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Trinuclear Mn(II) complex with paramagnetic bridging 1,2,3-dithiazolyl ligands†

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The first metal coordination complex of a radical ligand based on the 1,2,3-dithiazolyl heterocycle is reported. 6,7-Dimethyl-1,4-dioxo-naphtho[2,3-d][1,2,3]dithiazolyl acts as a bridging ligand in the volatile trinuclear $Mn(hfac)_2$-Rad–$Mn(hfac)_2$-Rad–$Mn(hfac)_2$ complex (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-). The Mn(II) and radical ligand spins are coupled anti-ferromagnetically (AF) resulting in an $S_T = 13/2$ spin ground state.

The ability to manipulate magnetic coupling between paramagnetic species is the key to creating new materials with desirable magnetic properties.[1] One possible method is the use of organic paramagnets as ligands: the so-called "metal–radical approach".[2,3] An unpaired electron on a ligand can couple strongly to unpaired electrons on a coordinated metal ion, particularly if there is significant spin density at the donor atom(s). If the ligand bridges multiple metal ions, a high-spin ground state can be achieved. New paramagnetic ligands continue to be reported, however these are often modifications of a few organic radical architectures, such as phenoxyls and semiquinones,[4] nitroxides and nitronylnitroxides,[5] verdazyls,[6] and triphenylmethyls.[7] Thiazyls and selenazyls have lately been added to this list with the use of 1,3,2-dithiazolyls[8] and 1,2,3,5-dithiadiazolyls[9–11] (and selenium analogues of the latter)[12] as radical ligand building blocks. As Veciana[2] recently articulated, the advancement of "spin science" requires structural diversity, and therefore it is important that new paramagnetic ligand designs be pursued and developed. To this end, we are reporting the first radical ligand based on the 1,2,3-dithiazolyl heterocycle and the first trinuclear metal complex of a thiazyl radical ligand, illustrated in Fig. 1.

6,7-Dimethyl-1,4-dioxo-naphtho[2,3-d][1,2,3]dithiazolyl **1** is a derivative of the 1,2,3-dithiazolyl-*p*-naphthoquinone radical that was observed in solution EPR by Mayer in 1981.[13] The latter is a structural isomer of the 1,3,2-dithiazolyl-*p*-naphthoquinone recently detected in solution EPR by Passmore.[14] We have incorporated methyl groups in the framework of ligand **1** in order to increase the sigma donor ability of the radical and ensure its function as a ligand. This alteration also promotes the solubility of the ligand in organic media, facilitating coordination syntheses.

Ligand **1** is prepared by treating 2-amino-3-bromo-6,7-dimethyl-1,4-naphthoquinone with excess S_2Cl_2 followed by reduction of the resulting dithiazolium chloride.† Purple crystals of **1** are grown by sublimation on a preparative scale.

As illustrated in Fig. 2, **1** is dimerized in the solid state. While this is expected for thiazyl radicals that have not been explicitly designed to do otherwise,[15] the dimerization motif is entirely new, characterized by short intermolecular S···O contacts (3.111(3) Å). This can be rationalized by invoking the *O*-radical resonance contributor. Computational analysis† of radical **1** predicts a delocalized π* SOMO (singly occupied molecular orbital) with a significant coefficient at atom O2 (Mulliken spin density *ca.* 13%; compare *ca.* 25% at N1). The *O*-radical resonance contributor also influences the crystallographic C–O bond lengths: C2–O1 (1.220(3) Å) is typical for a C=O double bond in a benzoquinone, whereas C9–O2 (1.234(3) Å) is long for this type of bond.‡

The dc susceptibility measurements indicate that dimers of **1** are diamagnetic over a temperature range of 1.8 to 300 K. No evidence for a thermally populated triplet excited state is observed by solid state X-band EPR (150 to 300 K).[16] The solution EPR spectrum of **1** (CH_2Cl_2) is a three-line pattern (hyperfine coupling to one ^{14}N nucleus) with small shoulders from hyperfine coupling to two ^1H nuclei on the naphthalene backbone. This spectrum is adequately simulated using: $a_N = 4.46$; $a_H = 0.32$; $a_{H'} = 0.53$ G; $g = 2.0095$.†

Coordination complex **2** was prepared by treating radical **1** with $Mn(hfac)_2(THF)_2$.[11] Crystalline material suitable for bulk analysis was grown by sublimation. The structure of **2** is shown in Fig. 3. Atom Mn2 is located at an inversion center, thus the two halves of the molecule are symmetry-related. The coordination geometry about Mn2 is roughly octahedral with the two radical ligands occupying axial positions *via* monodentate *O*-coordination. Like many monodentate *O*-coordinated Mn(II) complexes of nitronylnitroxides,[17] the Mn–O bond is not in the ligand

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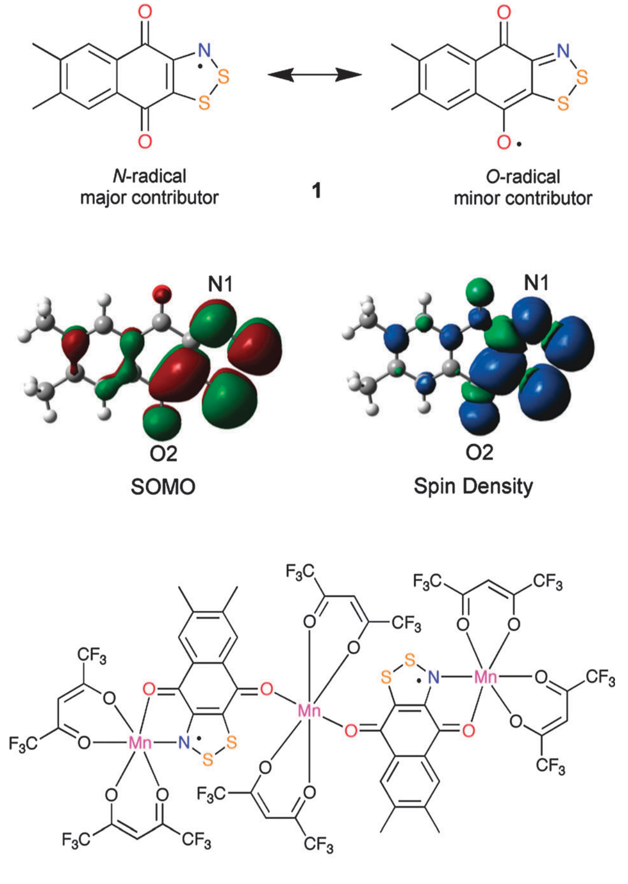

Fig. 1 Top: line drawing of **1** illustrating two possible resonance contributors. Middle: singly occupied molecular orbital (SOMO) and spin density distribution calculated† for **1**. Bottom: line drawing of **2**.

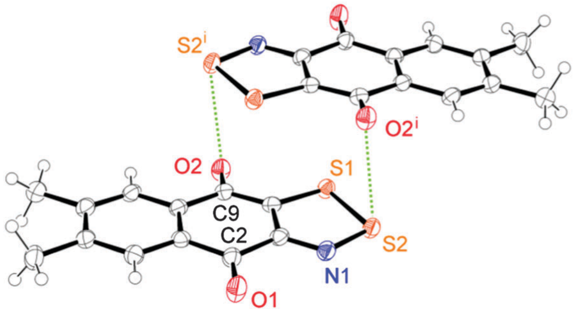

Fig. 2 Single crystal X-ray structure of **1**. Green dashed lines denote close S···O contacts that define the dimer. ORTEP thermal ellipsoids drawn at 50% probability. Symmetry code: (i) $1 - x$, $1 - y$, $-z$.

plane (C9–O2–Mn2, 139.0(2)°; C10–C9–O2–Mn2, 59.7(5)°). Bidentate chelation of Mn1 places this metal ion approximately in the ligand plane.

The magnetic properties of **2** were investigated between 280 and 1.8 K with an applied field of 1000 Oe (Fig. 4). At 280 K, the χT product is 13.1 $cm^3\ Kmol^{-1}$. Upon cooling, the χT product gradually decreases to 12.4 $cm^3\ Kmol^{-1}$ at 110 K, then increases to a maximum of 15.5 $cm^3\ Kmol^{-1}$ at 14 K. This thermal behaviour is consistent with significant antiferromagnetic (AF) coupling between the ligand and metal ion spins leading to a ferrimagnetic arrangement of the magnetic sites. Upon further cooling, the χT product decreases sharply to a minimum of 4.7 $cm^3\ Kmol^{-1}$ at 1.8 K, indicating additional AF intermolecular interactions. From the structure of **2**,

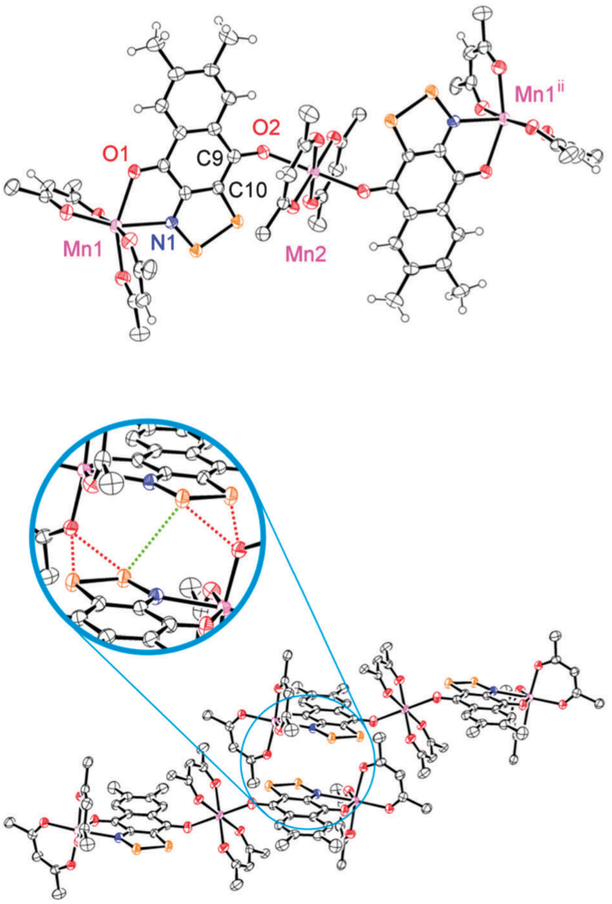

Fig. 3 Single crystal X-ray structure of **2**. ORTEP thermal ellipsoids drawn at 50% probability. F atoms omitted for clarity. Top: complete molecule; symmetry code: (ii) $-x$, $1 - y$, $-z$. Bottom: crystal packing between two molecules with the intermolecular S···S contact highlighted by a green dashed line and the S···O contacts by red dashed lines; H atoms omitted for clarity.

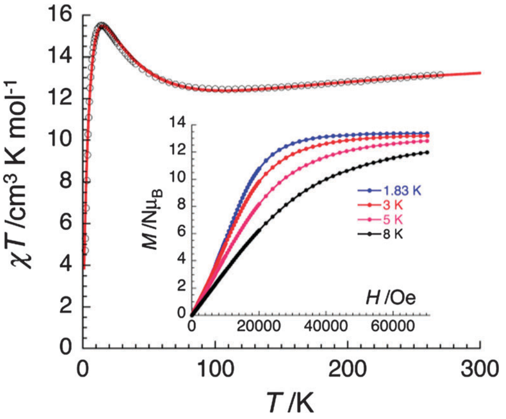

Fig. 4 Temperature dependence of the χT product for **2** at 1000 Oe (with χ defined as molar magnetic susceptibility equal to M/H per mole of complex **2**). Black circles indicate measured data and the red line represents best simulation obtained with the model described in the text. Inset: M *vs.* H data below 8 K.

the magnetic data were simulated numerically using MAGPACK software[18] with the following isotropic Heisenberg Hamiltonian: $H = -2J_{\mathrm{Mn1\text{-}Rad}}[S_{\mathrm{Mn1}} \times S_{\mathrm{rad}} + S_{\mathrm{Mn1(ii)}} \times S_{\mathrm{rad(ii)}}] - 2J_{\mathrm{Mn2\text{-}Rad}}[S_{\mathrm{Mn2}}(S_{\mathrm{rad}} + S_{\mathrm{rad(ii)}})]$, where $J_{\mathrm{Mn1\text{-}Rad}}$ and $J_{\mathrm{Mn2\text{-}Rad}}$ represent the exchange interactions between ligand **1** ($S = 1/2$) and Mn1 and Mn2 ($S = 5/2$) spins respectively, and S_{i} is the spin operator of each magnetic site. Introducing inter-complex interactions in the above model in the frame of the mean-field approximation (zJ'),§ an adequate simulation of the experimental data was obtained with $J_{\mathrm{Mn1\text{-}Rad}}/k_{\mathrm{B}} = -35(1)$ K, $J_{\mathrm{Mn2\text{-}rad}}/k_{\mathrm{B}} = -13(1)$ K, $zJ'/k_{\mathrm{B}} = -0.17(2)$ K, and $g_{\mathrm{iso}} = 2.05(2)$, suggesting an $S_{\mathrm{T}} = 13/2$ spin ground state for complex **2**. This ground state is confirmed by *M vs. H* data (inset Fig. 4) and the high field magnetization at 1.8 K that saturates at $13.4\mu_{\mathrm{B}}$.

Magnetic coupling between radical ligand and terminal Mn1 atom spins is larger than that between the radical and central Mn2 atom spins. This is likely a result of the larger spin density at N1 than at O2, and possibly also aided by the in-plane, bidentate coordination motif at Mn1. Short intermolecular S···O contacts like those apparent in complex **2** (2.915 and 3.188 Å; Fig. 3) have previously been shown to mediate AF coupling between a radical ligand and a neighbouring Mn(II) ion, thereby giving rise to a high spin ground state for a pair of complexes.[9] For **2**, however, the dominant intermolecular magnetic contacts appear to be the S···S contacts (3.388 Å; Fig. 3). Non-orthogonal overlap between neighbouring radical ligand SOMOs provides a mechanism for the AF couplings observed between the trinuclear complexes in the solid state.

Paramagnetic ligand 6,7-dimethyl-1,4-dioxo-naphtho[2,3-d]-[1,2,3]dithiazolyl, **1,** is shown to be capable of coordinating a metal ion in a monodentate fashion at atom O2 and in a bidentate chelating fashion at atoms N1 and O1. Owing to the significant spin density at both N1 and O2, strong antiferromagnetic coupling is observed between the ligand and the metal ions in both positions. The trinuclear coordination complex **2** is the first example of metal ion coordination to a 1,2,3-dithiadiazolyl radical and it is a very rare example of a linear "oligomeric" radical ligand coordination complex with more than two metal ions. This complex is robust and volatile, such that sublimation produces pure crystalline material on a preparative scale. The spin ground state of the complex **2** is $S_{\mathrm{T}} = 13/2$, the highest to date for any thiazyl–metal system.

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Notes and references

‡ For 86 measured benzoquinone species, the unweighted mean C═O bond length is 1.222 Å, the median is 1.220 Å with a standard deviation of 0.013 Å, and the upper quartile is 1.231 Å.[19]

§ In order to take into account the inter-complex interaction, the following definition of the susceptibility has been used:[20]

$$\chi = \frac{\chi_{\mathrm{Mn_3Rad_2}}}{1 - \frac{2zJ'}{Ng^2{\mu_{\mathrm{B}}}^2}\chi_{\mathrm{Mn_3Rad_2}}}$$

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