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A new dithiolene complex magnet: $[Ni(Cp^*Rubdt)_2][CF_3SO_3]$

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Abstract

The unique salt $[Ni(Cp^*Rubdt)_2][CF_3SO_3]$, containing the features of both a metal dithiolene complex and a metallocene, has been studied by d.c. and a.c. magnetic susceptibility measurements. This indicated ferromagnetism with $T_c = 3.5$ K as evidenced by splitting of the field-cooled and zero-field-cooled d.c. susceptibility, remnant magnetisation, a non-zero imaginary component and a peak in the real component of the a.c. susceptibility and magnetic hysteresis. Studies of magnetisation against field indicated superparamagnetic behaviour above the ordering temperature up to around 10–20 K, suggesting correlated behaviour of the spins in one or two dimensions before the onset of 3D order. In contrast to many mixed dithiolene complex—metallocene salts, the structure of the title compound ensures that no segregation of the dithiolene and metallocene components into separate stacks can occur, a structural feature that has previously led to interesting magnetic materials.

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1. Introduction

Metal complexes of 1,2-dithiolenes have been widely studied due to the cooperative electronic properties displayed in many of their salts. This has given rise to materials such as superconductors [1–3], ferromagnets [4] and a wide range of other conducting and magnetic materials [4,5]. These typically show structures composed of stacks of planar or approximately planar complexes, and the cooperative electronic interactions generally arise through short intermolecular interactions involving metal and sulfur atoms on the molecules.

In particular, the family of materials based upon salts of $[M(mnt)_2]^-$ complexes (M = Ni, Pt; mnt = maleonitriledithiolate) have yielded a number of systems where ferromagnetism was confirmed or where evidence for ferromagnetic or other unusual ordering was obtained [6–11]. Among these salts, $[NH_4][Ni(mnt)_2]\cdot H_2O$ was shown to display ferromagnetic ordering at 4.5 K at ambient pressure with T_c rising by 0.4 K $kbar^{-1}$ until an abrupt loss of ferromagnetism above 6.8 kbar [6]. Hysteresis, with a coercive field of around 100 Oe was observed with the magnetic field applied perpendicular to the stacking axis and the anisotropy observed is typical of salts containing stacked metal dithiolene complexes. Salts based on $[Ni(mnt)_2]^-$ have also been prepared incorporating organic electron donors where one or 3D ferromagnetic order, arising through the metal complexes, is combined with high conductivity [8] or metallic conductivity [9] within the organic sublattice. In addition, salts based on $[Pt(mnt)_2]^-$ have been shown to display ferromagnetic order within 1D stacks of the metal complexes [10] or bulk 3D ferromagnetism [11].

Metal bis-1,2-dithiolene anionic complexes have also been extensively used in salts comprising metallocene based cations where both components possess unpaired electrons. In excess of 60 such salts have been reported [4] and extensive studies have shown that formation of a mixed (alternating) stack of the metallocene and the dithiolene complex offers the best opportunity to achieve 1D ferromagnetic order within the stacks. Favourable interstack interactions have, in some cases, led to metamagnets [12] and, in related salts with other planar radical anions such as $[TCNE]^-$, to ferromagnets [13]. The magnetic interactions in materials composed of dithiolene complexes alone [6,9], those composed of salts with metallocene and dithiolene components [4]

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and those composed of metallocene and planar organic radical anions [13] have been interpreted in terms of the McConnell spin polarisation model where regions of positive and negative spin density on adjacent molecules interact to give overall ferromagnetic coupling between molecules within the stack [14]. This is illustrated in Fig. 1 where antiferromagnetic coupling between the spins on the radical anion (e.g. TCNE or dithiolene complex) and the small negative spin density on the Cp rings of the metallocene results in overall ferromagnetic exchange [15].

2. Results and discussion

Recently we reported the preparation of the first example of a metal dithiolene complex where the dithiolene ligands are modified to incorporate metallocene units [16]. The preparation of [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] was achieved through reaction of [N(Bu)$_4$][Ni(bdt)$_2$] with [Cp*Ru(CH$_3$CN)$_3$][CF$_3$SO$_3$] and is illustrated in Fig. 2. Synthesis of this complex ensures structural packing that must involve a mixed arrangement of the dithiolene and metallocene components as they are both incorporated in the same molecule. Dithiolenes are non-innocent ligands and their charge can be formally regarded between dianionic (dithiolate) and neutral (dithione) extremes. Formal assignment of the ligands as dianionic results in assignment of the metal centres as Ni(III) and Ru(II) indicating that one unpaired electron may be expected for the complex. This was confirmed by epr and in keeping with the conjugated structure, spectroelectrochemical and epr studies showed that delocalisation of the unpaired electron extends over the entire molecule with significant hyperfine coupling of 10.2 G to both the Ru centres [16]. This results in the possibility of cooperative electronic interactions between the paramagnetic molecules, analogous to behaviour observed in mixed-stack metallocene and dithiolene complex containing materials.

The d.c. and a.c. magnetic properties of [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] have been investigated using a SQUID magnetometer. Magnetisation against temperature was recorded (Fig. 3) with the sample field-cooled and zero-field cooled showing a clear divergence of the two measurements around 4 K. This is consistent with measurement of the remnant magnetisation, which persists also up to 4 K. Thus, clear evidence was obtained for the existence of 3D ferromagnetic order at low temperature.

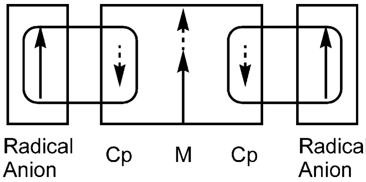

Fig. 1. Illustration of ferromagnetic coupling in 1D alternating stacks of metallocenes and radical anions through the McConnell spin polarisation model. The radical anions may be metal-bis-1,2-dithiolene complexes or organic electron acceptors. Redrawn from [15].

A plot of magnetisation against field at 1.7 K for a powder sample (Fig. 4) shows the presence of hysteresis with a coercive field of around 200 Oe. The saturation magnetisation for [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] with one unpaired electron would be anticipated to be 5750 emu mol^{-1} using $g = 2.06$ measured from epr data [16]. At 10 000 G, the magnetisation reaches a value of 2040 emu mol^{-1}, around 1/3 of the maximum saturation value that might be expected. It is not clear whether the magnetisation shown in Fig. 4 would continue to rise significantly at higher field or whether saturation at a value lower than 5750 emu mol^{-1} would occur. The latter situation has previously been observed in Ni-bis-1,2-dithiolene magnets [6].

The a.c. susceptibility was recorded at frequencies of 1, 30 and 100 Hz and is plotted against temperature in Fig. 5. This clearly indicates a non-zero imaginary component at temperatures below 8 K for all frequencies. A distinct peak in the real component observed at 3.5 K, which does not shift significantly with frequency, corresponds to the peak in susceptibility at the Curie temperature.

Magnetisation against field was measured at increasing temperatures up to 30 K and results are shown in Fig. 6. A clear non-linearity in the plot can be seen in temperatures up to 10 K and possibly up to 20 K. This is indicative of the onset of long-range correlated behaviour of the spins at temperatures well above the 3D ordering temperature and is consistent with the anisotropy that would be expected in a material formed from complexes such as [Ni(Cp*Rubdt)$_2$]$^+$ where face-to-face interactions between the complexes, for example in stacks, are typically stronger than side-by-side interactions. This superparamagnetic behaviour above the ordering temperature may also be reflected in the rise in the imaginary component of the a.c. susceptibility beginning around 8 K.

3. Conclusions

The salt [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] combines, in a single paramagnetic molecule, features of dithiolene complexes and metallocenes that have previously led to novel magnetic materials in mixed salts. Both a.c. and d.c. magnetic susceptibility measurements were consistent with the presence of bulk ferromagnetic order with $T_c = 3.5$ K. Measurement of magnetisation against field confirmed this with the observation of magnetic hysteresis and also indicated the presence of superparamag-

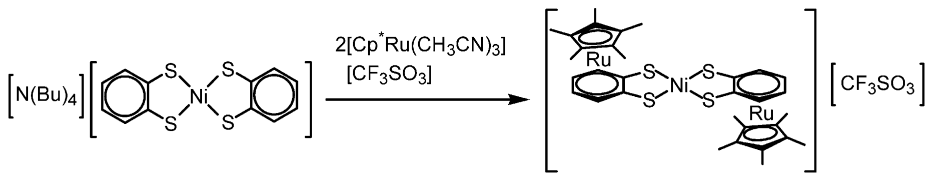

Fig. 2. Synthesis of [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] [16].

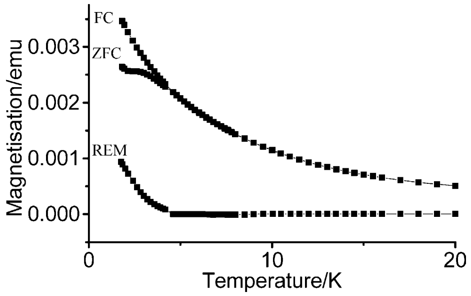

Fig. 3. Field-cooled (1000 G), zero-field cooled and remnant magnetisation.

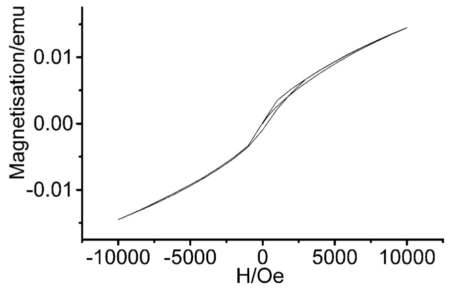

Fig. 4. A plot of magnetisation against field for [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$] at 1.7 K.

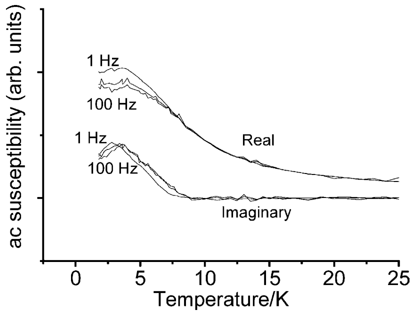

Fig. 5. Plots of the real and imaginary components of the a.c. susceptibility at 1, 30 and 100 Hz with zero d.c. bias for [Ni(Cp*Rubdt)$_2$][CF$_3$SO$_3$].

netic behaviour at temperatures above the ferromagnetic phase. Numerous attempts to obtain single crystal structural data have so far been unsuccessful. Future work will involve alteration of the counterion from $CF_3SO_3^-$, which in addition to altering the chances of obtaining structural data, will also allow modification of the magnetic properties and insight into the mechanism of magnetic exchange. A wide scope also exists for use of the (Cp*Rubdt)$^{2-}$ ligand in other bis-dithiolene and mixed ligand complexes.

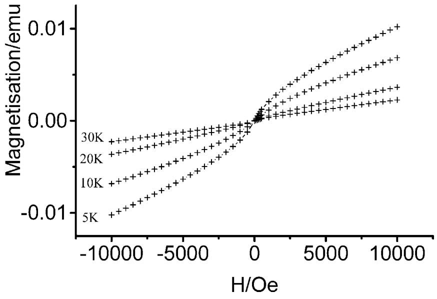

Fig. 6. Plots of magnetisation against field at temperatures of 5, 10, 20 and 30 K.

4. Experimental

All magnetic measurements were performed using a Quantum Design MPMS2 SQUID magnetometer at The University of Edinburgh.

Acknowledgements

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