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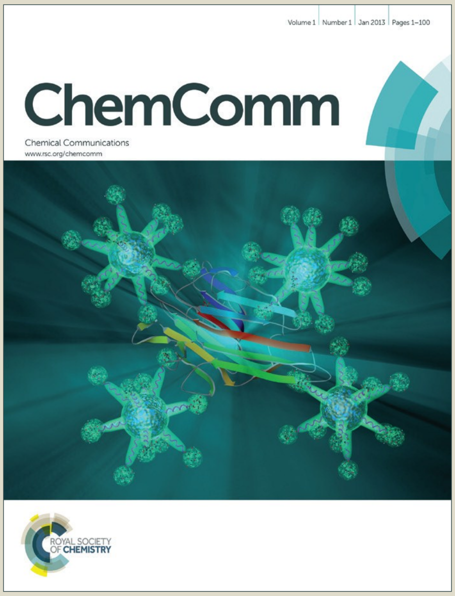

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Ferromagnetic Ordering of –[Sm(III)-Radical]$_n$– Coordination Polymers†

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[Sm(hfac)$_3$(boaDTDA)]$_n$ is the first coordination compound of a thiazyl-based neutral radical ligand to exhibit ferromagnetic ordering; T_C = 3 K. The [Sm(III)-radical]$_n$ species is soluble in common organic solvents and can be sublimed quantitatively. A McConnell I mechanism is implicated in local exchange pathways that contribute to cooperative magnetic properties.

Technological progress demands materials with novel or enhanced physical properties. Molecule-based materials are attractive because they provide flexibility of design and facile processing without the need for metallurgical techniques. In addition, they provide access to quantum phenomena, such as the qubit and qugate functionality of metal coordination complexes,[1] Single-Molecule Magnets (SMMs),[2] and Single Chain Magnets (SCMs).[3] For molecule-based materials with technologically relevant properties, the use of paramagnetic ligands is an important contemporary strategy. Milestones include magnetic ordering in metal-TCNE,[4] and metal-nitroxide species,[5] record magnetic blocking temperatures in N_2^{3-} bridged lanthanide SMMs,[6] and record exchange coupling in iron-azophenine SMMs.[7]

Our approach to radical ligand design employs thiazyl building blocks.[8] One of our primary goals is to take advantage of the impressive properties exhibited by thiazyl radicals, such as magnetic ordering of radical cation salts[9] and metal-free neutral radicals.[10] We aim to expand possible magnetic exchange pathways in metal-radical complexes and to develop new avenues to magnetically ordered materials. Herein, we report the first coordination compound of a thiazyl-based neutral radical ligand that exhibits a three-dimensional (3D) ferromagnetic (FM) order. Structurally characterized metal-radical coordination compounds that exhibit a FM ground state are relatively rare, and [Sm(hfac)$_3$(boaDTDA)]$_n$ **1** represents the first in a new family of such species. Furthermore, **1** is easily dissolved in common organic solvents and is thermally stable, such that it can be sublimed quantitatively. These properties are valuable for surface deposition and coatings.

Compound **1** is prepared from a stoichiometric mixture of the neutral radical boaDTDA ligand[11] and Sm(hfac)$_3$(DME);[12] hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; DME = 1,2-dimethoxyethane. Upon sublimation of the crude, purple product (120 °C, 10^{-2} Torr), **1** crystallizes in *Pbca* as lustrous green needles that can be re-sublimed quantitatively and readily dissolve in CH_2Cl_2.

Structural determination of **1** reveals a 1D coordination polymer comprised of alternating metal and radical components (Figure 1; Table S1). The coordination environment around the 9-coordinate Sm(III) ions is best described as a distorted mono-capped square antiprism, wherein the N1 atom is at the capping apical position.

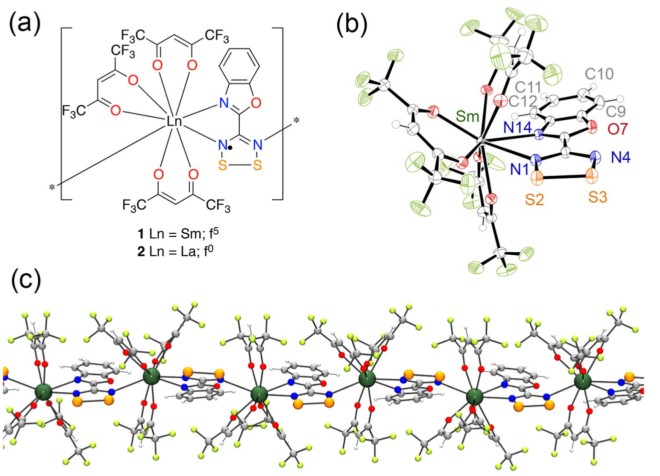

Figure 1. (a) Line drawing of the repeat unit of **1** and **2**; (b) ORTEP representation of the asymmetric unit of **1** (thermal ellipsoids for 150 K structure are shown at 50% probability); (c) 1D structure of **1**.

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†Electronic Supplementary Information (ESI) available: CIFs for **1** at 100, 150, 200, 250 and 300 K; experimental section for synthesis and characterization of **1**; additional magnetic data; Figures S1, S2 S3 and S4; Tables S1 and S2. See DOI: 10.1039/x0xx00000x

Species **1** is isomorphous with the analogous, paramagnetic $[La(hfac)_3(boaDTDA)]_n$ **2**.[13] Important similarities and subtle, but crucial, differences between the Sm(III) and La(III) structures help to rationalize the significant differences in magnetic properties (*vide infra*).

The magnetic properties of **1** have been studied in detail by dc and ac techniques, between 370 and 1.8 K, with applied field up to 7 T (Figures 2-4 and S1). At room temperature, the χT product per $Sm(hfac)_3(boaDTDA)$ unit is 0.47 cm^3 K mol^{-1} (inset Figure 2), consistent with the expected value for one Sm(III) metal ion ($4f^5$, $S = 5/2$, $L = 5$, $^6H_{5/2}$, $g_J = 2/7$; $\chi T = 0.09$ cm^3 K mol^{-1})[14] and one $S_{rad} = 1/2$ boaDTDA radical ($g = 2$; $C = 0.375$ cm^3 K mol^{-1}). Decreasing the temperature, the χT product increases progressively, suggesting local ferromagnetic interactions between spin carriers. Based on the structure, and for comparison with the analogous La(III) complex **2**,[13] Baker's model for a chain of FM coupled $S = ½$ spins (J being the magnetic interaction between the radicals) was used to fit the experimental data, considering the following spin Hamiltonian and neglecting the weakly paramagnetic Sm(III) centres (treated as an additional Curie contribution):[15]

$$\hat{H} = -2J\sum_{i} \vec{S}_i \cdot \vec{S}_{i+1}$$

As shown in Figure 2, an excellent fit is obtained down to 15 K with $g = 2.00(5)$ and $J/k_B = +2.2(1)$ K. The ferromagnetic interactions in **1** are one order of magnitude stronger than in the case of **2** (+0.29 K), highlighting the key role played by the Sm(III) centres to enhance the magnetic communication along the chain. The enhanced coupling is remarkable in light of the extremely small magnetic moment of Sm(III) and the inherently weak coupling arising from a superexchange mechanism.

Below 3.1 K, the magnetic susceptibility (Figure 3a), and thus the χT product (Figure 2), becomes strongly dependent on the applied dc field, indicating the stabilization of a magnetically ordered ground state. Accordingly, the ac susceptibility measurements of **1** (measured as a function of temperature at ac frequencies between 1 and 1500 Hz) reveal a marked out-of-phase signal below 3 K, consistent with a 3D magnetically ordered phase that possesses a spontaneous magnetization, i.e. a ferro- or ferri-magnetic state (Figure 3b and 3c).

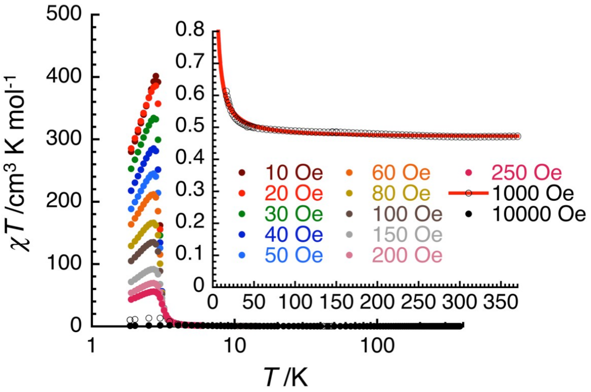

Figure 2. Semi-logarithmic plot of the temperature dependence of the χT product at different dc fields below 10000 Oe (χ is defined as molar magnetic susceptibility equal to M/H per mole); Inset: enlarged view of the χT product as a function of temperature at 1000 Oe. The solid red line indicates the best fit using the 1D model described in the text.

The field dependences of the magnetization shown in Figures 4 and S1 allow assignment of the ground state as ferromagnetic rather than ferrimagnetic because (i) no inflection point on the M vs. H data, indicative of possible antiferromagnetic interactions, was detected even at extremely low field, and (ii) the high field magnetization reaches 1.2 μ_B at 7 T and 1.86 K confirming the parallel alignment of the Sm(III) and boaDTDA radical moments. In addition, a hysteresis effect on the M vs. H curve is observed reproducibly in the ferromagnetic phase with a tiny coercive field of 20 Oe, below 2 K.

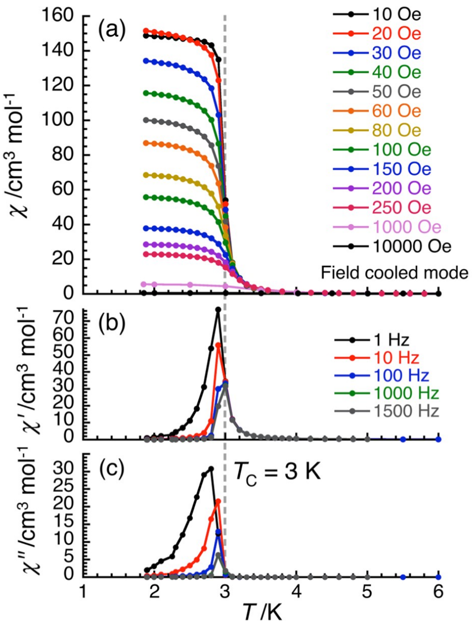

Figure 3. Temperature dependence of (a) the dc magnetic susceptibility at different dc fields below 10000 Oe (χ is defined as molar magnetic susceptibility equal to M/H per mole), and (b,c) ac susceptibility at different ac frequencies in zero-dc field. Solid lines are visual guides.

In order to rationalize the magnetic properties of **1**, it is helpful to examine relevant structural features and magnetic properties of related boaDTDA complexes. First, to understand contributions to the magnetic coupling along a 1D coordination polymer, it helps to consider the isomorphous La(III) species **2**,[13] which exhibits FM interactions between boaDTDA $S_{rad} = ½$ spins, but does not exhibit magnetic ordering above 1.8 K. Using a simple orbital overlap argument, a super-exchange mechanism provides a reasonable model for the observed magnetic properties.[13] FM coupling between two paramagnetic species (e.g., boaDTDA radicals), bridged by a diamagnetic species (e.g., La(III)), may be achieved via super-

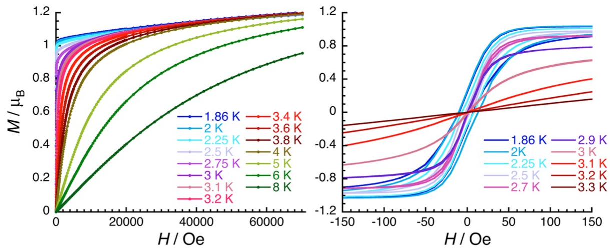

Figure 4. *M* vs. *H* data for **1**: (left) after cooling the sample in zero-dc field from 10 K to the indicated temperature with field scanning rates between 20 and 500 Oe min^{-1}; (right) highlighting the hysteresis effect in low fields with field scanning rates of 18 Oe min^{-1}. Solid lines are visual guides.

exchange if there is a difference in symmetry between the overlap of the magnetic orbital of each radical (ligand) with the (set of) orbital(s) of the bridging species (f^0 metal ion). As previously shown,[13] there is a ~32° angle relating the boaDTDA planes on either side of a bridging La(III) ion in **2**, and it is reasonable that the symmetry of the interaction of one ligand π* singly occupied molecular orbital (SOMO; Figure S2) with the empty 5d orbitals[‡] of the central La(III) ion is different from the symmetry of the interaction of the other ligand SOMO with the same 5d orbitals. Consequently, FM coupling is expected, and observed, between ligand spins in **2**. A similar argument can be made for the isostructural species **1** (Figures 1 and 5). Furthermore, all atomic orbitals on any given nucleus are necessarily orthogonal to one another, thus the empty 5d orbitals are orthogonal to the partially filled 4f^5 orbitals of Sm(III), and FM coupling between all ligand and lanthanide moments is anticipated in the 1D coordination polymer of **1**.

To achieve a FM ground state, however, there must be interactions between the moments of neighbouring chains in **1**. A conceptual design for FM ordered molecule-based materials was famously proposed by McConnell in the 1960s.[16] Now termed the McConnell I mechanism, FM exchange between net magnetic moments occurs via contact between α spin density (↑) on one molecule and β spin density (↓) on a neighbouring molecule.[§] FM interactions via a McConnell I mechanism were demonstrated in the Ni(II) complex of the boaDTDA radical ligand.[11] Specifically, contacts between the thiazyl S atoms (α spin density) and the benzoxazolyl C atoms (β spin density) were determined to be the primary intermolecular exchange pathway (Figure S3). These contacts also exist *between* 1D coordination polymers in **1**, as shown in Figure 5 (Table S2). Furthermore, they are all shortened in **1** compared with **2**, and they appear to compress with decreasing temperature (Table S2). The McConnell I mechanism may be a key pathway for FM interactions between the chains in **1**, stabilizing a FM ordered state below 3 K.

The first metal compound of a neutral thiazyl radical to exhibit FM ordering, **1** is a new milestone in the development of thiazyl-based materials (T_C = 3 K). Although the total combination of weak interactions resulting in cooperative magnetic properties may be complex and subtle, both a superexchange mechanism along the 1D coordination polymer and a McConnell I mechanism between polymers can be rationalized. Because the magnetic moment of Sm(III) is very small, the magnetic properties of **1** can be regarded as primarily "ligand centred". Nevertheless, it is clear that the contribution from Sm(III) is a key feature. Comparison with structurally similar species provides a good starting point for understanding the properties of **1**. Plans are currently underway to study a complete series of structurally analogous lanthanide coordination polymers, by computational methods, neutron diffraction, and spectroscopic techniques, in order to gain a more comprehensive understanding of the local magnetic moments and their relation to the proposed (super)exchange pathways.

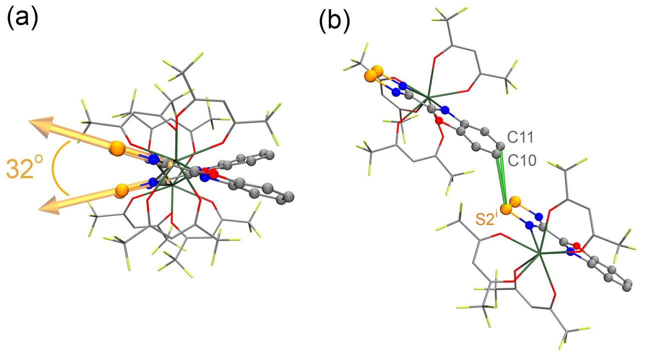

Figure 5. Excerpts from the crystal structure of **1** viewed down [010], illustrating (a) the angle between planes of boaDTDA ligands in the 1D coordination polymer, and (b) the close contacts (bright green lines) between benzoxazolyl carbon atoms C10 and C11 of a molecule in one chain and sulphur atom S2 of a molecule in a neighbouring chain; symmetry code: (i) *x*, 3/2 – *y*, *z* + 1/2.

Notes and references

‡ Although the 4f orbitals are nominally the frontier atomic orbitals, they are buried in the xenon core in most lanthanide trications. It is widely accepted that lanthanide-ligand interactions involve the empty 5d orbitals, primarily.

§ All paramagnetic molecules have regions of α (positive; up) spin density and regions of β (negative; down) spin density. For a doublet ground state, α is the majority spin density. Contact between α spin density on one molecule and β spin density on a neighboring molecule results in antiparallel alignment of these two moments, and therefore parallel alignment of all regions of α (majority) spin density on the two molecules, and thus ferromagnetic coupling.

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