

Synthesis and magnetic properties of a 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazolyl dimanganese complex†

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A spin-bearing bis-bidentate ligand, designed from a pyrimidyl-substituted R-CN₂S₂ neutral radical, is used to co-ordinate two Mn(II) metal centres yielding a thermally stable complex with antiferromagnetic coupling between the ligand-centred spin and the metal-centred spins, and thus an overall ferrimagnetic coupling scheme with a ground state $S = 9/2$.

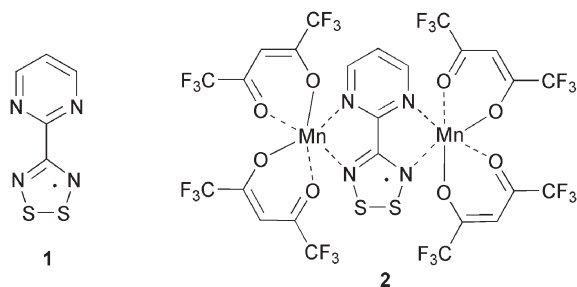
The coordination of paramagnetic metal ions to organic radicals is a promising design for the development of molecule-based magnets.^{1,2} There is, however, a limited number of organic radical building blocks from which suitable ligands can be developed. There is a greater dearth of designs incorporating a spin-bearing organic radical capable of coordinating two or more metal ions to ligand atoms of high spin density such that magnetic coupling between the metal centres is mediated *via* coupling to the ligand spin. Successful ligand designs of this nature include nitronyl nitroxide³ and verdazyl⁴ radical building blocks. We recently reported a metal complex of 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazole, demonstrating for the first time the use of the R-CN₂S₂ radical as an N-coordinating ligand.⁵ Herein, we report the first sulfur–nitrogen heterocyclic radical ligand capable of N-coordinating two metal ions **1**, and we evince the nature of the magnetic coupling between the unpaired electron on the ligand and those on two coordinated high-spin Mn(II) metal centres of a dimanganese complex **2** (Scheme 1). It is worth noting that coordination of Ph-CN₂S₂ to two nickel ions and to two iron atoms *via* the S atoms has previously been reported,⁶ however the mediation of magnetic

coupling between the metals cannot be achieved in the reported S-coordination geometry.

1,2,3,5-Dithiadiazolyl (DTDA) radicals, with a wide variety of substituents in the 4- position, have been studied for many years.⁷ They are known to be 7 π electron planar rings with the unpaired electron occupying a π^* molecular orbital that has high spin density on the S and N atoms and is nodal at the C atom. This spin distribution can be predicted by *ab initio* calculations and is borne out by solution EPR spectra.⁸ We chose the DTDA radical as our building block based on these attributes. The π^* singly occupied molecular orbital (SOMO) with high spin density on the nitrogen atoms facilitates strong magnetic coupling to a coordinated metal ion and the node at the carbon atom diminishes the electronic influence of any substituent at the 4-position. A further consideration in our choice of radical building block is the report that *p*-NC-C₆F₄-CN₂S₂ exhibits the onset of weak ferromagnetism at low temperature arising from intermolecular interactions in the solid state.⁹ This bodes well for the future of this project since the incorporation of *intermolecular* magnetic interactions may prove possible.

The synthesis of 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazole **1** was undertaken following standard preparatory procedures for such heterocycles¹⁰ and the physical properties of **1** were found to be comparable to those of other known DTDA radicals. The room temperature EPR of a solution of **1** in CH₂Cl₂ shows a 1 : 2 : 3 : 2 : 1 five line pattern consistent with coupling of one unpaired electron to two equivalent nitrogen atoms ($a_N = 5.12$ g, $g = 2.010(7)$). The cyclic voltammetry of **1** in dry CH₂Cl₂ (0.087 M *n*-Bu₄NPF₆) shows a reversible oxidation wave at $E_{1/2}(\text{ox}) = +1.22$ V (vs. SCE) and a reversible reduction wave at $E_{1/2}(\text{red}) = -0.79$ V (vs. SCE). There is also a temperature- and concentration-dependent irreversible reduction wave at $E_{\text{red}} = -0.54$ V (vs. SCE), probably associated with the redox properties of a small quantity of a dimer of **1** in solution.

Disorder in the crystalline state‡ suggests two possible modes of dimerization of the radical **1**. The first is cofacial dimerization (as shown in Fig. 1) with intermolecular S–S contacts of 3.035 Å and 3.148 Å (at 100 K). This mode of dimerization is common for RCN₂S₂ molecules in the solid state¹¹ and, given that the S–S contact distance is smaller than the sum of the van der Waals radii for two S atoms, it is expected that cofacial dimers of **1** in the crystalline state are diamagnetic. The second mode of dimerization that may be discerned from the disordered crystal structure is one in which the DTDA ring of one molecule is π -stacked with the pyrimidyl ring of the other molecule of a dimer pair. This mode of dimerization has no close intermolecular contacts between sites of high spin density and therefore is expected to give rise to a



Scheme 1 Radical ligand **1** and dimanganese complex **2**.

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† Electronic Supplementary Information (ESI) available: Experimental details and CIF files for **1** and **2** are included. MAGMUN modeling of the magnetic data is also available. See DOI: 10.1039/b512312g

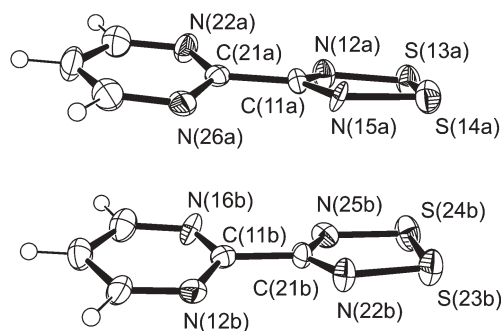


Fig. 1 An ORTEP drawing of a cofacial dimer of **1** representing one part of the 50/50 disordered structure. Data collected at $T = 100$ K. Selected bond distances (Å): S(13a)–S(14a), 2.093(3); S(23b)–S(24b), 2.086(3).

measurable amount of paramagnetism in the solid state. We are currently investigating the magnetic and conductive properties of **1**.

The dimanganese complex **2** was prepared by stirring two molar equivalents of $\text{Mn}(\text{hfac})_2 \cdot 2\text{THF}$ with one equivalent of **1** in dry THF at room temperature for 1 h. The crude product was recovered from the solution as a dark purple powder and sublimed under dynamic vacuum (10^{-2} Torr) in a gradient-temperature tube furnace (120°C) yielding small green crystals suitable for elemental analysis and magnetometry. Crystals suitable for X-ray analysis were grown by sublimation under static vacuum (10^{-2} Torr, 120°C).

The single crystal X-ray structure[‡] of **2** (Fig. 2) confirms the coordination of two manganese ions, with two hexafluoroacetylacetonato-ligands apiece, to the pyrimidine and DTDA nitrogen atoms of ligand **1**. The ligand remains intact and approximately planar (N53–C54–C55–N56 torsion angle $2.4(16)^\circ$). There is no significant change in the intramolecular S–S and S–N distances as compared with the free ligand **1**. The complex does not form dimers in the solid state.

The DC-SQUID magnetic susceptibility measurements were collected on a homogeneous solid sample of **2** (purity confirmed by elemental analysis) between 2 K and 300 K at a field strength of 1000 Oe. The magnetic data have been modeled as a three-spin system using an isotropic spin Hamiltonian ($\mathbf{H} = -J_1(2\mathbf{S}_{\text{Mn}}\mathbf{S}_{\text{DTDA}}) - J_2(\mathbf{S}_{\text{Mn}}\mathbf{S}_{\text{Mn}}) + g\beta\mathbf{S}\mathbf{H} - zJ' + \chi_{\text{TIP}}$).[§] The

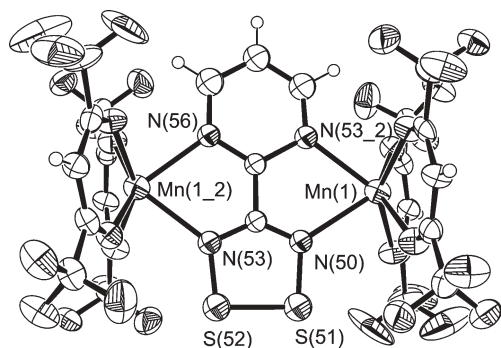


Fig. 2 An ORTEP drawing representing one part of the disorder for one of the two molecules of complex **2** observed in the single crystal X-ray data. Data collected at $T = 100$ K. Selected bond distances (Å): S(51)–S(52), 2.073(5); N(50)–Mn(1), 2.380(12); N(53)–Mn(1_2), 2.308(13); N(53_2)–Mn(1), 2.308(13); N(56)–Mn(1_2), 2.26(3).

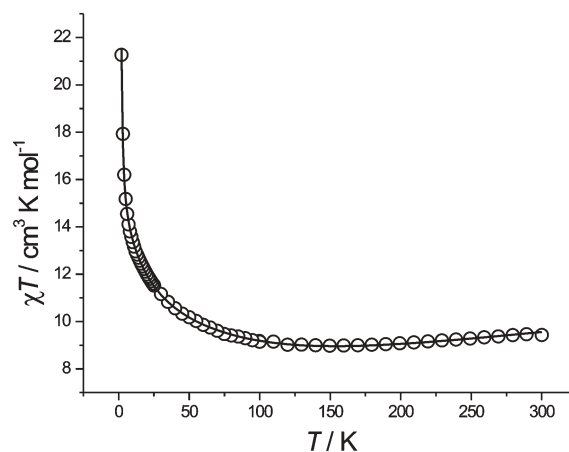


Fig. 3 Measured χT versus T data for complex **2** (○), collected at 1000 Oe. Magnetic susceptibility was measured from 2 K to 300 K and back to 2 K. As there was no variation between the field cooled and zero-field cooled measurements, a representative cycle (300 K to 2 K) is shown. The data were modeled as described in the text and the best fit is shown (—).

optimized fit parameters were found to be: $g = 2.03$, $J_1 = -65.7 \text{ cm}^{-1}$, $J_2 = -3.5 \text{ cm}^{-1}$, $zJ' = 0.034 \text{ cm}^{-1}$ and $\chi_{\text{TIP}} = 0.0043 \text{ cm}^{-1}$ where zJ' accounts for the intermolecular coupling in the solid state and χ_{TIP} is the temperature independent paramagnetism.

At 300 K, the measured χT is $9.4 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. 3). This compares well to the predicted high temperature limit of χT which is equal to the sum of the contributions of two isolated Mn(II) ions and one isolated organic radical (calculated to be $9.1 \text{ cm}^3 \text{ K mol}^{-1}$ for $g = 2$.) A small decrease in χT is observed as the temperature is decreased from 300 K to about 150 K, followed by a significant increase as the temperature is lowered further. This is consistent with the irregular spin state structure predicted for a system with antiferromagnetic coupling between the central site and the outer Mn(II) sites, resulting in a ground state ferrimagnetic coupling scheme with spin $S = 9/2$.² As the temperature is initially lowered, the first excited state to be depopulated is the highest spin state ($S = 11/2$) which results in a drop in the value of χT . Upon further cooling, excited states with lower spin than the ground state are depopulated resulting in an increase in χT . This is reminiscent of previously reported linear Mn(II)–Cu(II)–Mn(II) systems¹² and the Mn(II)–verdazyl–Mn(II) system.⁴

We have demonstrated that the 4-(2'-pyrimidine)-1,2,3,5-dithiadiazolyl neutral radical **1** can be used as a bis-bidentate ligand for the coordination of two metal cations. The resulting complex **2**, when Mn(II)(hfac)₂ is chelated to both ligand sites, is thermally stable and volatile, such that it can be purified by sublimation at elevated temperatures under dynamic vacuum. Furthermore, the unpaired electron associated with the π^* SOMO of the ligand is antiferromagnetically coupled to the unpaired electrons of both Mn(II) centres such that all the metal unpaired electrons are spin-aligned, generating a spin ground state $S = 9/2$.

Notes and references

[‡] Crystal data for **1**. $\text{C}_5\text{H}_3\text{N}_4\text{S}_2$, $M = 183.23$, monoclinic, $a = 7.1561(4)$, $b = 10.6746(5)$, $c = 10.1407(7)$ Å, $\beta = 116.994(3)^\circ$, $U = 690.24(7)$ Å³, $T = 100(2)$ K, space group $P2_1/c$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.696 \text{ mm}^{-1}$, 6572 reflections measured, 1216 unique ($R_{\text{int}} = 0.041$) which were used in

calculations. The compound was refined as a 50/50 disorder, verified by free-variable refinement. The 6-membered ring had three distinct distances refined as free variables [C(apical)–N 1.337(11); N–C 1.325(11); C–C 1.399(10)]. All non-hydrogen atoms were refined with anisotropic displacement parameters under “soft” restraints (ISOR, DELU, SIMU). The final $wR(F_2)$ was 0.0882.

Crystal data for 2. $C_{25}H_7F_{24}Mn_2N_4O_8S_2$, $M = 1121.35$, triclinic, $a = 8.9148(14)$, $b = 12.209(2)$, $c = 18.562(3)$ Å, $\alpha = 96.563(10)$, $\beta = 91.913(10)$, $\gamma = 110.860(9)^\circ$, $U = 1869.5(5)$ Å³, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.696$ mm⁻¹, 18090 reflections measured, 6570 unique ($R_{\text{int}} = 0.103$) which were used in calculations. In both of the crystallographically unique manganese complexes, the DTDA was refined at half-occupancy (it was located on a centre of symmetry.) The 6-membered ring was refined as a regular hexagon. The displacement parameters of the atoms of DTDA were refined isotropically with the symmetry related atoms having their displacement parameters restrained to be equal. The final $wR(F_2)$ was 0.0962. CCDC 283236 and 283237.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512312g

§ This modeling was performed using ChiT Pro 1.0 © 2004 developed by Prof. M.-H. Whangbo at North Carolina State University. For comparison, the data were also modeled using MAGMUN, a program written by Dr Zhiqiang Xu in collaboration with Prof. L. K. Thompson and Dr O. Waldmann. The results of the MAGMUN modelling are similar and can be found in the supplementary information.

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