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Very Strong Ferromagnetic Interaction in a New Binuclear μ-Methoxo-Bridged Mn(III) Complex: Synthesis, Crystal Structure, Magnetic Properties, and DFT Calculations

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The coordination chemistry of manganese is known for its important role in biological systems[1,2] and furthermore for its highly valuable catalytic uses in olefin epoxidation.[3,4] Moreover, some complexes can act as paramagnetic building blocks for single molecule magnets (SMM) and also for multidimensional expanded structures.[5] The magnetic behavior of a variety of such compounds has been explored during the past decades with the aim of designing SMM or single chain magnets.[6,7] The choice of binuclear transition metal building blocks with different exchange coupling patterns creates a number of exciting possibilities in this area.[8] Herein we report the preparation, crystal structure analysis, and a detailed magnetic study of exchange interaction between manganese centers of the dinuclear $\mathrm{Mn(III)_2(\mu\text{-}OMe)_2(HL)_4}$ ($\mathrm{H_2L}$ = 2-salicyloylhydrazono-1,3-dithiolane).

We have previously reported that the reaction of Mn(II) acetate tetrahydrate and Mn(II) acetylacetonate with the $\mathrm{H_2L}$ ligand yields $\mathrm{Mn(II)(HL)_2L'_2}$ (L′ = DMF, THF, Py) complexes.[9] The reaction of this ligand with Mn(III) acetate dihydrate in methanol at room temperature gives the monomer $\mathrm{[Mn(III)(HL)_3]\cdot 2CHCl_3}$ **1**.[10] The addition of base to the reaction mixture results in the formation of a new dimer, $\mathrm{Mn(III)_2(\mu\text{-}OMe)_2(HL)_4}$ **2**, obtained as brown crystals with good yield.

The molecular structure consists of a neutral asymmetric complex where each manganese ion is chelated by two $\mathrm{HL^-}$ bidentate ligands and bridged by two methoxy anions. This complex demonstrates an unexpected nonsymmetrical situation for both Mn(III) ions. In fact, Mn1 and Mn2 are in two different distorted octahedra with clear Jahn−Teller axial deformations ($\mathrm{N_2{-}Mn_1{-}N_4}$ and $\mathrm{N_6{-}Mn_2{-}O_9}$, Figure 1). The angle between these two deformed axes is approximately 100°, and the Mn1−O9−Mn2 and Mn1−O10−Mn2 angles are 100.1 and 104.0°, respectively. Around Mn1, the oxygen atoms O1−O3 are in a *cis* configuration and N1−N4 in a *trans* configuration. In contrary, the oxygen atoms O5−O7 are in a *trans* configuration around Mn2 and N6−N8 in a *cis* configuration. This unexpected situation probably has to be related to two intramolecular nonclassical H-bonds found between C9 and the centroid of the C22_C27 phenol group and C20 and the centroid of the C32_C37 phenol group (Figure 1).

The magnetic susceptibility of **2** is depicted in Figure 2a. The room temperature χT value of approximately 6.4 cm^3·K·mol^{-1} rapidly increases upon cooling to a maximum value of about 9.0 cm^3·K·mol^{-1} at 17.5 K before dropping back to approximately 8.0 cm^3·K·mol^{-1} at 1.8 K, and this behavior is indicative of ferromagnetic exchange between the metal centers, resulting in an $S = 4$ ground state (the expected value for χT for two uncoupled $\mathrm{Mn^{III}}$ ions is approximately 6.0 cm^3·K·mol^{-1}, whereas the expected value for χT for an $S = 4$ is approximately 10 cm^3·K·mol^{-1}, assuming $g = 2$). The low temperature decrease may be safely attributed to zero field splitting within the $S = 4$ ground state. Intermolecular antiferromagnetic interactions can be neglected on the basis of the rather large distance between two $\mathrm{Mn^{III}}$ centers from two different molecules (8.6 Å).

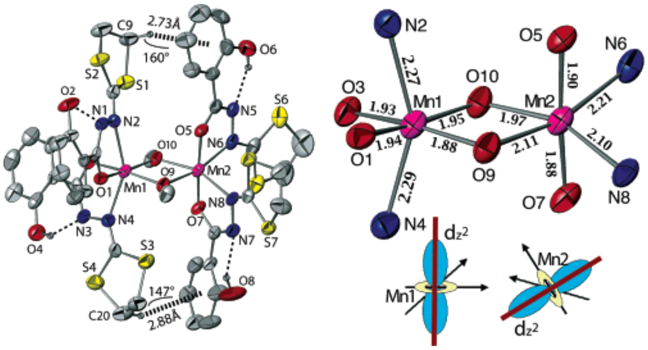

Figure 1. ORTEP view of **2** (left) showing specific intramolecular hydrogen bonds. The other hydrogen atoms have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density. Selected distances (Å) are gathered in the partial view of the molecular core (right) with an indication of the relative orientation of Jahn−Teller elongated (d_{z^2}) axes around both Mn(III) atoms.

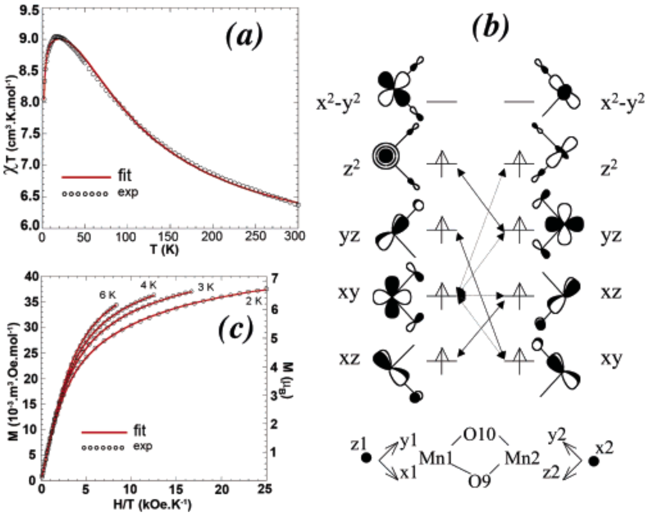

Figure 2. (a) χT versus T plot for complex **2**. (b) Simplified scheme of natural magnetic orbitals and dominant exchange pathways in complex **2**. Bold lines symbolize AF coupling, while dotted lines stand for F coupling (see Supporting Information). (c) Reduced magnetization M versus H/T plot for complex **2**.

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Therefore, we have fitted the data using the following spin Hamiltonian where all parameters have their usual meaning and the spin operator **S** is defined as $\mathbf{S} = \mathbf{S}_{\mathbf{Mn1}} + \mathbf{S}_{\mathbf{Mn2}}$:[11]

$$\mathbf{H} = -J\,\mathbf{S}_{\mathbf{Mn1}}\,\mathbf{S}_{\mathbf{Mn2}} + g\,\beta\,\mathrm{H}\,\mathbf{S}$$

Axial zero field splitting was introduced only in the ground state $S = 4$ using the following Hamiltonian:

$$\mathbf{H}_{\mathbf{ZFS}} = D_{S=4}\,[\mathbf{S}_{\mathbf{z}}^{\mathbf{2}} - S(S+1)/3]$$

The fit leads the following values: $J = +19.7$ cm^{-1}, $g = 1.90$, and $D_{S=4} = -0.83$ cm^{-1} with an excellent agreement factor ($R = 1.5 \times 10^{-5}$).[12] To our knowledge, this compound presents one of the strongest ferromagnetic interactions for binuclear Mn$^{\mathrm{III}}$ complexes.[6,13−15] As suggested by Hotzelmann and co-workers, the strong ferromagnetic interaction is most probably due to the existence of ferromagnetic interaction pathways which arise from the efficient “crossed interaction” between the singly occupied d_{xy} orbital on the left fragment and the empty $d_{x^2-y^2}$ on the right fragment (Figure 2b and Supporting Information).[11,14]

The ferromagnetic coupling is further supported by first-principles density functional theory (DFT) calculations. The complete molecule, including all hydrogen atoms, has been modeled for ferromagnetic and antiferromagnetic alignment of the two Mn spins. The ferromagnetic configuration is found to be lower in energy by 182 cm^{-1} than the antiferromagnetic one. Mapping this energy difference to the energy difference between the $S = 4$ and $S = 0$ states, which equals $10J$, we obtain $J = +18.2$ cm^{-1}, in very close agreement with the result from the fit.

To characterize more precisely the magnetic anisotropy of the ground state of this binuclear compound (in particular, to determine the sign of the axial parameter $D_{S=4}$ and the rhombicity $E/|D|$), we performed field-dependent magnetization measurements at different temperatures. The $M = f(H/T)$ plots for $T = 2$, 3, 4, and 6 K (for which we can consider that only the ground state $S = 4$ is populated) cannot be superimposed due to the presence of magnetic anisotropy within the complex (Figure 2c). The data were fitted by exact diagonalization of the energy matrices corresponding to the spin Hamiltonian

$$\mathbf{H} = g\,\beta\,\mathrm{H}\,\mathbf{S} + D_{S=4}\,[\mathbf{S}_{\mathbf{z}}^{\mathbf{2}} - S(S+1)/3] + E_{S=4}\,[\mathbf{S}_{x}^{\mathbf{2}} - \mathbf{S}_{y}^{\mathbf{2}}]$$

averaged over 120 orientations of the magnetic field.[16] The fitting was performed simultaneously for the four experimental temperatures. The best fit was obtained with $D_{S=4} = -0.85$ cm^{-1}, $E_{S=4}/|D_{S=4}| = 0.21$, and $g = 1.89$ ($R = 2.3 \times 10^{-5}$). To reduce the variable parameters during the fitting procedure, the [**g**] tensor was constrained to be isotropic. The quality of the fit is excellent, and the values obtained for g and for the axial anisotropy parameter $D_{S=4}$ are in remarkable agreement with those obtained from the fit of the $\chi T = f(T)$ curve (all attempts to fit the experimental data using a positive value for D were, indeed, unsuccessful). The amplitude of the anisotropy is considerably reduced compared to what is usually observed for monomeric Mn$^{\mathrm{III}}$ complexes ($|D| \sim 4$ cm^{-1}). This is probably due to the observed noncollinearity between the distortion axis of the two Mn$^{\mathrm{III}}$ centers.[17] Nevertheless, the anisotropy of the $S = 4$ ground state of this binuclear complex remains relatively large compared to what is observed in other ferromagnetically coupled dimeric Mn$^{\mathrm{III}}$ compounds.[6,15] The DFT calculations also confirm the negative sign of D; however, the calculated magnitude of D is too small ($D_{S=4} = -0.35$ cm^{-1}, $E/|D| = 0.19$). The underestimation of D by about a factor of 2 is similar to results obtained for a series of Mn monomers.[18]

In summary, we have reported the synthesis of a new binuclear Mn(III) complex which presents one of the strongest intramolecular ferromagnetic interactions. This strong interaction is supported by DFT calculations which also confirm the negative sign of the $D_{S=4}$ parameter. We are currently working on the modulation of the magnetic interaction by small modifications of the chemical bridge and/or peripheral ligand. Such binuclear complexes with very strong ferromagnetic interaction and axial magnetic anisotropy are excellent candidates to be incorporated into polymeric and/or supramolecular networks that could present interesting magnetic properties, if one achieves correctly designed interactions.[7]

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Supporting Information Available: Experimental and DFT calculation details and full ORTEP of **1** (PDF). Crystallographic data (excluding structure factors) in CIF format. The crystallographic material can also be obtained from the CCDC, the deposition number being CCDC 270924−270925. This material is available free of charge via the Internet at http://pubs.acs.org.

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