of **3.1** – **3.3** and three molecules of toluene, and there are two asymmetric units in the unit cell. In each of these structures, the molecule consists of twelve metal centres arranged in a highly distorted ring motif. Every



Figure 3.5: Left: Crystal structure of **3.2** backbone with [Cp']⁻ ligands omitted for clarity and thermal ellipsoids at 50%. Gd, green; S, yellow; C, grey. Right: Line drawing of **3.1** – **3.3** backbone with different Ln sites highlighted. Corner, blue; edge, green.

metal centre has similar geometry; there is a pseudo-tetrahedral arrangement of two [Cp']⁻ ligands and two bridging sulfur atoms for each. Each [tmme]³⁻ ligand unit bridges four metal centres in total.



Figure 3.6: Simple cartoon of **3.1 – 3.3**. Ln (corner), blue; Ln (edge), green; S, yellow; thick lines represent bonds while thin lines are merely a visual guide. The macrocycle as a whole can be described as forming the edges of a cuboid, with the corners and the centre of each of 4 long edges marked by the lanthanides (Figure 3.6). It could be argued that there are two separate metal environments within the molecule, despite their similar ligand geometry – eight sites on the 'corners' of the cuboid, where the metals are bridged by the same tmme unit, and four sites on the 'edges', where the metals link two different tmme units. ⁸⁹Y NMR spectroscopy was attempted in order to show this, but

the sample signal was not strong enough to observe any peaks.

	3.1 (Ln = Y)	3.2 (Ln = Gd)	3.3 (Ln = Dy)
Ln _c Ln _c	5.392(4) – 5.487(7)	5.480(3) – 5.530(4)	5.399(5) – 5.452(4)
Ln _c Ln _e	4.983(6) – 5.197(9)	4.894(3) – 5.191(3)	4.887(3) – 5.141(6)
Ln-S	2.706(5) – 2.823(4)	2.743(3) – 2.823(3)	2.704(3) – 2.798(3)
Ln-Cp' _{cent}	2.323(8) - 2.382(10)	2.374(6) - 2.411(5)	2.331(9) – 2.382(4)
S-Ln _c -S	92.41(15) - 95.44(14)	84.47(7) – 89.56(9)	84.58(9) – 87.67(10)
S-Ln _e -S	84.00(13) - 89.39(12)	91.15(9) – 97.30(8)	91.60(12) - 96.20(12)
Ln _c -S-Ln _c	165.13(17)–169.75(18)	167.54(11)-173.69(12)	166.17(13)–171.38(15)
Ln _c -S-Ln _e	124.83(15)–143.51(18)	122.37(9)–137.79(11)	123.83(12)–138.98(11)

Table 3.1: Selected bond lengths (Å) and angles (°) for **3.1**, **3.2**, and **3.3**. Ln_c and Ln_e are corner and edge sitesrespectively, and Cp'_{cent} is the centroid of the $[Cp']^{-}$ ring.

The data collected for **3.1** is of poor quality, and a sample is currently crystallising for a new data collection on a Cu-source diffractometer, to eliminate the possibility of Mo-source induced yttrium fluorescence which can severely degrade the quality of crystal data. Bond lengths and angles are therefore somewhat inaccurate, and can only be broadly compared with **3.2** and **3.3**, with which it shares most structural features. Y---Y distances also vary significantly between 'corner-to-corner' (5.392(4) - 5.487(7) Å) and 'corner-to-edge' (4.983(6) - 5.197(9) Å) dimensions, with corner-to-corner distances being longer by 0.195(9) – 0.504(7) Å. Y-S bond lengths fit well with those reported in the literature, at 2.706(5) – 2.823(4) Å, [42] with again no real pattern to the variations between sites. Y-Cp' centroid bonds vary little, and average to 2.353 Å (2.323(8) - 2.382(10) Å). Variations between bond angles on the Y₁₂S₁₂ backbone are similar to those observed in the other **Ln**₁₂ structures, whereby S-Y_{edge}-S angles ($84.00(13) - 89.39(12)^\circ$) are more acute than those for Y_{corner} sites

 $(92.41(15) - 95.44(14)^\circ)$ by $3.02(15) - 11.44(14)^\circ$. Variation between bond angles at sulfur is again more substantial, with Y_{edge}-S-Y_{corner} angles on long edges $(124.83(15) - 143.51(18)^\circ)$ more acute than Y_{corner}-S-Y_{corner} angles on short edges $(165.13(17) - 169.75(18)^\circ)$ by $21.62(18) - 44.92(18)^\circ$. Ln-S-Ln angles on short sides in **3.1** are the furthest from linear for the three complexes reported here.



Figure 3.7: Crystal structure of **3.2**; **3.1** – **3.3** are isostructural. Thermal ellipsoids are set at 50%. Ln, green; S, yellow; C, grey; H omitted and [Cp']⁻ rendered in wire frame for clarity. For bond lengths and angles see Table 3.1.

3.2 shows slightly less rotational disorder on $[Cp']^-$ ligands than **3.3**, although there are still a few rings with distorted ellipsoids due to rotation about the Gd-Cp' centroid axis and a few methyl groups showing partial occupancy of two different sites on the ring. Analysis of bond

lengths and angles shows similar site variations to those seen in **3.3**. Gd---Gd 'corner' to 'corner' distances (5.480(3) – 5.530(4) Å) are 0.289(3) – 0.636(4) Å longer than 'corner' to 'edge' distances (4.894(3) – 5.191(3) Å), which shows slightly more variation than for **3.3**. This is again significant, as the variation in distances is 5 – 12% of the longest distance. Gd-S bond lengths (2.743(3) – 2.823(3) Å) also have significant variation of 0.089(3) Å between them but again a pattern could not be observed. The average Gd-S bond length is 2.779 Å, which is normal. Gd-Cp' centroid lengths average 2.395 Å (2.374(6) – 2.411(5) Å); they are slightly longer than Dy-Cp' centroid lengths, as would be expected. Similar backbone bond angle variations are observed as in **3.3**. S-Gd-S angles at 'corner' sites (84.47(7) – 89.56(9)°) are 1.59(9) – 12.83(8)° smaller than at 'edge' sites (91.15(9) – 97.30(8)°). Gd-S-Gd angles show the same large variation, with the angle at short edge S sites ('corner'-to-'corner') being near-linear (167.54(11) – 173.69(12)°) and 29.75(11) – 51.32(12)° larger than at long edge S sites ('corner'-to-'cedge') (122.37(9) – 137.79(11)°).

There is considerable rotational disorder on the $[Cp']^{-1}$ ligands of **3.3**, which manifests in two ways: slight rotation of the entire ring around the Ln-centroid axis, resulting in distortion of the ring ellipsoids, and in some cases partial occupancy of the methyl group across multiple (usually two) sites around the ring. Analysis of bond lengths and angles at Dy centres confirms the hypothesis that the 'edge' and 'corner' Ln sites are geometrically distinct, especially with relation to their distance from their nearest-neighbour metal centres. The presence of two distinct metal environments could potentially affect the magnetic properties of the compound. 'Edge' to 'corner' Dy---Dy distances (4.887(3) – 5.141(6) Å) are shorter than 'corner' to 'corner' distances (5.399(5) – 5.452(4) Å) by 0.258(6) – 0.565(4) Å, which is a significant difference. At an average of 2.748 Å (2.704(3) – 2.798(3) Å), Dy-S bonds

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are a good match for literature values; [42] lengths vary by 0.094(3) Å between the longest and shortest bond but there is no particular pattern to the bond length variation, and so this does not adequately explain the Dy-Dy distances. There is little variation in Dy-Cp' centroid lengths, which average 2.354 Å (2.331(9) – 2.382(4) Å). S-Dy-S bond angles around Dy are noticeably different between 'edge' (91.60(12) – 96.20(12)°) and 'corner' sites (84.58(9) – 87.67(10)°), by 3.93(12) - 11.62(12)° with the 'corner' sites having the more acute angles. It has been shown that even small bond angle variations at the lanthanide can have an effect on SMM properties. [92] However, the dimension that is the probable cause of the difference in Dy-Dy distances is actually the Dy-S-Dy angle, which varies hugely between S atoms bridging 'corner' sites (on the short edges of the cuboid shown in Figure 3.5, 166.17(13) - 171.38(15)°) and S atoms bridging 'corner' and 'edge' sites (on the long edges, 123.83(12) - 138.98(11)°). The bond angle difference here is 27.19(13) - 47.55(15)°, with the Dy-S-Dy angle on the short edges approaching linearity.

The macrocycles **3.1** – **3.3** can be considered as generally isostructural when comparing both the overall geometry of the complex and the geometry at individual atom sites. They crystallise in the same space group, with the same number of solvent molecules and very similar unit cell dimensions. All distances and bond lengths in **3.2** are very slightly longer than in **3.3**, which is to be expected given the slightly larger ionic radius of Gd^{III} (the metal sites are again formally 8-coordinate: Gd^{III}, 105 pm; Dy^{III}, 103 pm). [6] Bond angles at comparable atom sites are similar, with variation between similar sites within each molecule being larger than variation between molecules.

3.4. NMR Spectroscopy Studies of 3.1

Despite the complexity of **3.1**, a simple analysis gives only five expected unique proton environments: three for Cp' (one for the methyl group and two on the ring) and two for tmme (one, again, for the methyl group and one for the CH₂ groups on the pendant arms). Initial experiments run on **3.1** – standard ¹H and ¹³C {¹H} NMR in d₈-THF – showed a much larger number of peaks than expected. A DOSY experiment (SI.2.2) was performed on the same sample which showed only the presence of a single molecule in solution, indicating that all major peaks in the ¹H NMR spectrum must be part of the same molecule. However, as the DOSY peak appears close to the solvent peak, it is possible that the molecule may fragment in THF solution. The most likely reasons for so many peaks to be observed are hindered rotation of [Cp']⁻ rings and site inequivalency, as explored through bond length and angle analysis of crystallographic data.



Figure 3.8: ¹H NMR spectrum of **3.1** in d₈-THF. See Table 3.2 for individual peak information.

The ¹H NMR and ¹³C {¹H} (SI.2.3) spectra can be partially assigned based on HMBC and HSQC 2-D NMR data (Figure 3.8, Table 3.2). Overlap between the assigned $[Cp']^{-}$ methyl peak at

2.55 ppm and $[\text{tmme}]^{3-}$ CH₂ peak at 2.57 ppm complicate integration. The splitting patterns of the $[Cp']^{-}$ Me peaks support the hypothesis that 'edge' and 'corner' LnCp'₂ sites are inequivalent: the 48-proton peak at 2.28 ppm fits corner sites, while the 18-proton peak at 2.17 and 6-proton peak at 2.55 ppm fit edge sites. This 8:3:1 ratio is also evident for the $[Cp']^{-}$ ring protons in the aromatic region, and combined with the 3:9 ratio of the $[\text{tmme}]^{3-}$ Me peaks, this suggests that one 'edge' may be inequivalent to the other three.

2D experiments can be used to differentiate the peaks for general sites (Figure 3.8 and SI.2.3, Table 3.2), but more detailed assignment was not possible with this data. An NOE experiment was run in an attempt to ascertain which peaks belonged to the same ligand moieties within the molecule, but the resolution was too low for this to be possible. ⁸⁹Y NMR was used in an attempt to find out how many inequivalent metal sites there are within the molecule, but again this experiment was unsuccessful; for several reasons, it is often not possible to obtain useful spectra from ⁸⁹Y NMR, [93] as was the case with this sample.

Site	¹ H Shift (ppm)	Integration	Multiplicity	¹³ C Shift (ppm)
Cp' ring	5.64	12	t	108.70, 110.79,
	5.79	12	t	111.79, 112.96,
	5.88	2	S	113.44, 113.77,
	5.99, 6.03, 6.13	60	s (broad), d (broad), t	114.83, 115.52,
	6.22	2	S	118.38
	6.34	4	t	
	6.52	4	t	
Cp' methyl	2.17	15	S	15.44, 15.84,
	2.18	3	s (broad)	16.17, 16.44,
	2.28	48	s (broad)	17.04
	2.55	6	s (broad)	
tmme CH_2	1.96	1	quad	39.23, 40.00,
	2.03	1	d	42.05, 42.29
	2.57	16	S	
	2.66	1	S	
	2.69	1	S	
	2.81	1	d	
	2.88	1	s (broad)	
	2.91	1	S	
	2.94	1	S	
tmme methyl	0.97	3	S	21.88, 22.69
	1.07	9	S	

Table 3.2: NMR data for **3.1.** ¹H peaks from 5.99-6.13 had too much overlap to consider separately.



Figure 3.9: Variable temperature ¹H NMR spectra of **3.1**. Top: All temperatures measured, in 10 °C intervals from -30 to 60 °C. Bottom: Only the highest and lowest temperatures are shown, with the original room temperature ¹H NMR for easier comparison.

To investigate the possibility of hindered [Cp']⁻ ring rotation, VT NMR was used (Figure 3.9). A quick comparison of the low and high temperature data shows that this hypothesis is at least partially correct, as the peaks resolve and converge (respectively) as expected, most noticeably in certain [Cp']⁻ ring signals (5.88 – 6.22 ppm) but also for the [Cp']⁻ and [tmme]³⁻ methyl groups. At lower temperatures, the [Cp']⁻ ring peak at 6.03 ppm, [tmme]³⁻ Me peak at 1.07 ppm and [Cp']⁻ Me peak at 2.28 ppm begin to split into multiple component peaks. At higher temperatures, this trend reverses; peaks for similar sites begin to converge, especially the [tmme]³⁻ and [Cp']⁻ methyl peaks. Interestingly, the peaks attributed to different sites within the structure (as explained in Figure 3.8 and Table 3.2: corner and edge [Cp']⁻ Me at 2.28 ppm and 2.17 ppm; [tmme]³⁻ Me 1.07 ppm and 0.97 ppm on different faces) also begin to converge, suggesting that at higher temperatures the overall spatial configuration of the macrocycle itself may fluctuate enough that these sites become equivalent.

3.5. Magnetic Property Measurements

Magnetic measurements of **3.2** were run on a polycrystalline sample suspended in eicosane by Dr. Thomas Pugh (a postdoctoral researcher in the Layfield group).

Direct current magnetic susceptibility measurements were performed in a static applied field of 1 kG. The $\chi_M T$ value of 87.7 cm³ K mol⁻¹ at 300 K agrees well with the calculated value of 90 cm³ K mol⁻¹ for 12 independent Gd ions in the ${}^8S_{7/2}$ ground state. [78]



Figure 3.10: Direct current magnetic susceptibility measurements for 3.2 in a static field of 1 kG. χ_M blue; $\chi_M T$ red.

Unfortunately, with such a large number of potentially interacting metal centres in a single molecule, it is currently not computationally feasible to extract *J* coupling values from this data due to likely over-parameterisation, and so the extent of interaction between the metals in **3.2** could not be determined. It was however possible to attempt to model $\chi_M T$ for **3.2** as a function of isolated Gd^{III} ions interacting with the ligand field, and this gave a poor match for the measured data (SI.2.4), showing that Ln-Ln superexchange via bridging thiolate ligands does indeed play a part in the magnetic behaviour of this molecule.

Magnetic measurements of **3.3** were performed on a polycrystalline sample by Dr. Marie-Emmanuelle Boulon of the University of Manchester. Direct current (d.c.) magnetic susceptibility measurements were performed in a static applied field of 1 kG. The $\chi_M T$ value of 172.1 cm³ K mol⁻¹ at 300 K agrees well with the calculated value of 170.04 cm³ K mol⁻¹ for 12 non-interacting Dy^{III} ions in the magnetic ground state ${}^{6}H_{15/2}$. [78]



Figure 3.11: Direct current magnetic susceptibility measurements of 3.3 in a static field of 1 kG. χ_M blue; $\chi_M T$ red.

No hysteresis was observed at 2 K. This is quite usual for dysprosium compounds due to extensive quantum tunnelling between magnetic ground states or intramolecular dipolar interactions between metal centres, the latter of which can be eliminated by magnetic dilution.



Figure 3.12: Magnetic hysteresis chart for 3.3 at 2 K. No hysteresis is observed.





Figure 3.13: Zero d.c. field out-of-phase (χ " vs ν , top) and in-phase (χ ' vs ν , bottom) data plots for **3.3** at a range of temperatures in a 1.55 G a.c. field.



Figure 3.14: Cole-Cole plots of χ' vs χ'' for **3.3**. The maxima of these curves give the lifetime τ , which is plotted against T to find U_{eff}. Only the data sets from 4 K to 20 K are used, as the others do not reach maxima.



Figure 3.15: Magnetisation lifetime τ plotted vs T^{-1} for **3.3**. The best fit for the linear high temperature region (black line) gives the energy barrier to reversal of magnetisation U_{eff}.

The out-of-phase susceptibility shows clear temperature-dependent response in zero external field (Figure 3.13, top), which confirms that this compound exhibits slow magnetic relaxation. The maximum of each isotherm is at a higher frequency with each temperature increase, indicating that there is indeed an energy barrier to reversal of magnetisation and that the mechanism of relaxation has a thermal component.

After data processing using the equation $\tau = \tau_0 e^{(\text{Ueff}/kT)}$, the linear high-temperature (thermally activated) region of the resulting chart gives an effective energy barrier U_{eff} of 97 K, or 69 cm⁻¹, and a τ_0 value of 1.36 µs. This energy barrier is approximately half that of **1.6** $(U_{eff} = 135 \text{ cm}^{-1})$, [47] and a τ_0 value on the order of microseconds is not at all unusual. [41]

Other Dy_{12} complexes have also been shown to be SMMs, although poor ones. [94] Where energy barriers were extracted, they do not exceed 5 cm⁻¹. [95] The presence of antiferromagnetic superexchange in the Gd_{12} analogues was also noted, but could not be quantified due to the complexity of the system, as in this work. [94]

3.6. Conclusions and Future Work

Three macrocyclic sulfur-bridged compounds **3.1** – **3.3** were synthesised. The structures are broadly similar, differing only in the metal used and minor variations in bond lengths and angles. ¹H NMR of **3.1** suggests some interesting behaviour of the structure in solution at different temperatures, hinting at not just $[Cp']^{-}$ ring rotation but perhaps fluctuation of the structure of the entire molecule. Further investigation by ⁸⁹Y NMR of a larger sample may be useful. **3.3** shows slow magnetic relaxation in zero external d.c. field, with an energy barrier to reversal of magnetisation of 69 cm⁻¹.

There are three possible avenues for further work. Firstly, the reaction stoichiometry can be varied, and some of this work is explored in the following chapter. The [Cp']⁻ ligands on the metal moiety can be changed to make them larger or smaller which, in the likely case that steric hindrance is the main reason for the formation of the macrocycle structure, may have an effect on the nuclearity of the complex. This has also been shown in a recent work to directly affect the magnetism itself, by subtly altering the electronics of the ligand environment. [96] Finally, the ligand itself can be altered to have different coordinating groups - Se especially may be interesting in light of a recent report [36] - or longer pendant arms, which could again change the nature of the structure formed. Incorporation of a donor group on the fourth arm may also give some interesting structures. Preliminary investigations with the equivalent triol MeC(CH₂OH)₃ were unsuccessful, as the triol has low solubility in dry solvents and no reaction occurs.

4. Lanthanide Dimers with Sulfur Bridging and Ligand Cyclisation

4.1. Introduction

This work follows on directly from the lanthanide macrocycles discussed in the last chapter. The previously reported sulfur-bridged dimers are perhaps even more relevant here, considering the structural similarities between $[(Cp'_2Dy{\mu-SSiPh_3})_2]$ (**1.6**) [47] and the new compounds reported in this chapter.

1.6 is synthesised by the salt metathesis reaction of $DyCp'_3$ and $LiSSiPh_3$. As a reminder, **1.6** was the first sulfur-bridged lanthanide SMM, and has $U_{eff} = 135$ cm⁻¹.



At the time, this was the highest known value for Figure 4.1: Structure of 1.6.

polymetallic lanthanide SMMs, but since then many more impressive compounds have been reported. [34] The use of soft ligands was intended to investigate whether greater orbital overlap between ligand and metal might help to improve SMM properties by enhancing magnetic exchange between sites. The study of an isostructural Gd^{III} compound showed that there was weak antiferromagnetic exchange between the two sites ($J = -0.105 \text{ cm}^{-1}$).

4.2. Synthesis of Sulfur-Bridged Lanthanide Dimers

Following the formation of the macrocycles 3.1 - 3.3, it seemed logical to investigate the effect of a simple change in stoichiometry. As such, instead of a 3:1 stoichiometric ratio of LnCp'₃ to tmmeH₃, a 1:1 ratio was used. The effect of the extra ligand in the system was difficult to predict, but it was anticipated that it may form larger networks by linking macrocycles together. This did not happen; instead, the reaction formed a dimer of LnCp'₂

bridged by two tmme units. In the absence of a metal with which to bind, the two free pendant arms on each tmme ligand have coupled together to form a five-membered heterocycle. (For experimental details, see Section 7.4.)



Figure 4.2: Proposed reaction scheme for 4.1 – 4.3. Ln = Y (4.1), Gd (4.2), Dy (4.3).

Synthesis of 4.1 - 4.3 is a nominally simple deprotonation reaction between one equivalent of LnCp'₃ and one equivalent of tmmeH₃, eliminating one equivalent of Cp'H. Based on the formula of the reaction, it would be sensible to expect that cyclisation of tmme eliminates one equivalent of H₂; NMR spectroscopy experiments were therefore carried out to investigate the ring closure mechanism. The reaction proceeds quickly at room temperature, with an almost immediate loss of colour upon ligand addition (similar to that observed in synthesis of 3.1 - 3.3) and then a gradual return to a pale yellow over the course of approximately one hour with stirring. The product is purified by crystallisation.

It is possible to isolate clean 3.1 - 3.3 without crystallisation by complete evaporation of solvent under vacuum and washing with hexane; for 4.1 - 4.3 this does not give a clean (by

elemental analysis) isolated product, so it is possible that there is some unknown side product which is not precipitated during crystallisation.

Transformation of 1,3-dithiopropane into 1,2-dithiolane is a known reaction with many synthetic routes reported in the literature, and it is known that the unsubstituted dithiolane is susceptible to photolysis. [97] The dithiolate ring is known to form as a result of oxidation of the dithiol by: heterogeneous or polyoxometalate-bound potassium permanganate [98]; alkyl tin halides [99]; Ti^{IV} and NaI [100]; dimethyldisulphide, [101] among others; or by a radical photochemical mechanism which can be catalysed by copper hydroxyphosphate. [102] Many of these mechanisms involve intermolecular polymerisation of the dithiol as a side reaction to formation of the dithiolate ring.

4.3. Description of Crystal and Molecular Structures

For crystal data, see SI.3.1. **4.1** – **4.3** is a lanthanide Cp'_2 dimer bridged by two thiolate ligands. Each metal centre exists in a pseudo-tetrahedral geometry, with bonds to two $[Cp']^{-}$ rings and two bridging sulfur atoms. At 2.7511(18) – 2.8456(17) Å, the Ln-S bonds are within the range of Ln-S bond lengths reported for thiolate-bridged lanthanide complexes. [42] The most interesting feature of the structure is that the tmme ligand has cyclised; the two free thiol groups have formed a sulfur-sulfur bond, presumably eliminating one molecule of H₂. NMR studies were carried out to investigate the mechanism. At 2.030(3) – 2.0940(16) Å, the length of this sulfur-sulfur bond is a good match to the literature value of 2.10 Å for such bonds within a 4- or 5-membered heterocycle. [103]



 Table 4.1: Selected bond lengths (Å) and angles (°) for 4.1 – 4.3.

Figure 4.3: Molecular structure of **4.1**, with thermal ellipsoids at 50%. Y = blue; S = yellow; C = grey; H omitted for clarity. For bond lengths and angles see Table 4.1.

4.1 crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit contains half of the molecule (one YCp'₂ unit and one bridging ligand) and so the two halves of the molecule are symmetry generated. There are two molecules in the unit cell.



Figure 4.4: Molecular structure of **4.2**, with thermal ellipsoids at 50%. Gd = green; S = yellow; C = grey; H omitted for clarity. For bond lengths and angles see Table 4.1.

4.2 crystallises in the orthorhombic space group *Pbca*. As with **4.1**, the asymmetric unit consists of half the molecule (one $GdCp'_2$ unit and one bridging ligand). The unit cell contains four molecules in total.



Figure 4.5: Molecular structures of **4.3**, with thermal ellipsoids at 50%: top, Type 1; bottom, Type 2. Dy = green; S = yellow; C = grey; H omitted for clarity. For bond lengths and angles, see Table 4.1.

4.3 crystallises in the triclinic space group *P-1*. The unit cell contains two different molecules, and the asymmetric unit consists of one half of each of these molecules. One of these molecules has two disordered sites on the bridging ligand where the CH_2 group is bent in a different direction in approximately one third of molecules (Figure 4.5). One molecule in the unit cell adopts a geometry similar to that of **4.1** (which will be referred to as Type 1), and the other is more similar to **4.2** (Type 2). See Table 4.1 for comparisons.

While essentially isostructural, there are a few structural differences between 4.3 and 4.1 that are important to note. 4.1 crystallises in the centrosymmetric space group $P2_1/c$, with only half of the molecule in the unit cell. 4.3, however, crystallises in the triclinic space group P-1, with two half molecules in the unit cell; while the two metals within each molecule are symmetrically related, there are still two separate metal environments in the **4.3** unit cell. As noted, the geometries around the Dy centres differ greatly between the two molecules, especially relating to bond angles, which could affect any magnetic properties displayed by the material. One molecule has an S-Dy-S angle of 82.62(6)° and a Dy-S-Dy angle of 97.37(6)°, which gives a Dy---Dy distance of 4.140(2) Å. In the other molecule, the S-Dy-S angle is 64.35(5)° and the Dy-S-Dy angle is 115.65(5)°, which pulls the Dy centres further apart and increases the Dy---Dy distance significantly, to 4.736(1) Å. As the easy axis of magnetisation of these dimers is likely to be directed mostly by the position of the [Cp']⁻ groups, [47] this may not have too much of an effect on the magnetic study of these molecules, but it may be useful to keep in mind in case of unexpected results. The variation of Ln-S bond lengths between 4.3(1) (2.7511(18) - 2.7609(17) Å) and 4.3(2) (2.7910(14) -2.8046(15) Å) is an order of magnitude greater than between the Ln-S bond lengths of the 4.3 and 4.1 (2.7539(9), 2.7561(8) Å) molecules with similar geometry, so this difference

between the **4.1** and corresponding **4.3** structures is negligible. Due to the relative amounts of metal present in the system, 10%Dy@**4.1** (**4.4**) is likely to crystallise in the same way as **4.1**, and so any issues presented by the differing **4.3** molecules should be eliminated and the material will be more directly comparable to $[(Cp'_2Dy{\mu-SSiPh_3})_2]$ (**1.6**); the bond lengths and angles around the metal in **4.1** are almost identical to those reported for **1.6**. [47] The Ln-S-Ln angle (97.68(3)° in **4.1**, 101.43(6) in **1.6**) is smaller by 3.75(6)° in **4.1**, and the S-Ln-S bond angle (82.32(3) in **4.1**, 78.57(5) in **1.6**) is larger by 3.75(5)° in **4.1**. All Ln-ligand bond lengths match well: Ln-S lengths are 2.7539(9), 2.7561(8) Å in **4.1** and 2.7500(15), 2.7761(16) Å in **1.6**; Ln-Cp' centroid lengths are 2.355(1), 2.357(1) Å in **4.1** and 2.353(12), 2.364(15) Å in **1.6**.

Bond lengths in **4.2** that involve Gd are 0.0113(17) - 0.0945(18) Å longer than the corresponding bonds in **4.1** and **4.3**, as would be expected for a slightly larger metal (metal centres in the Type 1 coordination mode are formally 8-coordinate: Y^{III}, 102 pm; Dy^{III} 103 pm; metal centres in the Type 2 coordination mode are formally 9-coordinate: Gd^{III}, 111pm; Dy^{III}, 108 pm). [6] Ln-S lengths are 2.7539(9), 2.7561(8) Å in **4.1**, 2.8159(17), 2.8456(17) Å in **4.2** and 2.7511(18) – 2.8046(15) Å in **4.3**; Ln-Cp' centroid lengths are 2.355(1), 2.357(1) Å in **4.1**, 2.424(1), 2.431(2) Å in **4.2** and 2.355(3) – 2.399(2) Å in **4.3**. There are significant differences in bond angles between **4.2** and **4.1**; where there are two **4.3** molecules with different geometries, one is comparable to **4.1** (Type 1) and the other is comparable to **4.2** (Type 2). The metal-metal distances differ between the two **4.3** geometries (4.140(2), 4.736(1) Å) by 0.596(2) Å, while the difference between **4.2** (4.793(2) Å) and the Type 2 **4.3** molecule is only 0.057(2) Å, a similar comparison as with **4.1**. This can be attributed to the changes in Ln-S-Ln and S-Ln-S bond angles. In the **4.2**-type geometry, the Ln-S-Ln angle

 $(115.65(5)^{\circ} \text{ in 4.3}, 115.70(6)^{\circ} \text{ in 4.2})$ is larger by $17.97(5) - 18.33(6)^{\circ}$ than in the 4.1-type geometry $(97.37(6)^{\circ} \text{ in 4.3}, 97.68(3)^{\circ} \text{ in 4.1})$. The S-Ln-S angle is also smaller by $17.97(5) - 18.32(6)^{\circ}$ in the 4.2 $(64.30(6)^{\circ} \text{ in 4.2}, 64.35(5)^{\circ} \text{ in 4.3})$ than in the 4.1-type geometry $(82.32(3)^{\circ} \text{ in 4.1}, 82.62(6)^{\circ} \text{ in 4.3})$. This therefore holds the metal sites further apart (the Gd---Gd distance of 4.793(2) Å is 0.644(2) Å longer than the Y---Y distance of 4.149(1) Å).

One particularly interesting feature is the position of the heterocyclic ring in relation to the metal centre. In the **4.1**-type geometry, the ring is held far away from the metal, so there is little to no interaction between the metal and the sulfur of the ring (a Y-S distance of 4.555(2) Å and Dy-S distance of 5.245(2) Å). However, in the **4.2**-type geometry, the ring is bent to sit much closer to the metal, and there is the possibility of an interaction between $S_{(2)}$ on the ring and the metal (a significantly shorter Gd-S distance of 2.985(1) Å, and Dy-S distance of 2.977(2) Å), which will of course greatly change the ligand environment of the metal and therefore the magnetic behaviour of the compound. This interaction may also be the source of the geometric differences between the two molecules, as a higher coordination number will necessitate smaller bond angles at the metal. It is not clear at this point what causes the change in position of the ring with respect to the metal. Perhaps the larger size of Gd^{III} makes the higher coordination number more stable compared to Y^{III}. A comparison of the structures in sphere packing mode may support this (Figure 4.6).


Figure 4.6: Comparison of **4.1** (left) and **4.2** (right) sphere packing, showing the two different chelating modes of the ligand. In **4.2**, ring sulfur 2 is coordinated to the metal, while in **4.1** the ring is free. Y, navy; Gd, green; S, yellow; C, grey.

4.4. NMR Spectroscopic Studies of 4.1

As observed in the crystal structure, the formation of the **4.1** – **4.3** dimer involves cyclisation of the $[\text{tmme}]^{3^{-}}$ ligand, and it was essential to perform NMR studies to analyse the reaction mechanism. All significant peaks in the ¹H (Figure 4.7) and ¹³C (¹H) (SI.3.2) NMR spectra of isolated **4.1** can be assigned with the help of HMBC and HSQC 2-D NMR techniques (SI.3.3). These assignments are given in Table 4.2. The protons in the ring of the bridging ligand are diastereotopic, as shown in the COSY spectrum in Figure 4.8. The H-H coupling constant for the doublets at 2.78 and 3.26 ppm corresponding to the diastereotopic protons is 10.8 Hz. Unfortunately, a pristinely clean NMR spectrum could not be obtained by the time of writing, despite attempts to purify **4.1** by recrystallization from toluene. Reasons for this difficulty are explored shortly.

Site	¹ H Shift (ppm)	Integration	Multiplicity	¹³ C Shift (ppm)
Cp' methyl	2.17	6	S	15.32
Cp' ring C	N/A	N/A	N/A	123.38
Cp' ring CH 1	5.93	4	s (broad)	110.44
Cp' ring CH 2	5.95	4	s (broad)	112.43
tmme CH ₂ 1	3.02	2	S	41.71
tmme C	N/A	N/A	N/A	55.01
tmme methyl	1.27	3	S	24.63
tmme ring CH ₂	2.77, 3.26	2, 2	d, d	49.99

Table 4.2: ${}^{1}H$ and ${}^{13}C$ { ${}^{1}H$ } data for 4.1 in d₈-THF.



Figure 4.7: : ¹H NMR spectrum of **4.1** in d₈-THF.



Figure 4.8: COSY NMR spectrum of **4.1** in d₈-THF zoomed in to show coupling between diastereotopic protons 2.78 and 3.26 ppm (site 6 in Figure 4.7). No other coupling between sites is present in the spectrum.

A room temperature reaction of YCp'₃ with tmmeH₃ in C₆D₆ was performed on a 20 mg scale in a Young's NMR tube and followed by ¹H NMR spectroscopy, to ascertain the possible mechanism of the ligand cyclisation. The ¹H NMR spectra are displayed at 2 hours, 8 hours, 16 hours, 32 hours, 50 hours, and 3 days into the reaction (Figure 4.9). The last two spectra are identical, so at this point the reaction has stopped. If H₂ is evolved during the reaction, as speculated, a small broad peak should appear at approximately 4.3 ppm. This peak is not observed however, so it is likely either that the reaction proceeds via some other mechanism or that any H₂ evolved reacts immediately with an unidentified species in solution.

The starting materials and *in situ* spectra are taken in C_6D_6 to avoid solvent-product peak overlap in the aliphatic region of the spectrum. The isolated product is shown in d₈-toluene for solubility reasons; once isolated, **4.1** has poor solubility in benzene. As well as the product, it would be expected that Cp'H is formed in the reaction mixture, and the presence of two distinct peaks at 1.87 ppm (likely the Me group of coordinated [Cp']⁻) and 1.90 ppm (free Cp'H) supports this. However, there are far more peaks in the Cp' ring region than anticipated; this may be due to dimerization of Cp'H, or there may be unknown Cp'Ycontaining intermediate species in solution. Due to the complexity of the 2.0-2.5 ppm region, where the bridging ligand CH₂ groups lie, this second possibility is quite likely. Additionally, the triplet at 0.89 ppm which is associated with the thiol protons in the starting material spectrum is still evident even when the reaction appears to have ended, although this may be confused by overlap with the tmme Me group in the end product. Unfortunately, concrete assignment of peaks is complicated by the low solubility of the isolated product in C₆D₆, so the chemical shifts do not adequately match the reaction sample.



Figure 4.9: Synthesis of **4.1**, as followed by ¹H NMR spectroscopy (the reaction proceeds from bottom to top).

After leaving the sample at room temperature for 2 weeks, the ¹H NMR spectrum is still unchanged from the measurement at 3 days' reaction time, and some peaks corresponding to the starting materials are still observed. The sample was then heated at 80 °C for 6 hours, and another ¹H NMR spectrum was taken (SI.3.5). There is a large change in the spectrum but the sample has obviously not converted cleanly to the isolated product.

It is difficult to draw a solid conclusion from these data. This reaction seems to lead to a mixture of products of which only 4.1 - 4.3 significantly crystallises from toluene at -30 °C, which may partially account for the low yields obtained. This also does not make it easy to explain the origin of the ring closure, as it seems that the mechanism is quite complex and may involve several intermediates and side products, which would explain the complexity of the *in situ* NMR spectra. This would also account for the difficulty in obtaining a clean isolated NMR spectrum, whereas 3.1 - 3.3 requires very little purification.

4.5. Magnetic Property Measurements

All magnetic measurements were performed on microcrystalline samples suspended in eicosane by Dr. Thomas Pugh (a postdoctoral researcher in the Layfield group).

Direct current (d.c.) magnetic susceptibility measurements were performed for **3.2** in static fields of 1 kG and 0.1 kG. The $\chi_M T$ value at 300 K is 15.78 cm³ K mol⁻¹ in a 1 kG field, and 15.85 cm³ K mol⁻¹ in a 0.1 kG field. This fits well to the expected value of 15.76 cm³ K mol⁻¹ for two independent Gd^{III} ions in the ${}^8S_{7/2}$ ground state. [78]



Figure 4.10: Direct current magnetic susceptibility measurements for **4.2** in a 1 kG static field. χ_M blue; $\chi_M T$ red.

The magnetic susceptibility data was fitted to extract the *J* coupling and g values for **3.2**, using the fitting program PHI [79] and the isotropic spin Hamiltonian $H = -2J[S_{Gd1} \cdot S_{Gd2}]$ where S_{GdN} denotes the spin on each Gd^{III} centre. Values of J = -0.115 cm⁻¹ and g = 1.992 give a good fit for the experimental 0.1 and 1 kG magnetic susceptibility data (Figure 4.11). The simulated and experimental magnetisation data also fit well (SI.3.5). This indicates weak antiferromagnetic superexchange between the Gd^{III} ions via the bridging sulfur atoms, which fits well with the value of J = -0.105 cm⁻¹ obtained for the magnetic exchange between Gd^{III} ions in [(Cp'₂Gd)(μ -SSiPh₃)]₂. [47] As with **2.3** (Section 2.4), a similar fit could not be replicated by simulating the interaction of a single Gd^{III} ion with the crystal field.



Figure 4.11: Data fitting for **4.2**. Blue squares and green triangles are experimental magnetic susceptibility data in 1 kG and 0.1 kG static field respectively. The solid blue line is the calculated fit given by the parameters $J = -0.115 \text{ cm}^{-1}$ and g = 1.992.

Direct current (d.c.) measurements were performed for **4.3** in a static applied field of 1 kOe. The $\chi_{\rm M}T$ value of 28.47 cm³ K mol⁻¹ at 300 K agrees well with the calculated value of 28.34 cm³ K mol⁻¹ for two independent Dy^{III} ions in the magnetic ground state ${}^{6}{\rm H}_{15/2}$. [78]



Figure 4.12: Direct current magnetic susceptibility measurements of 4.3 in a static field of 1 kOe. χ_M blue; $\chi_M T$ red.

A narrow butterfly-shaped hysteresis was observed at 1.8 K with loop openings at +/- 10 kOe. Closure of the hysteresis loop in zero field is common for lanthanide SMMs, due to efficient fast magnetic relaxation via quantum tunnelling.



Figure 4.13: Butterfly-type magnetic hysteresis measured for 4.3 at 1.8 K. Narrow openings are observed at +/- 10 kOe.



Figure 4.14: Zero d.c. field out-of-phase (χ'' vs ν , top) and in-phase (χ' vs ν , bottom) data plots for **4.3** at a range of temperatures in a 1.55 G a.c. field.



Figure 4.15: Cole-Cole plots of χ' vs χ'' for **4.3**. The maxima of these curves give the lifetime τ , which is plotted against T to find U_{eff}. The curves plotted at 2 K and 4 K show more than one relaxation process, and the curves from 23 K up do not reach maxima, so only the values from 6K to 22 K are used.



Figure 4.16: Magnetisation lifetime τ plotted vs T^{1} for **4.3**. The best fit for the linear high temperature region (black line) gives the energy barrier to reversal of magnetisation U_{eff}.

The out-of-phase susceptibility shows a temperature dependent response in zero field (Figure 4.14, top), which confirms that **4.3** is an SMM. It appears that there may be more than one relaxation process at very low temperatures (multiple maxima observed for 2 K and 4 K in Figure 4.14 top and Figure 4.15) but only one is present at the higher temperatures measured. This is fairly common, and indicates the presence of non-thermal relaxation processes at low temperature (usually quantum tunnelling).

After data processing using the equation $\tau = \tau_0 e^{(\text{Ueff}/kT)}$, the linear high-temperature (thermally activated) region of the resulting chart gives a lifetime $\tau_0 = 1.16 \ \mu\text{s}$ and an effective energy barrier U_{eff} = 125 K or 87 cm⁻¹. Both values are within the range for Ln SMMs [41] and U_{eff} is approximately 2/3 of the value obtained for **1.6** of 135 cm⁻¹. [47]

Measurements were also performed on a magnetically dilute sample of 10%Dy@4.1 (4.4). At this dilution level, 1% of the sample would consist of Dy₂, 18% would consist of the species of interest DyY, and 81% would consist of diamagnetic Y₂. The single-Dy species will therefore provide the overwhelming majority of the magnetic response in such a sample, allowing for a study of the system with intramolecular magnetic interactions removed.

Direct current measurements of **4.4** were performed in an unoptimised static applied field of 1 kOe. The $\chi_M T$ value of 1.33 cm³ K mol⁻¹ at 300 K (with diamagnetic correction applied) is slightly low compared to the calculated $\chi_M T$ value of 1.42 cm³ K mol⁻¹ for 0.1 independent Dy^{III} ions in the ⁶H_{15/2} ground state. [78]



Figure 4.17: Direct current magnetic susceptibility measurements for **4.4** in a 1 kG static field. χ_M blue; $\chi_M T$ red.

Hysteresis measurements of **4.4** show similar butterfly-shaped openings to **4.3**, again with a closed loop at zero field, but the openings are much wider than for the pure sample and are evident up to 3.4 K. The remaining loop closure at zero field indicates that quantum tunnelling is still active, but the improved hysteresis at higher temperatures than in **4.3** shows that removing metal-metal interactions does deactivate some relaxation mechanism within the system; the specifics of this are discussed shortly.



Figure 4.18: Magnetic hysteresis measured for 4.4. Loops are observed at approximately +/- 1.5 kOe up to a temperature of 3.4 K, with a closure at zero field.



Figure 4.19: Zero d.c. field out-of-phase (χ'' vs ν , top) and in-phase (χ' vs ν , bottom) data plots for **4.4** at a range of temperatures in a 1.55 G a.c. field. The low frequency peaks in the 2K data are machine artefacts which often arise from weak and diluted samples.



Figure 4.20: Cole-Cole plots of χ' vs χ'' for **4.4**. The maxima of these curves give the lifetime τ , which is plotted against T to find U_{eff}. The curves plotted at 2 K and 4 K may again show more than one relaxation process, and the curves from 21 K up do not reach maxima, so only the values from 6K to 20 K are used.



Figure 4.21 Magnetisation lifetime τ plotted vs 1/T for 4.4. The black line gives the energy barrier to reversal of magnetisation U_{eff}.

The 2 K a.c. measurement for **4.4** shows an unusual feature (the peak noted in the caption for Figure 4.19) at low frequency in both χ' and χ'' measurements, which can happen for weak samples such as this. Measurements at 4 K and higher temperatures are normal. The main relaxation process at 2 and 4 K appears to be temperature-independent in the out-ofphase measurement, but becomes temperature-dependent at higher temperatures; as usual, this is likely due to quantum tunnelling at low temperature. Data for temperatures between 6 and 20 K are used for calculation of the energy barrier, as these are the temperatures with both a single temperature-dependent relaxation process and a maximum in the Cole-Cole plot.

Using the equation $\tau = \tau_0 e^{(U = ff/kT)}$, it is again possible to extract U_{eff} for this compound. The U_{eff} value of 122 K or 85 cm⁻¹ agrees well with the U_{eff} of 87 cm⁻¹ obtained for the pure compound, suggesting that thermal relaxation processes within this system are not affected by interaction between Dy^{III} ions. τ_0 for **4.4** is 0.34 µs, which is again within the expected range for lanthanide SMMs. [41] The noted improvement in hysteresis is seen at lower temperature (< 3.4 K) than those at which the thermal relaxation pathway dominates (> 6 K). Comparison of Cole-Cole plots for **4.3** (Figure 4.15) and **4.4** (Figure 4.20) shows that at low temperature (< 6 K), there are two relaxation processes in **4.3** but only one in **4.4**; removing this competing relaxation pathway is the likely mechanism to the improved hysteresis observed upon magnetic dilution.

Complete Active Space Self-Consistent Field (CASSCF) calculations were performed by Dr. Nick Chilton of the University of Manchester using MOLCAS 8.0 [83] on the experimental **4.3** crystal structure reported here with no structural optimisation. Each Dy^{III} centre was studied independently, with the other replaced by the closed-shell Lu^{III}. The basis sets were chosen

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from the ANO-RCC library; [88] the Dy^{III} centre of interest had VTZP quality, the first coordination sphere had VDZP quality and all other atoms had VDZ quality. The active space consisted of the 7 4*f* orbitals, with 9 active electrons. 21 sextets, 224 quartets and 490 doublets were considered in the orbital optimisation; 21 sextets, 128 quartets and 130 doublets were mixed by spin-orbit coupling. The results of these calculations are given in Table 4.3.

Table 4.3: Calculated values for ground and excited states in 4.3: energy above the ground state, anisotropic g-values, angle of easy axis of magnetisation in the excited states compared to the ground state. Dy in Type 1coordination with monodentate S-ligand (Dy in Type 2 coordination with chelating S-ligand)

State	Energy (cm ⁻¹)	<i>g</i> _x 1 (2)	g _y 1 (2)	g _z 1 (2)	Angle (°) 1 (2)
Ground	0 (0)	0.00 (0.02)	0.00 (0.05)	19.34 (18.88)	
1 st	121 (95)	0.01 (0.07)	0.01 (0.11)	16.95 (16.73)	1.9 (3.8)
2 nd	268 (236)	0.07 (0.80)	0.14 (2.66)	14.80 (15.91)	5.8 (87.2)
3 rd	309 (250)	1.16 (0.16)	1.48 (4.90)	17.08 (12.11)	86.7 (16.8)
4 th	339 (297)	0.31 (1.07)	3.04 (1.67)	10.05 (10.54)	8.3 (6.3)
5 th	371 (334)	3.96 (4.37)	6.52 (7.16)	10.48 (9.97)	86.8 (82.9)
6 th	403 (374)	0.24 (0.08)	1.54 (0.73)	15.35 (15.75)	82.9 (87.3)
7 th	555 (500)	0.06 (0.15)	0.10 (0.21)	19.73 (19.47)	88.4 (88.6)



Figure 4.22: The two different types of coordination mode for the bridging ligand of 4.3.

As suggested earlier, interaction between the metal centre and the sulfur on the ligand ring does indeed create a less axial ligand environment which negatively affects the SMM properties of the compound. In the Type 2 coordination sphere where the bridging ligand is chelating (Figure 4.22), the excited states are lower by 26 - 59 cm⁻¹ and the anisotropy of the ground state is lowered compared to the Type 1 coordination sphere. For Dy^{III} to show good SMM properties, the ground state needs to have maximum anisotropy where $g_z \approx 20$ and $g_x \approx g_y \approx 0$ (*i.e.* the easy axis of magnetisation is completely confined to the z axis and cannot deviate towards the x or y axis); this is true for Type 1 coordination, but not for Type 2. This may account for the differences in low temperature behaviour noted in 4.3 and 4.4; the pure compound has a competing fast relaxation pathway corresponding to the Type 2 metal centre, which is absent from the diluted sample where only the Type 1 centre is present due to the influence of the majority **4.1** species. Additionally, for the magnetisation to relax via an excited state above the first, the states by which it does not relax must also have $g_z \approx 20$ and $g_x \approx g_y \approx 0$, as well as an easy axis of magnetisation which is parallel to that of the ground state (0°). The first excited state of **4.3** does not have these qualities, and so the magnetisation must relax via the first excited state.

4.6. Conclusions and Future Work

A sulfur-bridged lanthanide dimer was synthesised and characterised for Ln = Y, Dy, and Gd. The synthesis involved formation of a heterocyclic ring on the bridging ligand, the mechanism of which was investigated by NMR spectroscopy. These experiments were inconclusive, and a far more involved study may be necessary to fully understand the method of ring closure in this molecule. Isolation and characterisation of side products may be helpful, although difficult. **4.3** was found to be a single molecule magnet with $U_{eff} = 87 \text{ cm}^{-1}$ and narrow magnetic hysteresis at 1.8 K. The magnetically dilute **4.4** showed no significant change in U_{eff} , but magnetic hysteresis was much improved up to 3.4 K. These results are within the expected range for lanthanide-based single molecule magnets [41] and are explained by calculations. **4.2** shows weak antiferromagnetic superexchange between the metal sites in the complex, although due to differences in the coordination sphere between the **4.1** and **4.2** type structures, it is not possible to say definitively whether this applies to all Ln versions of this complex. Similarity to exchange observed in $[Cp'_2Gd(\mu-SSiPh_3)]_2$, however, indicates that this is likely.

5. Lanthanide Alkoxide Cluster Compounds

5.1. Introduction

This thesis focuses mainly on lanthanide complexes with soft bridging ligands; however, as a

continuation of the exploration of unusual structural motifs with the potential for interesting magnetic behaviour, oxygen-ligated lanthanide systems should not be neglected. Lanthanide clusters incorporating alkoxide ligands can be a rich source of such structural variety, and some have also been shown to possess excellent SMM properties.



Figure 5.1: Crystal structure of 1.3. [74] Dy, green; O, red; C, black.

Lanthanide alkoxides can be easily formed in several ways, with the general synthesis proceeding by reaction of the metal or a lanthanide amide $[Ln(N{SiMe_3}_2)_3]$ with an alcohol ROH, or the metal chloride $LnCl_3$ with a potassium alkoxide ROK under anhydrous anaerobic conditions. [5] However, these syntheses may not be as simple as they seem. $[Ln_5O(O^iPr)_{13}]$ was assumed for a long time to be the simple lanthanide isopropoxide salt $[Ln(O^iPr)_3]$, until the structure was confirmed by crystallography as a square-based pyramid of lanthanide



Figure 5.2: Crystal structure of **1.2**. [34] Dy, purple; K, green; O, red; C, black.

ions with a μ_5 -oxide-bridged base, [67] [104] a structural motif which will be revisited later in this work. Other lanthanide alkoxide compounds, assumed to be monomeric salts, also form complex cluster structures; a lanthanide centre is unlikely to be coordinatively saturated by three alkoxide ligands, unless they are extremely bulky. [105] Lanthanide alkoxide compounds have been considered promising for use in catalysis [106] and are commonly used as precursors in the production of ceramics or for metal oxide deposition. [107] Several siloxide-bridged lanthanide compounds have been reported, the majority of which use the bulky [Ph₃SiO]⁻ ligand and so form low-nuclearity complexes. [64]

Recently, lanthanide alkoxide cluster compounds have been revealed as an area of interest in molecular magnetism. Two compounds in particular, **1.3** [74] and **1.2**, [34] set new records at the time of their reports for energy barriers of polymetallic dysprosium-based SMMs (Table 1.1), and these are still some of the highest energy barriers in the field.



Figure 5.3: Reaction scheme for synthesis of 1.3. [74]



Figure 5.4: Reaction scheme for synthesis of 1.2. [34] Although not reported, addition of one equivalent of H₂O and elimination of two equivalents of HCl would balance the equation.

There is a lot of scope for experimentation with the synthesis. As seen for **1.3** and **1.2**, even a minor change to the ligand (addition of a single methyl group) can alter the structure of the product. A few other small changes in the reaction conditions are also evident. In the synthesis of **1.3**, the potassium salt of the ligand (KOⁱPr) is generated *in situ* and stoichiometric H₂O is added to the reaction mixture to ensure the presence of the oxide in the final structure. For **1.2**, the potassium salt used (KO^tBu) is commercially available, and was used as supplied. No extra water is added to this reaction and yet the central oxide is still evident in the structure, possibly due to either KOH contamination of the potassium *t*butoxide starting material or wet solvent. Another likelihood is that the oxide is generated via the Bradley reaction, [108] where two ligated alkoxides react to form an oxide and an ether, which is eliminated (Figure 5.5). Isolated yields for both of these reactions are low to middling, ranging from 9% to 46%, probably due to difficulties with crystallisation.



Figure 5.5: The Bradley reaction for formation of oxide and ether from two alkoxide ligands. [108]

For this thesis, the cheap and easily available silanol Me₃SiOH was chosen as the precursor to the siloxide ligand [Me₃SiO]⁻. The difference between this and the [Bu^tO]⁻ used in previous work is again very minor (simple substitution of a carbon atom for a silicon) and it would be useful to see the effect of this variation on the product structure, given the apparent sensitivity of this chemistry to small changes in the reaction conditions.

5.2. Synthesis

For experimental details, see Section 7.4. KOSiMe₃ was initially synthesised using potassium metal reacted with HOSiMe₃ in solution. In toluene, KOSiMe₃ proved insoluble and the metal surface became coated with the salt, stopping the reaction at low completion even with the aid of sonication. The use of Et₂O as a solvent (in which KOSiMe₃ is soluble) was more successful, but the reaction is still quite slow and unreacted metal is present even after three days. Using KN(SiMe₃)₂ as the potassium source gives a much cleaner, faster reaction and pure KOSiMe₃ was easily isolated in good yield (79%).

K(s) + HOSiMe₃
$$\xrightarrow{\text{toluene or Et}_2O}$$
 KOSiMe₃ + H₂

 $K(N(SiMe_3)_2) + HOSiMe_3 \xrightarrow{pentane} KOSiMe_3 + HN(SiMe_3)_2$

Figure 5.6: Reaction schemes for synthesis of KOSiMe₃.



Figure 5.7: Top: reaction scheme for synthesis of 5.1. Bottom: Crystal structure of 5.1, with methyl groups omitted for clarity. Dy, green; K, blue; O, red; Si, orange.

5.1 was synthesised in toluene at reflux overnight, and the product was purified by extraction into and crystallisation from hexane. The experiment was performed on a small scale and the isolated yield was low, at only 20 mg and 21% of the theoretical total yield, so there was not enough material for further analysis after determination of the crystal structure. This yield is comparable to some of those reported for analogues of **1.2**, [34] and can be attributed to the difficulty of crystallising the product of a small scale reaction, especially a product with high solubility.



Figure 5.8: Top: reaction scheme for synthesis of **5.2**. Bottom: crystal structure of **5.2**, with methyl groups omitted for clarity. Dy, green; K, blue; O, red; Si, orange.

5.2 was formed in an attempt to scale the previous reaction up (1.6 mmol DyCl₃) in order to collect enough **5.1** to perform full characterisation, given the low yield of the synthesis. At 21.3%, this reaction had the highest isolated yield of all syntheses reported in this chapter. Similar reaction and isolation conditions to the synthesis of **5.1** were used; the stoichiometry of the reaction was not different between the two, and the slight change given in the reaction schemes is intended to reflect the difference in the structures formed. The main difference between these two syntheses is the concentration of the reaction mixture, which is almost 4 times higher in the synthesis of **5.2**. One unreacted equivalent of KOSiMe₃ in the synthesis of **5.1** would account entirely for the difference in stoichiometry, and is plausible given the much lower concentration of that reaction. Insertion of a fourth KOSiMe₃ unit into the cage is also a plausible consequence of an increase in reaction concentration.



Figure 5.9: Top: reaction scheme for synthesis of 5.3. Bottom: crystal structure of 5.3, with methyl groups omitted for clarity. Y, navy; K, blue; O, red; Si, orange.

5.3 is the result of performing a similar reaction at room temperature as another variation in reaction procedure, and changing the metal to Y^{III} in the hope of characterising the product using NMR (this ultimately proved unsuccessful). The change in metal is unlikely to give such a dramatic change in structure as that observed between **5.2** and **5.3**. Y^{III} is often used as a diamagnetic substitute for Dy^{III}; its reactivity and ionic radius are similar to that of Dy^{III} and their compounds from the same reaction are usually close to isostructural. The difference in reaction temperature, from reflux (135 °C in toluene) to room temperature, is far more likely to be at least partially responsible due to potentially differing energy barriers to formation of different clusters. However, the most likely culprit for formation of this cluster is accidental contamination of the reaction mixture with air or moisture, which is suggested by the six oxides within the structure. The -6 charge on the cluster and absence of counter-ions in the crystal structure suggests that these may in fact be hydroxides. Whichever they are, water is the probable source. [109]



Figure 5.10: Top: reaction scheme for synthesis of **5.4**. Bottom: Crystal structure of **5.4**, with methyl groups omitted for clarity. Dy, green; K, blue; O, red; Si, orange.

Due to NMR proving ineffective for characterisation of these clusters, Dy^{III} was again used as the lanthanide to make magnetic characterisation possible, if the product could be obtained in sufficient yield. Deliberate introduction of stoichiometric water into the reaction mixture was performed, which gave **5.4** rather than the analogous Dy version of **5.3**. As before, the siloxide salt stoichiometry given in Figure 5.10 is indicative of that which makes sense for the product formed, rather than what was actually used (2 Ln : 9 K). Other than the deliberate introduction of water and use of DyCl₃ rather than YCl₃, the actual reaction mixture was identical between **5.3** and **5.4**. It is possible that the **5.3** reaction requires its oxides to come from a different source, or to be present in a different concentration than was used here. As before, the cluster is not charge-balanced, and it is possible that there is an extra proton incorporated within the cluster that cannot be identified by crystallography; there is one proton unaccounted for in the reaction scheme, originating from the water.



Figure 5.11: Summary of the reaction conditions for synthesis of 5.1 – 5.4. Ln = Dy (5.1, 5.2, 5.4), Y (5.3)

What is clear is that minor changes in the reaction conditions result in the formation of vastly different compounds. Unfortunately, this meant that purity, yield and reproducibility were problems for this study.

5.3. Description of Crystal and Molecular Structures

	C	0		
	5.1 (Dy)	5.2 (Dy)	5.3 (Y)	5.4 (Dy)
Ln-O(oxide)	N/A	N/A	2.261(4)-2.415(4)	2.362(7)-2.379(7)
Ln-µ₄O(Si)	2.357(12)-2.406(7)	N/A	N/A	2.246(8)-2.267(9)
Ln-µ₃O(Si)	N/A	2.237(8)-2.270(8)	2.208(4)-2.235(4)	2.180(9)-2.216(8)
Ln-µ₂O(Si)	2.143(11)-2.222(9)	N/A	2.146(5)-2.161(4)	N/A
Ln-O(Si)	N/A	2.145(10)	N/A	N/A
K-O(oxide)	N/A	N/A	2.736(4)-3.018(5)	2.395(11)-3.397(11)
K-O(Si)	2.650(11)-2.917(11)	2.715(6)-2.759(8)	2.725(5)-2.962(5)	2.573(10)-3.177(9)
LnLn	3.4191(11)	5.265(10)	4.495(13)-4.562(10)	4.704(7)-4.727(8)
LnK	3.591(5)-3.675(8)	3.853(2)-3.871(2)	3.522(15)-3.794(18)	3.553(3)-3.656(6)
КК	5.278(13)-5.695(10)	3.963(8)-4.028(7)	3.799(16)-5.722(17)	2.876(9)-3.857(6)

Crystal data for all compounds is listed in SI.4.1 and SI.4.2.

Table 5.1: Bond length ranges and metal-metal distances (Å) in 5.1 – 5.4.



Figure 5.12: Crystal structure of 5.1; right, carbon removed for clarity. Dy, green; K, blue; O, red; Si, orange; C, grey; H omitted for clarity. See Table 5.1 for bond lengths.

5.1 crystallises in the orthorhombic space group *Pbcm* as a siloxide-bridged trigonal bipyramid of metals. There are 4 molecules in the unit cell, with half a molecule in the asymmetric unit. The plane of symmetry runs through both Dy atoms, O1 and K3; K1 and K2, as well as O2 and O3, are symmetry related. Dy centres are six-coordinate in a pseudo-octahedral configuration with significant distortion in all O-Dy-O bond angles, which range from 72.7(3) – 108.3(3)° (Figure 5.16) compared to the 90° angle of an ideal octahedral geometry. The maximum O-Dy-O angle for opposing ligands is 158.5(4)°, which again is much smaller than the 180° separation in an ideal octahedral geometry. The K centres are four-coordinate, with ligands forming the base of a square pyramid of which the metal comprises the peak; there is however some interaction with carbon atoms, especially those positioned directly within the plane formed by the 3 K centres where K-C distances range

from 1.984(4) – 2.539(5) Å, which is in agreement with literature values for such agostic interactions. [110] All trimethylsilyl groups are somewhat disordered, with this disorder being especially pronounced on the three 'inner' ligands (O1-3). The methyl groups directly in the 3-potassium plane are disordered over two sites in a roughly 50:50 distribution, with each site allowing for interaction with a different potassium centre. This is the origin of the apparently five-coordinate silicon atoms shown in Figure 5.12.

Dy^{III} centres in this molecule are held very close together, with a separation of only 3.4191(11) Å. Dy^{III} is bound more closely to the 'outer' siloxide ligands (O4-9) (2.143(11) – 2.222(9) Å) than the 'inner' ligands (O1-3) (2.357(12) – 2.406(7) Å) by 0.135(12) – 0.263(11) Å. This is likely due to the number of other metals bound to each ligand; the μ_2 siloxides O4-9 are more closely bound than the μ_4 ligands O1-3, and this type of bond length variance is well established for such alkoxide cluster systems. [64] However, bonds between K centres and ligands do not show the same pattern; both ligand sites have a similarly wide range of bond lengths to K centres (2.650(11) – 2.917(11) Å), implying that ligand placement is more strongly affected by the more highly-charged Dy^{III} centres. Dy-O (2.143(11) – 2.406(7) Å) bonds are significantly shorter than K-O bonds by 0.244(11) – 0.774(11) Å, as would be expected given the high charge density and oxophilic nature of the lanthanides.



Figure 5.13: Crystal structure of 5.2; right, carbon omitted for clarity. Dy, green; K, blue; O, red; Si, orange; C, grey; H omitted for clarity. See Table 5.1 for bond lengths.

Compound **5.2** crystallises in the orthorhombic space group *Pnnm* as a siloxide-bridged octahedron of metals. There are 2 molecules in the unit cell, with a quarter of a molecule in the asymmetric unit: half a dysprosium and one potassium site. Dy sites are five-coordinate, in a slightly distorted square-based pyramidal configuration. The Dy-O bond to the terminal siloxide ligand (O1,2) is tilted slightly out of the Dy-Dy axis, causing $O_{terminal}$ -Dy- $O_{bridging}$ bond angles (104.3(4) – 115.8(3)°) to vary by 11.5(4)°, while O-Dy-O bond angles between bridging siloxide ligands (O3-10) vary by less than one degree (83.04(19) – 83.74(19)°). K sites are again four-coordinate as the peak of a pyramid of which the ligands form a square

base, allowing for some stabilising interaction between K and methyl groups; K-C distances are 3.270(2) - 3.854(6) Å, which is slightly long.

The Dy---Dy distance in **5.2** is the longest of all the complexes covered in this chapter, at 5.265(10) Å. The Dy-O bond to the terminal siloxide (2.145(10) Å) is shorter by 0.092(10) – 0.125(10) Å than Dy-O bonds to the μ_3 -bridging ligands (2.237(8) – 2.270(8) Å), which is again due to a combination of electrostatic and steric factors and is part of an established literature pattern. [64] As before, Dy-O bonds (2.145(10) – 2.270(8) Å) are shorter than K-O bonds (2.715(6) – 2.759(8) Å) by 0.445(8) – 0.614(10) Å because of the much higher charge density of Dy, and the strong affinity of lanthanide ions for oxygen.

This compound can be compared to the literature example **1.2** (see Figure 5.2). [34] In **5.2** the two Dy metals are situated trans to one another within the octahedron of metals, while in **1.2** the K metals are cis to one another. **1.2** also has an oxide ligand in the centre of the metal cluster, whereas the **5.2** cluster is empty. This particular difference will prove crucial in understanding differences in the magnetic behaviour of these clusters. The alkoxide ligands used are similar: $[OSiMe_3]^-$ in **5.2**, and $[OBu^t]^-$ in **1.2**; the only difference is substitution of a carbon for a silicon, and so there is very little difference between these ligands in terms of sterics, which is the main factor in formation of these clusters. Dy-O_{terminal} bonds are 0.053(10) - 0.077(10) Å longer in **5.2** (2.145(10) Å) than in **1.2** (2.068(10) - 2.092(9) Å), [34 (SI)] while Dy-O_{bridging} bonds in **5.2** are less varied than in **1.2** (2.237(8) – 2.270(8) Å in **5.2** vs 2.213(11) – 2.515(10) Å in **1.2**). [OBu^t]⁻ bonds to K in **1.2** are also more variable and shorter on average than $[OSiMe_3]^-$ bonds to K in **5.2** (2.715(6) – 2.759(8) Å in **5.2** vs 2.611(11) – 2.756(11) Å in **1.2**). It is possible that the presence of the central oxide causes the cluster to contract as the metals bond with the ligand, bringing all parts of the

cluster closer together. Dy---Dy distances are of course much shorter in **1.2** considering the geometry of the metal arrangement within the cluster. Metals arranged cis to one another are 3.4208(11) - 3.467(11) Å apart, while the metal pair trans to one another (Dy3 and Dy4 in Figure 5.19) are separated by 4.773(10) Å. Compared to the 5.265(10) Å Dy---Dy separation in **5.2**, it would seem that the **1.2** central cluster is indeed more compact.



Figure 5.14: Crystal structure of 5.3; bottom, carbon omitted for clarity. Y, navy; K, pale blue; O, red; Si, orange; C, grey; H omitted for clarity. See Table 5.1 for bond lengths.

Compound **5.3** crystallises in the triclinic space group *P-1*. One molecule of **5.3** and two molecules of hexane crystallise in the asymmetric unit, with two asymmetric units in the

unit cell. The core of the structure could be described in two ways: as a capped cube, or as two joined square-based pyramids (this description is most useful for comparison with **1.3**). In the first interpretation, the compound consists of a cube of Y^{III} and K metal ions, with Y^{III} occupying opposing corner sites and the faces bridged by oxygen donors (either oxides, or again potentially hydroxides given the charge imbalance on the complex). On the top and bottom of the cube, the μ_5 oxide (O1, 2) sits exactly within the plane of the face, with a $178.7(2) - 178.92(19)^{\circ}$ Y-O-Y bond angle; the μ_4 oxides on the other four faces (O3-6) bow out of the plane somewhat, giving Y-O-Y angles of 141.1(2) - 142.9(2)°. The edges of the cube are bridged by μ_2 siloxide ligands (O7-10). The top and bottom faces of the cube each have a capping K ion (K1, 6), which attaches to the cube by bonding with the oxygen on the face (O1, 2), and by coordination to four μ_3 siloxide ligands, which bridge each triangular face of the pyramid formed on this site (O11-18). Each Y^{III} ion has a highly distorted octahedral coordination, with bonds to three oxide and three siloxide ligands. As with 5.4, the O-Y-O bond angles are extremely variable although not as large on the high end of the range (74.81(14) - 114.53(17) Å), and so the Y^{III} sites appear more fully coordinatively saturated compared to the Dy^{III} sites in **5.4**. The K ions on the cube have a similar coordination sphere, while the capping K ions are coordinated to four siloxide ligands in a distorted square. The open top face of the capping K ion may be stabilised by interaction with the methyl groups that extend above the plane.

The Ln---Ln distance in **5.3** is 4.495(13) – 4.562(10) Å: a little longer than in **5.4**. As with the other compounds described in this chapter, Y^{III} bonds more closely to the less congested ligand – again, the siloxide – by 0.031 – 0.269 Å: Y^{III} to μ_4 or μ_5 oxide bond lengths are 2.261(4) – 2.415(4) Å; $Y-\mu_3O$ siloxide bond lengths are 2.208(4) – 2.235(4) Å; $Y-\mu_2O$ siloxide
bond lengths are 2.146(5) – 2.161(4) Å. Ligands are bonded more closely to Y^{III} than to K (K-oxide bond lengths are 2.736(4) – 3.018(5) Å; K-siloxide bond lengths are 2.725(5) – 2.962(5) Å) by 0.321 – 0.816 Å, again most likely due to charge differences (the negative ligand being more attracted to a +3 ion vs +1).

As mentioned, it is possible to consider 5.3 as two M_5 pyramids with bases joined by oxides and siloxides, and so it may be compared to the 1.3 pyramid reported in the literature (see Figure 5.1). [74] The main difference to note is that 1.3 has a terminal alkoxide ligand on each metal site, while 5.3 has a siloxide bridge between pyramids taking up the equivalent position on each metal site of the pyramid base (bonded more closely to Y than to K) and no such ligand on the capping K site. The geometry at each metal in 5.3 is therefore distorted further from the ideal octahedral configuration than are the metal sites in 1.3. The base edge-bridging [O^IPr]⁻ ligand sites in **1.3** are replaced by oxides in **5.3**. All metal-metal sites are further apart in 5.3 than in 1.3. Cap-base distances in 1.3 average to 3.43 Å, while the equivalent distance in 5.3 averages to 3.80 Å. Neighbouring base-base distances are more similar; in **1.3** these distances average to 3.40 Å, whereas the average in **5.3** is 3.53 Å. This indicates that the 1.3 pyramid is flattened compared to 5.3, which is confirmed by comparing the cap-oxide distance: 2.60 Å in **1.3**; an average of 2.746 Å in **5.3**. As the capping metal in 5.3 is K rather than a lanthanide, this can be attributed to a simple charge difference. Y-oxide distances (2.261(4) – 2.415(4) Å) are comparable to Dy-oxide bond lengths (2.25 – 2.60 Å). If the pure dysprosium version of this compound could be synthesised, there are two ways in which the differences between 1.3 and 5.3 might affect the magnetic behaviour of **5.3**. In **1.3**, neighbouring metal sites interact, lowering the energy barrier of the pure compound; in 5.3, all lanthanoid sites are neighboured only by potassium, and so interaction between magnetically active metal sites will not be so much of a concern. However, the difference in the coordination sphere of the metals may cause a difference in the easy axis of magnetisation. In **1.3**, the easy axis on each metal is calculated to point along the terminal alkoxide-Dy-oxide bonds. [34] In **5.3**, Y is bonded to three oxides and three siloxides, which means that the orientation of the easy axis is less clear-cut; since the different ligand types are arranged on opposite sides of the metal (*fac* arrangement of the ligands), there is still anisotropy in the coordination sphere, but it is difficult to predict what effect this will have on the magnetic behaviour of the compound. Additionally, it is not clear whether the 'oxides' are actually hydroxides, in which case the anisotropy in the coordination sphere will be even less pronounced, negatively affecting the magnetic behaviour of the complex.



Figure 5.15: Crystal structure of **5.4**; bottom, carbon omitted for clarity. Dy, green; K, blue; O, red; Si, orange; C, grey; H omitted for clarity. See Table 5.1 for bond lengths.

Compound **5.4** crystallises in the monoclinic space group $P2_1/c$, as an oxide-bridged triangle of dysprosium sandwiched between two flattened trigonal pyramids of potassium. There are two molecules of **5.4** in the unit cell, with one molecule of **5.4** and one molecule of pentane in the asymmetric unit. Dy sites are six-coordinate in a highly distorted pseudooctahedral geometry, with two bonds to oxides and four to siloxides. O-Dy-O bond angles in the $[Dy_3O_3]$ central arrangement are slightly larger than the 60° expected for a regular triangle, ranging from 65.8(3) – 70.3(3)°. Other O-Dy-O bond angles are extremely varied, ranging from 80.4(3) – 130.5(4)°. There are two distinct K environments: one makes up the base of the pyramid (K2-4, K6-8), where K is five-coordinate, with bonds to two oxides and three siloxides; the other makes up the apex of the pyramid (K1, K5), where K is sixcoordinate, with bonds to three oxides and three siloxides. In both of the K sites, all K-O bonds are positioned on the same face of the metal, again leaving the other face open for agnostic interaction with methyl groups. **5.4** is a 1- charged cluster, and due to the absence of a counter-ion in the crystal structure, it is likely that there is a proton somewhere within the structure but this could not be confirmed.

The Dy---Dy distance in **5.4** is 4.704(7) – 4.727(8). Dy-oxide bonds are actually the longest of the Dy-O bond types within this molecule at 2.362(7) – 2.379(7) Å; the oxide ligands are μ_{6^-} bridging to two Dy and four K centres, compared to the μ_4 siloxide ligand (O10-15) bridging one Dy and three K centres at the next longest Dy-'sandwich' site with bond length ranging between 2.246(8) – 2.267(9) Å. The shortest Dy-O bonds are to the 'equatorial' siloxide sites (O4-9), with bond lengths of 2.180(9) – 2.216(8) Å and μ_3 -coordination to only one Dy and two K centres. As with other compounds in this class, it seems that the coordination state of the ligand directly affects the bond length to the lanthanide: more coordination, longer bond; less coordination, shorter bond. [64] Unlike other compounds discussed here, the bond lengths to K centres are similarly affected. While K-O bonds to the less congested equatorial siloxide sites are not uniformly shorter as for the equivalent dysprosium bonds, there is still a difference at the longer end of the bond ranges: 2.782(11) – 2.911(9) Å for equatorial sites, compared to 2.794(9) – 3.111(10) Å for 'sandwich' sites. However, K-oxide

bonds are much shorter than either at 2.362(7) - 2.379(7) Å. K-O bond lengths seem to be more affected by the charge on the ligand than Dy-O bond lengths.



Figure 5.16: Ln-O coordination spheres showing ligand bridging modes, and representative bond lengths (Å) and angles (°). a) **5.1** b) **5.2** c) **5.3** d) **5.4**.

Similar syntheses have led to the formation of a range of compounds with diverse geometry. There is huge variation in overall cluster geometry between complexes, and so there is also large variation in important dimensions (Figure 5.16, Table 5.1), such as metal-metal distances, metal-ligand bond lengths, and the geometry of the lanthanide coordination spheres. The lanthanide-lanthanide distance has the largest difference seen here, varying by almost 2 Å between the smallest (**5.1**, 3.4191(11) Å) and largest (**5.2**, 5.265(10) Å) measurement.

The coordination geometry at the metal centre varies hugely between these complexes. Lanthanide sites are six-coordinate pseudo-octahedral in all complexes shown here except **5.2**, which is five-coordinate square pyramidal. In **5.1** and **5.2**, all ligands are siloxides, with ligands differentiated only by the number of metals to which they are bonded. In **5.4**, four ligands on each Dy site are siloxides and two are oxides, which sit cis to one another. In **5.3**, three ligands on each Y site are siloxides and three are oxides in a *fac* arrangement. With very small synthetic changes, the effect of differences in the coordination sphere of the metal on magnetic behaviour could be investigated.

5.4. Magnetic Property Measurements

The only sample which was suitable for magnetic measurement in terms of yield and purity was **5.2**. Magnetic measurements were performed on a microcrystalline sample by Dr. Floriana Tuna of the University of Manchester.

Direct current (d.c.) measurements were performed in a static applied field of 1 kG. The $\chi_{M}T$ value for **5.2** of 28.64 cm³ K mol⁻¹ at 300 K agrees well with the calculated value of 28.34 cm³ K mol⁻¹ for two non-interacting Dy^{III} ions in the magnetic ground state ⁶H_{15/2}. [78]



Figure 5.17: Direct current magnetic susceptibility measurements for 5.2 in a static field of 1 kG. χ_M blue; $\chi_M T$ red.

In the low temperature preliminary a.c. susceptibility measurements, one temperatureindependent maximum in the out-of-phase measurement is observed for the very low temperature data (<3 K), which disappears on further warming. No temperature-dependent features are observed. Therefore, this compound does not display SMM behaviour.



Figure 5.18: Preliminary in-field (χ' , left) and out-of-field (χ'' , right) low-temperature measurements for 5.2 in a 1.55 G a.c. field. A 1 kG external d.c. field was applied.

The lack of SMM properties in **5.2** is likely to arise from a simple structural factor. This can be attributed to the empty core of the molecule, which is easy to illustrate by comparison with the previously reported **1.2**, which has a central oxide and a large energy barrier (220 and 481 cm⁻¹ in the pure compound due to two competing thermal relaxation mechanisms, 585 cm⁻¹ magnetically diluted as 5%Dy@Y₄K₂). Ignoring the central oxide, the dysprosium coordination spheres in **5.2** and **1.2** have similar geometry, as noted in earlier structural discussion. [34] CASSCF calculations revealed that each Dy site in **1.2** possesses a pure m_J = ±15/2 magnetic ground state. The first excited state m_J = ±13/2 is also pure, with alignment of the easy axis of magnetisation parallel to the ground state, and the second excited state must be reached before significant state mixing is encountered, allowing the magnetism to relax. This accounts for the high energy barrier in this complex.

The magnetic anisotropy axes in **1.2** are aligned along the Dy-oxide axis for each Dy site (Figure 5.19), and this is also true for **1.3**, which also has a high energy barrier and similarly pure magnetic ground state (367 cm⁻¹ for the pure compound, 559 cm⁻¹ magnetically diluted as 5%Dy@Y₅). [74] [34] The easy axis of magnetisation in both cases would appear to be controlled by the position of the bond between the metal and the more negatively charged oxide ligand. In contrast, the dysprosium in **5.2** is surrounded by five almost identical ligands (Figure 5.13), with no particular direction giving an easy axis of magnetisation. A very slightly shorter bond to the terminal siloxide ligand than to the bridging ligands is not sufficient to stabilise one orientation of the magnetic ground state relative to the others, and so SMM behaviour in this compound is not observed.



However, if a similar cluster with an oxide centre could be synthesised, it may show enhanced magnetic behaviour compared to **1.2**. In the pure compound, neighbouring Dy sites with magnetic axes transverse to one another interact and allow relaxation via either thermal or quantum tunnelling mechanisms to occur at a lower energy than would otherwise

Figure 5.19: Crystal structure of **1.2**, with calculated easy axes of magnetisation. [34]

be possible; elimination of this interaction in the magnetically dilute compound is the main cause of the increase in the energy barrier. In an oxide-centred version of **5.2**, the magnetic axes of the Dy centres are likely to be parallel, so dipolar interactions may not lead to lowered barriers to magnetic relaxation. This possibility may be worth investigating.

5.6. Conclusions and Future Work

Through small variations in reaction conditions, four different lanthanide trimethylsiloxide cluster compounds were synthesised and structurally characterised. Difficulties with reproducibility, purity and yield were a consistent theme throughout this chemistry, and so further investigation was stopped in favour of the more easily repeatable and higheryielding chemistry that makes up the rest of this work. However, it would be worth persevering to gain an understanding of how the chemistry may be better controlled, and to take advantage of the huge range of structures that may be accessed. Methodical variation of a range of reaction conditions – concentration, temperature, solvent, water content, and of course metals and ligands used – could give a wealth of results.

It would of course also be worth attempting full characterisation of the compounds reported here, especially with regards to their magnetic behaviour. In particular, if it is possible to incorporate a central oxide into the **5.2** cluster, its magnetic behaviour may be interesting to compare with that of **1.2**. Once that synthetic hurdle is overcome, it would then be interesting to attempt to vary the element in the centre of the cluster to explore what effect it has on the magnetism; sulfur and selenium may be good choices. This chemistry would however add even more challenge to an already difficult synthetic area.

6. Closing Remarks

6.1 Conclusions

In this thesis, the chemistry, structure and magnetism of soft-ligand-bridged lanthanide complexes have been investigated. The new erbium and gadolinium versions of the primary phosphine adduct [Cp'₃Ln(H₂PMes)] (**2.1** and **2.2**) and the cyclic phosphide trimer [Cp'₂Ln(μ -PHMes)]₃ (**2.3** and **2.4**) are reported and structurally and magnetically characterised, and the magnetic superexchange between Gd^{III} centres in **2.3** is calculated; parameters J = - 0.138 cm⁻¹ and g = 1.998 are extracted, showing weak antiferromagnetic coupling between Gd^{III} ions in a frustrated spin system.

The novel sulfur-bridged lanthanide macrocycle **3.1** – **3.3** is reported for Ln = Dy, Y, Gd; the compounds are characterised by crystallography, NMR spectroscopy (**3.1**) and magnetometry (**3.2**, **3.3**). Compound **3.3** is a single molecule magnet with $U_{eff} = 69 \text{ cm}^{-1}$. Varying the stoichiometry of the reaction gives the sulfur-bridged dimer **4.1** – **4.3** for Ln = Dy, Y, Gd, where the two free arms of the tripodal ligand tmme have cyclised. The complexes are characterised by crystallography, NMR spectrometry (**4.1**) and magnetometry (**4.2**, **4.3**), and the mechanism of ligand cyclisation is investigated by NMR spectrometry. Compound **4.3** is also a single molecule magnet with $U_{eff} = 87 \text{ cm}^{-1}$, and the magnetically dilute **4.4** shows closed-waist magnetic hysteresis to 3.4 K. The magnetic superexchange between Gd^{III} centres in **4.2** is calculated, and the parameters *J* = -0.115 cm⁻¹ and *g* = 1.992 are extracted which again show weak antiferromagnetic coupling between Gd^{III} ions.

Comparing the Gd^{III} superexchange parameters reported here and for other soft-ligandbridged lanthanide systems, [47] it would seem that soft bridging ligands do not necessarily improve the exchange coupling in lanthanide systems, despite the predicted effect of their more diffuse electron orbitals compared to hard ligand donors such as oxygen. *J* couplings remain small, at 0.105 [47] – 0.138 cm⁻¹ for the systems studied.

Additionally, the beginnings of an investigation into the reactivity and structure of siloxideand oxide-bridged lanthanide complexes are reported. Four new siloxide-bridged lanthanide clusters 5.1 - 5.4 are reported, and are characterised by crystallography and magnetometry (5.2). It has long been known that alkoxide- and siloxide-bridged lanthanide compounds take more complex structures than were initially thought, [64] [66] and here it is shown that changes in reaction conditions (concentration, temperature, water content and source) can have a significant effect on the morphology of the cluster.

6.2 Future Work

The use of soft ligand donors in lanthanide single molecule magnetism has been somewhat overlooked until relatively recently, but the field is beginning to fill out. As well as the sulfur and phosphorus bridged systems covered here, single molecule magnets with bridging arsenic and selenium ligands [36] have now been reported, and current work within the group involves the synthesis of similar complexes incorporating antimony and tellurium.

As well as simply switching the bridging donor atom for increasingly exotic elements, the more subtle effects of ligand variation on coordination geometry may well prove interesting. It is known that the single molecule magnetism of lanthanide complexes depends heavily on electrostatic interactions of the ground m_J state with the ligand

environment, [111] and the SMM behaviour of all reported soft ligand bridged complexes can be rationalised using these principles. In particular, the easy axis of magnetisation arises from the [Cp']⁻ ligands (which are almost ubiquitous in this soft ligand work) exerting an axial ligand field, which stabilises the Dy^{III} m_J ground state ±15/2; the degree to which the bridging ligands introduce equatorial electron density appears to be the main factor in the magnetic differences between these systems. [47] [35] [36]

Changing ligand bulk to force differences in complex nuclearity or geometry at the metal centre may allow for increased tunability of SMM properties. As mentioned, all soft donor bridged complexes reported by this group have incorporated methylcyclopentadienyl ligands; switching these for pentamethylcyclopentadienyl [Cp*]⁻ or other large Cp derivatives may change the magnetic properties of the complex. Changing the substituent on the bridging ligand may also allow for new structural and magnetic behaviour, as observed when switching from [Ph₃SiS]⁻ [47] to the trimeric [tmme]³⁻ or heterocyclic [(S₂H₄MeC₃)CH₂S]⁻ ligands reported here. Changing bridging ligand bulk can lead to different nuclearity lanthanide clusters, as is currently being explored within the group, and using multi-dentate ligands can give unexpected new structures. Clearly, there are many potential avenues of exploration for the application of soft bridging ligands to single molecule magnetism of the lanthanides.

A deeper and more systematic investigation into the formation of alkoxide- or siloxidebridged lanthanide clusters may also be worthwhile. The sensitivity of these reactions means that a huge variety of structures may be accessible from relatively easily-acquired starting materials. Considering that small variations in the structure of a compound can have significant effects on its magnetic properties, this could be an interesting (if time-

consuming) avenue of exploration. Further experimentation with the conditions (concentration, temperature, solvent, water content) of the reaction between KOSiMe₃ and LnCl₃ may be a place to start, and can be followed by more significant alterations: mixtures of KOSiMe₃ and HOSiMe₃, other non-lanthanide metals, different lanthanide precursors, and of course varied alkoxide ligands can be used. The scope for further work in this area is enormous.

7. Experimental Details

Unless otherwise specified, all work was performed under anaerobic anhydrous conditions using standard glove box and Schlenk line techniques. Solvents were dried as follows: toluene was dried by refluxing over potassium; THF and hexane were dried by refluxing over NaK; Et₂O was dried by refluxing over potassium with benzophenone indicator; pentane was dried using a solvent purification system. All solvents were stored under argon over either molecular sieves or a potassium mirror. Deuterated solvents for NMR spectroscopy were dried by refluxing over potassium and stored under argon.

Crystal data for **2.2** were collected on an Oxford X-Calibur 2 X-ray diffractometer, and data for **2.1**, **2.3**, **2.4**, **3.1** - **3.3**, **4.1** – **4.3**, and **5.1** – **5.4** were collected on an Agilent SuperNova X-ray diffractometer. Both machines use a MoK α X-ray source. All structures were solved using Olex2 [112] and ShelXT [113] software. All NMR spectra were collected on a Bruker Avance-III 400 MHz spectrometer. IR spectra were recorded as Nujol mulls in KBr discs on a Perkin Elmer Spectrum RX1 spectrometer. Magnetic properties were measured using a Quantum Design MPMS-7 SQUID magnetometer. Microcrystalline samples (suspended in eicosane, where noted) were transferred to an NMR tube under glove box conditions; the tube was then flame sealed. Elemental analyses were carried out by Mr Stephen Boyer of London Metropolitan University.

7.1. Synthesis of LnCp'₃: LnCp'₃ was synthesised by a modified literature procedure. [26] $(Cp'H)_2$ was cracked by heating to 72 °C under a flow of N₂ in a distillation kit. Cp'H (100 mL approx.) was collected as a colourless oil and approximately one third of the volume removed under vacuum at -30 °C to remove CpH impurities. Cp'H was stored under N₂ at -80 °C. NaH (2.40 g, 0.1 mol) was suspended in THF (50 mL). Cp'H (20.5 mL, 19.27 g, 0.24 mol)

was added very slowly at room temperature with stirring; hydrogen gas was evolved, the solution became warm, and the white suspension became a clear, deep red solution. LnCl₃ ((e.g. 8.90 g DyCl₃), 33.1 mmol) was suspended in THF (100 mL) and sonicated for 10 minutes to encourage dispersion. The NaCp' solution was then slowly transferred to the LnCl₃ suspension by cannula and stirred at reflux (70 °C) for 18 hours; the suspension became cloudier and yellow. THF was removed under vacuum. The crude solid was purified by multiple sublimations at 10^{-2} mbar/170 °C. A crystalline yellow solid ((e.g. 5.87 g DyCp'₃), 15.3 mmol, 46% yield) was collected and stored under Ar. Elem. Anal. for YC₁₈H₂₁ Calc. C 66.3, H 6.4, N 0 %, Found C 64.5, H 7.8, N 0 %; Elem. Anal. for GdC₁₈H₂₁ Calc. C 54.8, H 5.3, N 0 %, Found C 53.1, H 6.4, N 0 %; Elem. Anal. for DyC₁₈H₂₁ Calc. C 54.1, H 5.3, N 0 %, Found C 53.6, H 6.0, N 0 %; Elem. Anal. for ErC₁₈H₂₁ Calc. C 53.4, H 5.2, N 0 %, Found C 51.9, H 5.9, N 0%.

7.2. Phosphorus-Bridged Lanthanide Compounds

7.2.1. Synthesis of MesPH₂: MesPH₂ was synthesised by literature procedure. [114] PCl₃ (2.1 mL, 3.31 g, 24 mmol) was degassed under N₂, dissolved in THF (20 mL), and cooled to -78 °C. MesMgBr (24 mL, 1 M in Et₂O, 24 mmol) was added dropwise at -78 °C. The mixture was warmed slowly to room temperature and stirred at r.t. for 18 hours to form a cloudy, pale orange solution. Solvents were removed under vacuum to yield an orange paste, which was extracted into pentane (30 mL) and filtered by cannula to give a pale yellow solution. Pentane was removed under vacuum and the resulting orange oil was distilled at <10⁻¹ mbar/70 °C to give MesPCl₂ (2.5 g, 11 mmol, 46% yield) as a pale yellow oil. LiAlH₄ was purified by extraction in Et₂O and dried under vacuum. LiAlH₄ (0.50 g, 13 mmol) was dissolved in Et₂O (20 mL) and cooled to -78 °C. MesPCl₂ (2.5 g, 11 mmol) was dissolved in

Et₂O (20 mL) and added slowly to the LiAlH₄ solution at -78 °C. The mixture was slowly warmed to room temperature and stirred at r.t. for 18 hours to give a cloudy white suspension. Et₂O was removed under vacuum to give a white paste, which was extracted into pentane (30 mL) and filtered by cannula to give a clear, colourless solution. Pentane was removed under vacuum and the resulting colourless oil was distilled at <10⁻¹ mbar/70 °C. MesPH₂ (1.08 g, 8.7 mmol, 76% yield) was collected, dissolved into toluene in a 0.5 M standard solution, and stored under Ar. ³¹P NMR in C₆D₆ relative to H₃PO₄: -153.8 ppm.

7.2.2. Synthesis of Cp'₃Ln(H₂PMes) (2.1 and 2.2): Cp'₃Ln (150 mg GdCp'₃ for 2.1; 154 mg ErCp'₃ for 2.2, 0.38 mmol) was taken in a Schlenk and dissolved in dry toluene (10 mL). To this was added H₂PMes (0.76 mL, 0.5 M in toluene, 0.38 mmol) dropwise at room temperature, and stirred for 2 hours. The clear solution underwent a colour change: for 2.2, from peach to pink; for 2.1, from bright yellow to paler yellow. The solution was concentrated under vacuum until a precipitate formed, which was then warmed back into solution and cooled to room temperature. This was then cooled at -30 °C for 3-5 days. Large crystals were isolated. 2.1: square white plates, 26 % yield; Elem. Anal. for GdPC₂₇H₃₄ Calc. C 59.31, H 6.22, N 0%, Found C 59.12, H 6.17, N 0%. 2.2: pink cubes, 66 % yield, Elem. Anal. for ErPC₂₇H₃₄ Calc. C 58.25, H 6.11, N 0%, Found C 58.08, H 6.01, N 0%. IR: P-H stretch for 2.1 at 2354 cm⁻¹.

7.2.3. Synthesis of $[(Cp'_{2}Ln)(\mu$ -PHMes)]_{3} (2.3 and 2.4): 2.1 (202 mg, 0.37 mmol for 2.3) or 2.2 (206 mg, 0.37 mmol for 2.4) was taken in a Schlenk, dissolved in dry toluene (10 mL) and cooled to -78 °C. To this was added *n*-BuLi (0.25 mL, 1.6 M in hexane, 0.40 mmol) dropwise with stirring. The solution was stirred for 2 hours with slow warming to room temperature. A fine precipitate of LiCp' was formed, and the solution underwent a colour change: for 2.4,

from pink to yellow/orange; for **2.3**, from pale yellow to colourless. The solution was filtered by cannula and concentrated under vacuum until a precipitate formed, which was then warmed back into solution and cooled to room temperature. This was then cooled at -30 °C for 3-5 days. Small crystals were isolated. **2.3**: orange cubes, 41 % yield, Elem. Anal. for Gd₃P₃C₆₃H₇₈ Calc. C 54.05, H 5.58, N 0%, Found C 53.85, H 5.70, N 0%. **2.4**: bright pink cubes, 71 % yield, Elem. Anal. for Er₃P₃C₆₃H₇₈ Calc. C 52.91, H 5.46, N 0%, Found C 52.79, H5.57, N 0%. IR: P-H stretch for **2.3** at 2314 cm⁻¹.

7.2.4. Attempted Synthesis of $[(Cp'_2Ln)_3(\mu$ -PMes)_3Li][Li(THF)_2]_2: 2.3 (125 mg, 0.09 mmol) or 2.4 (129 mg, 0.09 mmol) was taken in a Schlenk, dissolved in dry THF (10 mL) and cooled to - 10 °C. To this was added *n*-BuLi (0.19 mL, 1.6 M in hexane, 0.30 mmol) dropwise with stirring. The solution was stirred for 1 hour with slow warming to room temperature. In both cases the solution darkened upon reaction and remained clear. The solution was concentrated until a lot of precipitate formed, which was warmed into solution and cooled to room temperature. This was then cooled at -30 °C for 2-3 days. If crystals do not form on cooling, the solution may be layered with dry Et₂O to encourage crystallisation.

7.3. Sulfur-Bridged Lanthanide Macrocycles

7.3.1. Synthesis of tris(mercaptomethyl)ethane (tmmeH₃): Tris(mercaptomethyl)ethane was synthesised according to literature procedure. [90] *p*-TsCl (30 g, 0.15 mol) was dissolved in pyridine (100 mL). MeC(CH₂OH)₃ (6 g, 0.05 mol) was dissolved in pyridine (50 mL). The solutions were added together slowly at room temperature with vigorous stirring at 0 °C, warmed slowly to room temperature and left to stand at r.t. for 18 hours to give a cloudy white suspension. Pyridine was removed by rotary evaporation. The solid was extracted with CHCl₃ (100 mL) and H₂O (150 mL); the organic portion was then washed with 10%

H₂SO₄ in H₂O (100 mL) and 5 x H₂O (100 mL). This was dried over MgSO₄, filtered, and concentrated to approximately 50 mL. A white solid was precipitated by addition of cold MeOH, filtered, and washed with more cold MeOH. White needles of MeC(CH₂OTs)₃ (11.4 g, 20 mmol, 40% yield) were collected. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, 6H), 7.35 (d, 6H), 3.76 (s, 6H), 2.46 (s, 9H), 0.88 (s, 3H) ppm.

Na₂S.9H₂O (3 g, 12.5 mmol) was dissolved in H₂O (25 mL) at 30 °C. CS₂ (0.75 mL, 0.95 g, 12.5 mmol) was added and the mixture was stirred at 40 °C overnight, turning from colourless to bright orange. $MeC(CH_2OTs)_3$ (1.5 g, 2.5 mmol) was dissolved in dimethylformamide (50 mL) and the Na₂CS₃ solution was added slowly at room temperature. The mixture was stirred at reflux (110 °C) for 5 hours to form a clear yellow solution. The solution was cooled to room temperature and H₂SO₄ (1 M in H₂O, 25 mL) was added, turning the solution cloudy. The solution was extracted into CHCl₃ (150 mL) and washed with H_2O (4 x 100 mL). CHCl₃ was removed by rotary evaporation to give a yellow oil. HgCl₂ (0.32 g, 1.2 mmol) and Zn powder (0.35 g, 5.4 mmol) were suspended in H₂O (25 mL) and concentrated HCl (1 mL) added. This was stirred at room temperature for 20 minutes to give Zn amalgam. The yellow oil was dissolved in THF (10 mL) and added to the amalgam. Concentrated HCl (5 mL) was added and the mixture was stirred at reflux (80 °C) for 2 hours to give a pale, cloudy suspension. This was cooled to room temperature and extracted into CHCl₃ (100 mL), washed with H₂O (4 x 100 mL), and dried over MgSO₄. CHCl₃ was removed by rotary evaporation to give tmmeH₃ as a yellow oil (0.23 g, 1.4 mmol, 56 % yield). TmmeH₃ was stored under N₂ as a 0.5 M solution in toluene. ¹H NMR (400 MHz, CDCl₃): δ 2.61 (d, 6H), 1.22 (t, 3H), 1.01 (s, 3H) ppm.

7.3.2. Synthesis of [(Cp'₂Ln)₃{{μ-SCH₂}₃CMe)]₄ (**3.1** – **3.3**): LnCp'₃ (130 mg YCp'₃ for **3.1**; 158 mg GdCp'₃ for **3.2**; 160 mg DyCp'₃ for **3.3**, 0.40 mmol) was taken in a Schlenk and dissolved in toluene (10 mL). TmmeH₃ (0.26 mL, 0.5 M in toluene, 0.13 mmol) was added dropwise at room temperature with stirring, causing an immediate change in the colour of the reaction solution from bright yellow to very pale or colourless. The solution was then concentrated under vacuum until a large volume of precipitate formed, which was then warmed gently into solution and left to cool to room temperature, before cooling at -30 °C for 5-7 days. If crystal quality is not a concern, the solution can be taken to dryness under vacuum and washed with hexane for comparable purity and much higher yield, as reported for **3.2**.

Small pale crystals of [(Cp'₂Ln)₃(MeC{CH₂S}₃)]₄ (**3.1** – **3.3**) were isolated. **3.1**: 56 % yield; Elem. Anal. for Y₁₂S₁₂C₁₆₄H₂₀₄ Calc. C 54.30, H 5.63, N 0%, Found C 54.12, H 5.41, N 0%. **3.2**: 86 % yield; Elem. Anal. for Gd₁₂S₁₂C₁₆₄H₂₀₄ Calc. C 44.29, H 4.59, N 0%, Found C 44.40, H 4.70, N 0%. **3.3**: 44 % yield; Elem. Anal. for Dy₁₂S₁₂C₁₆₄H₂₀₄ Calc. C 43.68, H 4.53, N 0%, Found C 43.52, H 4.42, N 0%.

7.4. Sulfur-Bridged Lanthanide Dimers

7.4.1. Synthesis of $[Cp'_{2}Ln(\mu-SCH_{2}\{C_{3}S_{2}H_{4}\})]_{2}$ (4.1 – 4.4): LnCp'₃ (121 mg YCp'₃ for 4.1; 146 mg GdCp'₃ for 4.2; 148 mg DyCp'₃ for 4.3; 109 mg YCp'₃ and 15 mg DyCp'₃ for 4.4, 0.37 mmol) was dissolved in toluene (10 mL). TmmeH₃ (0.78 mL, 0.5 M in toluene, 0.39 mmol) was added at room temperature and stirred. The clear yellow solution paled in colour almost immediately before gradually darkening back to yellow, and in the case of 4.3, a large amount of white precipitate formed which was warmed back into solution. The sample was crystallised by concentration and cooling at -30 °C. Small crystals were isolated. 4.1: small pale yellow crystals, 21% yield; Elem. Anal. for Y₂S₆C₃₄H₄₆ Calc. C 49.51, H 5.58, N 0%,

Found C 49.34, H 5.43, N 0%. **4.2**: small pale yellow crystals, 36% yield; Elem. Anal. for $Gd_2S_6C_{34}H_{46}$ Calc. C 42.47, H 4.82, N 0%, Found C 42.29, H 4.67, N 0%. **4.3**: small peach crystals, 49% yield; Elem. Anal. for $Dy_2S_6C_{34}H_{46}$ Calc. C 42.02, H 4.74, N 0%, Found C 41.89, H 4.88, N 0%. **4.4**: small yellow crystals, 33% yield; ICP Dy 2.15%, Y 19.23% (1:9 Dy:Y); Elem. Anal. for $Dy_{0.2}Y_{1.8}S_6C_{34}H_{46}$ Calc. C 49.08, H 5.53, N 0%, Found C 48.85, H 5.39, N 0%.

7.5. Lanthanide Alkoxide Cluster Compounds

7.5.1. Synthesis of KOSiMe₃: K(N{SiMe₃}₂) (3.13 g, 15.7 mmol) was suspended in pentane (60 mL). HOSiMe₃ (1.5 mL, 1.49 g, 16.7 mmol) was added dropwise at room temperature and stirred for 18 hours. The cloudy suspension was left to settle and the yellow solution was decanted. The white powder was then washed with pentane (40 mL), collected on a frit, washed with pentane (20 mL) and dried under vacuum for 3 hours. KOSiMe₃ was collected as a white powder (1.6 g, 12.5 mmol, 79% yield). Elem. Anal. for KOSiC₃H₉ Calc. C 28.1%, H 7.0%, N 0%; Found C 28.3%, H 7.5%, N 0%.

7.5.2. Synthesis of [Dy₂K₃(OSiMe₃)₉] (5.1): KOSiMe₃ (139 mg, 1.07 mmol) and DyCl₃ (65 mg, 0.24 mmol) were suspended in toluene (20 mL) and stirred at reflux (110 °C) for 18 hours. After cooling to room temperature, the solvent was removed under vacuum. Hexane (10 mL) was added and the solution was filtered through Celite to give a clear, colourless solution and a white residue. The solution was concentrated under vacuum and cooled at - 30 °C for 9 days. Colourless square crystals were collected (20 mg, 0.016 mmol, 21% yield). Not enough material was available for further analysis.

7.5.3. Synthesis of $[Dy_2K_4(OSiMe_3)_{10}]$ (5.2): KOSiMe₃ (1.03 g, 8 mmol) and DyCl₃ (437 mg, 1.6 mmol) were suspended in toluene (35 mL) and stirred at reflux (110 °C) for 18 hours.

After cooling to room temperature, the solvent was removed under vacuum. Hexane (20 mL) was added and the solution was filtered through Celite to give a clear, pale yellow solution and a brown residue. The solution was concentrated under vacuum and cooled at - 30 °C for 5 days. Colourless square plate crystals were isolated (234 mg, 0.17 mmol, 21.3% yield). Elem. Anal. for $Dy_2K_4O_{10}Si_{10}C_{30}H_{90}$ Calc. C 20.4%, H 5.1%, N 0%; Found C 20.2%, H 4.8%, N 0%.

7.5.4. Synthesis of [Y₄K₆(OH)₆(OSiMe₃)₁₂] (5.3): YCl₃ (340 mg, 1.7 mmol) and KOSiMe₃ (1.1 g, 8.6 mmol) were suspended in toluene (40 mL) and stirred at room temperature for 18 hours. The solvent was removed under vacuum and hexane (20 mL) added. Filtration through Celite gave a clear, colourless solution and a cream-coloured residue. The solution was concentrated under vacuum and cooled at -30 °C for 12 days. Colourless cubic crystals were isolated (152 mg, 0.09 mmol, 13% yield). Elem. Anal. for Y₄K₆O₁₈Si₁₂C₃₆H₁₁₄ Calc. C 24.5%, H 6.5%, N 0%; Found C 21.3%, H 6.0%, N 0%.

7.5.5. Synthesis of [Dy₃K₈O₃(OSiMe₃)₁₂]⁻ (5.4): KOSiMe₃ (1.05 g, 8.2 mmol) and DyCl₃ (470 mg, 1.57 mmol) were suspended in toluene (40 mL). H₂O (40 μL, 40 mg, 1.67 mmol) was added and the mixture was stirred at room temperature for 18 hours. The solvent was removed under vacuum and pentane (20 mL) added. Filtration by cannula gave a clear, colourless solution and off-white residue. The solution was concentrated under vacuum and cooled at -30 °C for 10 days. Colourless crystals were isolated (103 mg, 0.05 mmol, 9% yield). Elem. Anal. for Dy₃K₈O₁₅Si₁₂C₃₆H₁₀₈ Calc. C 22.0%, H 5.5%, N 0%; Found C 20.2%, H 5.1%, N 0%.

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Supporting Information

SI.1. Phosphorus-Bridged Lanthanide Complexes

SI.1.1: Crystallographic data for **2.1** and **2.3**:

Empirical Formula	C ₂₇ H ₃₄ GdP (2.1)	Gd ₃ P ₃ C ₆₃ H ₇₄ (2.3)
Formula Weight (g mol ⁻¹)	546.76	1489.02
Temperature (K)	150.03(10)	150.03(10)
Crystal System	Monoclinic	Monoclinic
Space Group	P2 ₁ /c	Сс
Colour	Pale yellow	Yellow
a (Å)	13.5980(4)	14.9335(4)
b (Å)	24.8641(6)	18.6062(4)
c (Å)	14.7021(4)	23.6497(5)
α (°)	90	90
β (°)	109.224(3)	103.074(3)
γ (°)	90	90
Volume (Å ³)	4693.6(2)	6400.9(3)
Z	8	4
ρ_{calc} (kg m ⁻³)	1.547	1.545
R1 [I>2.0σ(I)]	0.0335	0.0359
wR2 (all data)	0.0590	0.0616

Empirical Formula	C ₂₇ H ₃₄ ErP (2.2)	C ₆₃ H ₇₆ Er ₃ P ₃ (2.4)
Formula Weight (g mol ⁻¹)	555.76	1518.04
Temperature (K)	293(2)	150.02(10)
Crystal System	Monoclinic	Monoclinic
Space Group	P2 ₁ /n	Сс
Colour	Pale pink	Pink
a (Å)	8.1714(3)	14.8060(6)
b (Å)	24.6855(10)	18.7100(7)
c (Å)	11.4921(6)	23.6952(9)
α (°)	90	90
β (°)	94.859(4)	105.883(4)
γ (°)	90	90
Volume (ų)	2309.79(17)	6313.5(5)
Z	4	4
ρ_{calc} (kg m ⁻³)	1.598	1.597
R1 [I>2.0σ(I)]	0.0340	0.0370

0.0804

0.0681

SI.1.2: Crystallographic data for 2.2 and 2.4:

wR2 (all data)



SI.1.3: Infra-red spectra for 2.2 (black) and 2.4 (red) on KBr discs in Nujol:

SI.1.4: Magnetisation data for **2.2**, **2.3** and **2.4** (with calculated fit for exchange parameters $J = -0.138 \text{ cm}^{-1}$ and g = 1.998 for **2.3**):




SI.2. Sulfur-Bridged Lanthanide Macrocycles

Empirical Formula	$C_{185}H_{228}S_{12}Y_{12}$ (3.1)	C ₁₈₅ H ₂₂₈ S ₁₂ Gd ₁₂ (3.2)	C ₁₈₅ H ₂₂₈ S ₁₂ Dy ₁₂ (3.3)
Formula Weight (g mol ⁻¹)	3903.45	4723.58	4786.58
Temperature (K)	150.03(13)	150.01(11)	150.02(10)
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	P-1
Colour	Colourless	Colourless	Pale yellow
a (Å)	16.6022(7)	16.8976(5)	16.7661(5)
b (Å)	18.1305(8)	17.0624(7)	16.8633(5)
c (Å)	31.5718(14)	31.5662(11)	31.1650(9)
α (°)	98.515(4)	79.800(3)	79.579(3)
β (°)	91.546(4)	82.521(3)	82.245(2)
γ (°)	104.680(4)	84.140(3)	84.719(2)
Volume (Å ³)	9071.1(7)	8851.7(6)	8566.0(4)
Z	2	2	2
ρ _{calc} (kg m ⁻³)	1.429	1.772	1.860
R1 [I>2.0σ(I)]	0.1242	0.0705	0.0789
wR2 (all data)	0.3123	0.1308	0.1979

SI.2.1: Crystallographic data for 3.1, 3.2, and 3.3:

SI.2.2: DOSY NMR spectrum for **3.1** in d₈-THF:



SI.2.3: $^{13}C \{^{1}H\}$ NMR for **3.1** in d₈-THF:



SI.2.4: $\chi_M T$ data for **3.2** modelled as interaction of individual Gd^{III} ions with the crystal field, with no interaction between metal centres (solid lines). This gives a poor fit for the experimental data (symbols), and so exchange interactions must be present within the compound.



SI.3. Lanthanide Dimers With Sulfur Bridging and Ligand Cyclisation

Empirical Formula	$C_{34}H_{46}S_{6}Y_{2}$ (4.1)	C ₃₄ H ₄₆ S ₆ Gd ₂ (4.2)	$C_{34}H_{46}S_6D\gamma_2$ (4.3)
Formula Weight (g mol ⁻¹)	824.89	961.57	972.07
Temperature (K)	150.01(11)	150.02(16)	150.01(11)
Crystal System	Monoclinic	Orthorhombic	Triclinic
Space Group	P2 ₁ /c	Pbca	P-1
Colour	Pale yellow	Colourless	Yellow
a (Å)	11.0065(4)	12.2664(5)	9.0542(4)
b (Å)	12.8734(3)	13.3689(7)	11.4943(4)
c (Å)	13.3265(4)	21.5519(10)	17.1714(6)
α (°)	90	90	93.086(3)
β (°)	108.017(4)	90	90.769(3)
γ (°)	90	90	96.088(3)
Volume (Å ³)	1795.66(10)	3534.0(3)	1774.08(12)
Z	2	4	2
ρ_{calc} (kg m ⁻³)	1.526	1.807	1.820
R1 [I>2.0σ(I)]	0.0435	0.0503	0.0443
wR2 (all data)	0.0893	0.0884	0.0762

SI.3.1: Crystallographic data for 4.1, 4.2 and 4.3:



SI.3.3: HMBC and HSQC (respectively) 2D NMR spectra for 4.1 in d₈-THF:





SI.3.4: ¹H NMR *in situ* reaction spectrum of **4.1**, after heating at 80 °C for 6 hours.







SI.4. Lanthanide Alkoxide Cluster Compounds

Empirical Formula	Dy ₂ K ₃ O ₉ Si ₉ C ₂₇ H ₈₁ (5.1)	$Dy_2K_4O_{10}Si_{10}C_{30}H_{90}$ (5.2)
Formula Weight (g mol ⁻¹)	1245.02	1373.31
Temperature (K)	151(2)	149.95(3)
Crystal System	Orthorhombic	Orthorhombic
Space Group	Pbcm	Pnnm
Colour	Colourless	Colourless
a (Å)	14.7357(7)	14.9860(7)
b (Å)	20.5995(13)	18.0994(8)
c (Å)	18.2568(10)	12.9261(13)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	5541.8(5)	3506.0(4)
Z	4	2
ρ_{calc} (kg m ⁻³)	1.492	1.301
R1 [I>2.0σ(I)]	0.0659	0.0686
wR2 (all data)	0.1933	0.2290

SI.4.1: Crystallographic data for 5.1 and 5.2:

Empirical Formula	Y ₄ K ₆ O ₁₈ Si ₁₂ C ₃₆ H ₁₀₈ (5.3)	Dy ₃ K ₈ O ₁₅ Si ₁₂ C ₃₆ H ₁₀₈ (5.4)
Formula Weight (g mol ⁻¹)	1828.60	1918.60
Temperature (K)	150.04(18)	139(15)
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P2 ₁ /c
Colour	Colourless	Colourless
a (Å)	13.8828(4)	21.3487(10)
b (Å)	15.2354(4)	12.9174(8)
c (Å)	24.9767(7)	31.3784(19)
α (°)	79.092(2)	90
β (°)	81.770(2)	91.649(5)
γ (°)	65.421(3)	90
Volume (Å ³)	4705.0(3)	8649.6(9)
Z	2	4
ρ_{calc} (kg m ⁻³)	1.291	1.473
R1 [I>2.0σ(I)]	0.0684	0.0678
wR2 (all data)	0.1629	0.1925

SI.4.2: Crystallographic data for 5.3 and 5.4:



