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A Unique Asymmetric [Mn_3^{II}] Triple-Stranded Helicate from a Symmetric Pentadentate Ligand**

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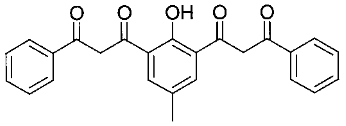
One of the richest parcels of supramolecular chemistry is that where the various components of a complex assembly recognize and associate with each other "via" the intermediacy of coordination bonds.[1] In this area, the specific coordination requirements of transition metals are combined with the electronic and structural features of new ligands in the design and construction of unprecedented molecular architectures displaying novel and exciting properties. This approach has been relatively unexplored in the field of molecular magnetism.[2] We have recently started a program aimed at the design and preparation of novel multidentate ligands as a means of assembling transition metal centers into species displaying new topologies and innovative magnetic properties. In this context, we have built in the same molecule two β-diketone units and a phenol group to produce a symmetric O-pentadentate ligand (H_3L).[3] The preparation of some related molecules and their use as dinucleating ligands have been reported in the literature.[4] We intended to use a basic form of H_3L as a template to bring in proximity a number of transition metals in discrete, molecular arrays. Examples of such systems involving oligo-α-pyridylamine ligands are known.[2e, 5] We now report the first case with an oxygen donor ligand and introduce an unprecedented asymmetric topology within the context of coordination helicates.



Reaction of H_3L with one equivalent of $Mn(AcO)_2 \cdot 4H_2O$ in the solvent mixture MeOH/py (2/1, v/v) leads to a yellow crude product upon precipitation with hexanes. Recrystallization of this product from CH_2Cl_2/Et_2O/hexanes affords yellow needles of [$Mn_3(HL)_3$] (**1**) in an overall yield of 15%. The structure of **1**[6] (Figure 1) consists of a trinuclear array of Mn^{II} ions chelated and bridged by three HL^{2-} ligands wrapped around the molecular axis in an irregular helical

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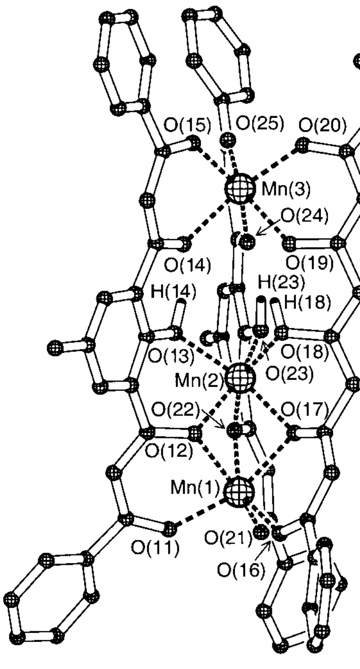

Figure 1. Pluton representation of complex **1**.

manner. The three metal centers are quasi colinear (Figure 2; the Mn(1)-Mn(2)-Mn(3) angle being 179.20(3)°) and display three distinct Mn$\cdots$Mn vectors with distances of 3.024(17), 5.044(2), and 8.076(3) Å for Mn(1)$\cdots$Mn(2), Mn(2)$\cdots$Mn(3), and Mn(1)$\cdots$Mn(3), respectively. This topological asymmetry of the metals along the molecular axis is what makes this compound unique amongst the family of metallohelicates.[7] To the best of our knowledge, this is the first asymmetric homometallic helicate obtained from a ligand with idealized C_{2v} symmetry. In addition, it constitutes a new addition to the smaller subset of compounds within this category that are based on oxygen donor ligands.[4b,c, 7b, 8] The peripheral metals of the complex are chelated by the β-diketonate units of the ligands. Evidence of the high degree of conjugation within these chelate rings is their quasi planarity. The central metal ion is bridged to Mn(1) by the three inner oxygen donors of the corresponding diketonate groups, with the oxygen atoms from the phenol units completing the hexacoordination around this ion in the form of six-membered chelate rings. In contrast to the case of the external Mn ions, the chelate rings involving Mn(2) display a distorted chair conformation. The coordination around the Mn centers is intermediate between octahedral and trigonal prismatic, with twist angles[9] and Mn–O distances within the ranges of 16.55–34.87° and 2.092(4)–2.261(4) Å, respectively. The +2 oxidation state of all the Mn ions is consistent with valence bond sum analysis, the elemental analysis[10] of the compound, and its magnetic behavior (see below). The cavity left between Mn(2) and Mn(3) is the most likely location of the three protons necessary to insure the electroneutrality of the complex, and indeed residual electron density was found in this area during the crystal structure determination.[6] The O–H$\cdots$O contacts between O(13), O(18), O(23) and O(14), O(19), O(24), respectively, (2.409(6), 2.382(6), and 2.385(6) Å) are slightly shorter than in organic molecules containing an equivalent moiety[11] and fall within the range found in coordination complexes displaying the M–O–H$\cdots$O–M unit.[12] These hydrogen-bond interactions are undoubtedly influencing the overall stereochemistry of the molecule (see below). The topological asymmetry of **1** translates into the presence of different helical domains. The irregularity of the helix is further brought about by the change of chirality of the metals along the chain. These show the Λ, Δ, and Λ configurations[13] for Mn(1), Mn(2), and Mn(3), respectively (Figure 3); the $\Delta\Lambda\Delta$ form exists in the crystal in an equal amount by virtue of the inversion center present within the *Pccn* space group. This alternation of configuration leads to the change of helicity through the molecular axis that renders this helicate amphiverse (Figure 2).

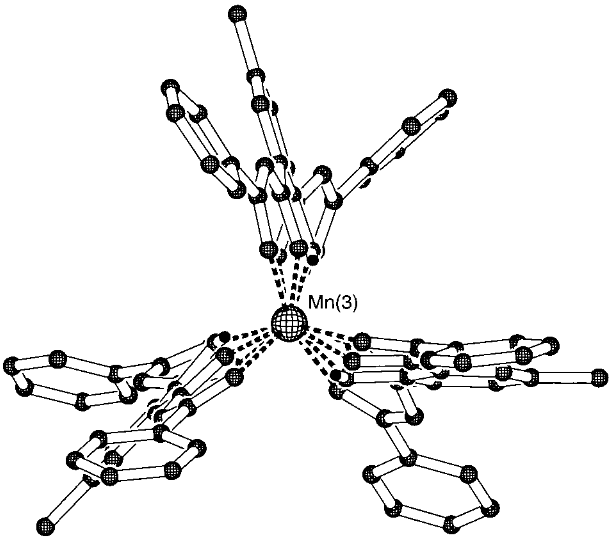

Figure 2. Pluton representation of **1** down the molecular axis emphasizing the amphiverse helical nature of the complex.

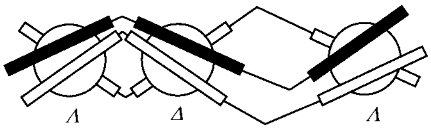

Figure 3. Stereochemistry along the axis of helicate **1**.

Consistent with the relatively slow electronic relaxation of the Mn^{II} ion,[14] the ^{1}H NMR spectrum of **1** in $CDCl_3$ shows only very broad, paramagnetically shifted signals. This precludes the study of the enantiomerization dynamics of this new type of helicate using that technique. Diamagnetic versions of **1** with a built in stereochemical probe in the form of diastereotopic protons could be used for that purpose, and this is currently being explored.

Variable-temperature magnetic susceptibility measurements were performed on powdered **1** in the 5–300 K range under a constant magnetic field of 20 kG. A plot of the effective magnetic moment (μ_{eff}/μ_B) versus temperature (T/K) is shown in Figure 4. The value of μ_{eff} at room temperature (10.1) is very close to the spin-only value (10.25 μ_B) expected for three uncoupled Mn^{II} ions per molecule with $g = 2.00$, and the value decreases monotonically to reach 5.87 μ_B at 5 K. This behavior indicates the presence of antiferromagnetic

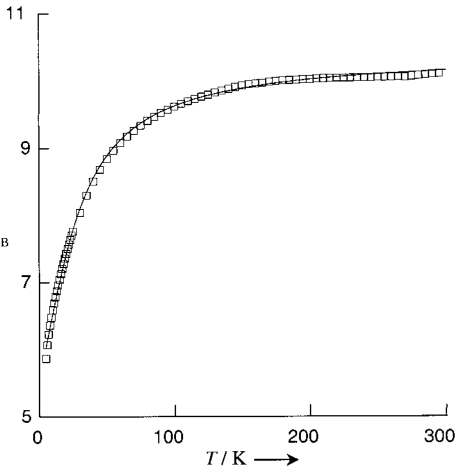

Figure 4. Plot of the effective magnetic moment (μ_{eff}) per molecule versus T for **1** in a 20.0 kG field. The solid line is a fit of the data to the appropriate theoretical equation; see the text for the fitting parameters.

interactions within this system. The magnetic data have been fit to a theoretical expression obtained by use of the van Vleck equation,[15] the Kambe vector coupling method,[16] and the spin Hamiltonian given in Equation (1).

$$\mathscr{H} = \mu_{\mathrm{B}} g_3 \hat{S}_3 \vec{B} + \mu_{\mathrm{B}} g_{12} \hat{S}_{12} \vec{B} - 2J \hat{S}_1 \hat{S}_2 \qquad (1)$$

This Hamiltonian results from consideration of a simple model consisting of the presence of an exchange-coupled $\mathrm{Mn^{II}}\cdots\mathrm{Mn^{II}}$ pair next to a third, uncoupled $\mathrm{Mn^{II}}$ center. In Equation (1), S_i is the spin of $\mathrm{Mn_i}$, with $S_1 = S_2 = S_3 = 5/2$, J is the exchange constant of the $\mathrm{Mn_1}\cdots\mathrm{Mn_2}$ coupling, g_{12} and g_3 are the Landé factors of the $\mathrm{Mn_{12}}$ pair and the $\mathrm{Mn_3}$ ion, respectively, μ_{B} is the Bohr magneton, and B is the external magnetic field. The best fit (Figure 4, solid line) was found for $J = -2.38(2)\ \mathrm{cm^{-1}}$, $g_3 = 2.08(2)$, and $g_{12} = 1.90(2)$. A temperature-independent paramagnetism parameter (TIP) was held constant at $600 \times 10^{-6}\ \mathrm{cm^3\,K\,mol^{-1}}$. A detailed analysis of the magnetic susceptibility data by use of a full-matrix diagonalization method will be necessary in order to evaluate the importance of the three possible Mn2–O–H⋯O–Mn3 additional pathways for the magnetic super-exchange.

The unique triple-stranded helicate **1** is the first crystallographically characterized complex with a deprotonated form of $\mathrm{H_3L}$. The study of the coordination properties of this ligand is currently being extended to other metals.

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[6] Crystal Data for **1**: $\mathrm{C_{75}H_{54}Mn_3O_{15}}$ + solvent (see below). Several crystallization batches yielded only weakly diffracting crystals. Final data were collected on a yellow block-shaped crystal ($0.2 \times 0.2 \times 0.3$ mm), orthorhombic, space group *Pccn* (no. 56), $a = 21.998(3)$, $b = 32.757(10)$, $c = 20.784(3)$ Å, $V = 14977(5)$ Å^3, $Z = 8$, 106973 reflections measured, 15572 independent, $R_{\mathrm{int}} = 0.112$, $R_\sigma = 0.103$, $1.6° < \theta < 27.0°$, $T = 150$ K, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å on a Nonius KappaCCD diffractometer on a rotating anode with no absorption correction. The structure was solved by automated direct methods (SHELXS86), and refined on F^2 (SHELXL-97). The electron density in disordered solvent areas (two voids of 1783 Å^3 each, filled with a mixture of $\mathrm{CH_2Cl_2}$, $\mathrm{Et_2O}$, and hexane) was taken into account in the refinement by PLATON/SQUEEZE. A total number of 949 electrons per unit cell was found. One of the phenyl rings (C(211) – C(216)) is disordered. Since no suitable disorder model could be obtained with the present data set, an ideal phenyl ring with isotropic displacement parameters was fitted in this electron density. Hydrogen atoms were included on calculated positions riding on their carrier atoms. Between atom pairs O(13)–O(14), O(18)–O(19), and O(23)–O(24) residual density peaks were observed, which correspond to three symmetric O–H⋯O hydrogen bonds. As a result of the low crystal quality, these hydrogen atoms could not be refined. Instead, the hydrogen atoms were introduced at ideal hydroxyl positions riding O(13), O(18), and O(23), respectively. Refinement of 793 parameters converged at a final $wR2$ value of 0.2216, $R1 = 0.0956$ (for 7734 reflections with $I > 2\sigma(I)$), $S = 1.042$, $-0.70 < \Delta\rho < 1.20\ \mathrm{e\,Å^{-3}}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163316. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] The twist angles are the three smallest angles between the projection of the bonds on a plane normal to an idealized C_3 axis, in this case, taken as the Mn⋯Mn vector beween the metal of interest and the closest one.

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