Metallacryptate Magnets

Synthesis and Magnetic Properties of a Metallacryptate that Behaves as a Single-Molecule Magnet**

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Metallamacrocyles have been intensively studied over the past decade. These molecules have already been used in applications as diverse as catalysis,[1] sensors,[2] or as chiral building blocks for two- and three-dimensional solids.[3] Metallamacrocyles include complexes such as metallacrowns,[3,4] molecular squares,[1,2] metallacalixarenes,[5] and metallahelicates.[6] Metallacrowns (MC), the inorganic structural and functional analogs to crown ethers, are usually formed with transition-metal ions incorporated into the metallamacrocyclic ring, thus providing the attractive feature that they concentrate a large number of metal ions per unit volume. This large metal-ion concentration may lead to interesting magnetic behavior.[4,7]

Since the recognition of single-molecule magnets (SMMs) in 1993, the field has gained considerable attention as a study of both classical and quantum effects.[8,9] SMMs of cobalt,[10] vanadium,[11] nickel,[12] iron,[13] and a mixed-metal system[14] have been studied. However, the best known and most intensely studied SMMs are the manganese carboxlyate clusters, which range in size from Mn_4 to Mn_{30}.[15] Herein we report the synthesis (Scheme 1) and characterization of the second[16] known Mn_{26} complex $[Mn^{II}_4Mn^{III}_{22}(pdol)_{12}(\mu_3\text{-}CH_3O)_{12}(\mu_3\text{-}O)_{10}(\mu_4\text{-}O)_6(N_3)_6]$ (**1**; $pdol^{2-}$ = dipyridylketone-

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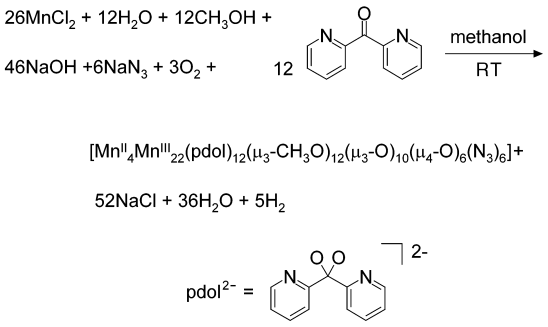

Scheme 1.

diolate ion), a highly symmetric metallacryptate that exhibits an imaginary component in the low-temperature ac susceptibility data that is consistent with SMM behavior.[17]

The crystal structure of **1** is shown in Figure 1. A core composed of 16 Mn^{III} ions, 12 methoxide, and 16 oxide groups is surrounded by strands of Mn ions and $pdol^{2-}$ ligands, which

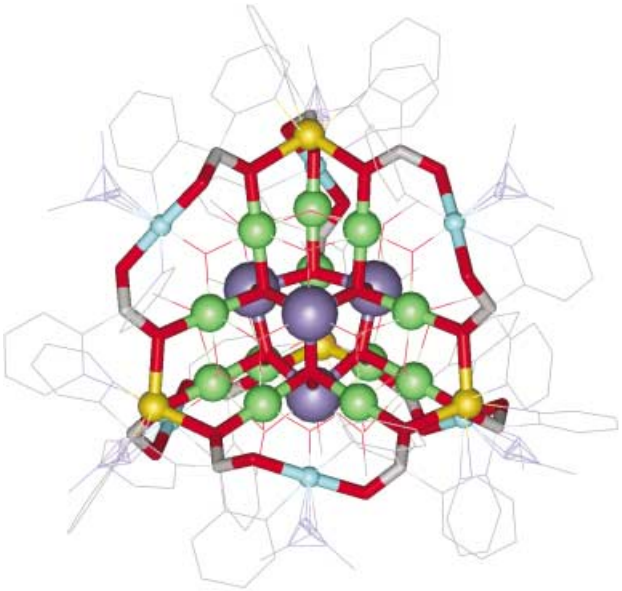

Figure 1. Crystal structure of **1**. The core and ring connectivity have been highlighted with thick tubes; Mn1 (gold spheres); Mn2 (aqua spheres); Mn3 (green spheres); Mn4 (navy blue spheres); C (gray tubes); O (red tubes). Bound azide groups are shown over all disordered positions.

form the metallacryptand (a three-dimensional version of a metallacrown). Figure 2 highlights the connectivity between the strands and the inner core. These strands, with the inner core removed, are shown as stereoviews oriented along the crystallographic twofold and threefold axes (Figure 3). The metallacryptand has an adamantoid structure[18] with four Mn^{II} ions on threefold axes that are bridged by pdol-Mn^{III}-pdol links; thus, **1** is a [4]metallacryptand, in which the $\{Mn_{16}(O^{2-})_{12}(MeO^{-})_{16}\}$ core is encapsulated (Figure 4). While **1** contains 26 metal ions, there are only four crystallographically unique manganese ions (Figure 5).

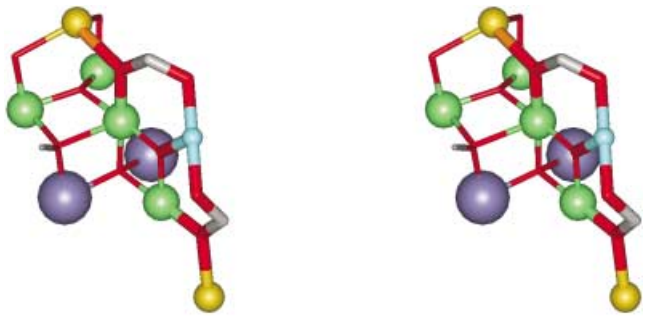

Figure 2. Steroview from the X-ray crystal structure of **1** highlighting the connectivity of strands to the core. The strand and connection points are represented by thick tubes, and the core connectivity is represented by thin tubes. The Mn3 atoms of the core are linked to the strand of the metallacrypate by a $pdol^{2-}$ ligand. Another link to the metallacryptate outer strand occurs through a μ_3-oxide bridge between one Mn2 and two Mn3 centers. Linkages within the core include a μ_3-oxide group that connects three Mn3 centers together and a μ_3-methoxide group that joins two Mn3 centers to one Mn4 center. A μ_4-oxide group links two Mn3 and two Mn4 centers. See Figure 1 for color scheme.

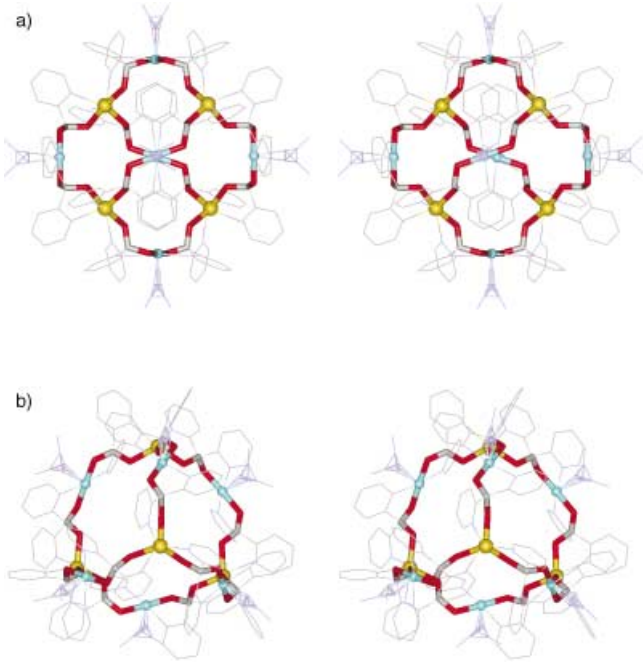

Figure 3. Stereoviews of **1** taken from its X-ray crystal structure, with the inner core removed. a) Along the twofold axis; b) along the threefold axis. See Figure 1 for color scheme.

Mn1, Mn2, and the 12 $pdol^{2-}$ ligands form the metallacryptand. The four seven-coordinate Mn1 centers (on threefold rotational axes) interact with three pyridyl nitrogen atoms (N1), three μ-oxygen atoms from the $pdol^{2-}$ ligand (O1), and a μ_3-oxide oxygen atom (O4) that links the metallacryptand to the core (Figure 5a). This face-capped octahedral polyhedron forms a Λ propeller, which results in a chiral molecule.[19] From the average Mn–N/O bond length of 2.32 Å, it appears that the manganese centers are in the +2 oxidation state. In comparison, seven-coordinate Mn^{III} ions

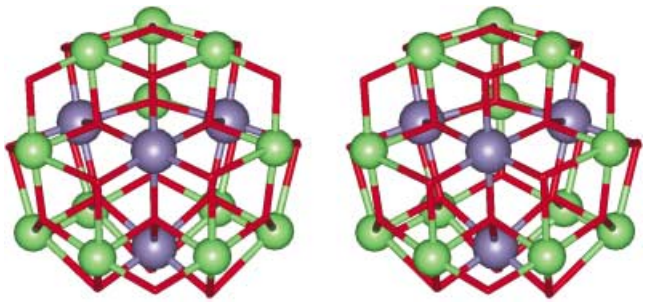

Figure 4. Steroview from the X-ray crystal structure of the core with carbon atoms of methoxide groups removed. See Figure 1 for color scheme.

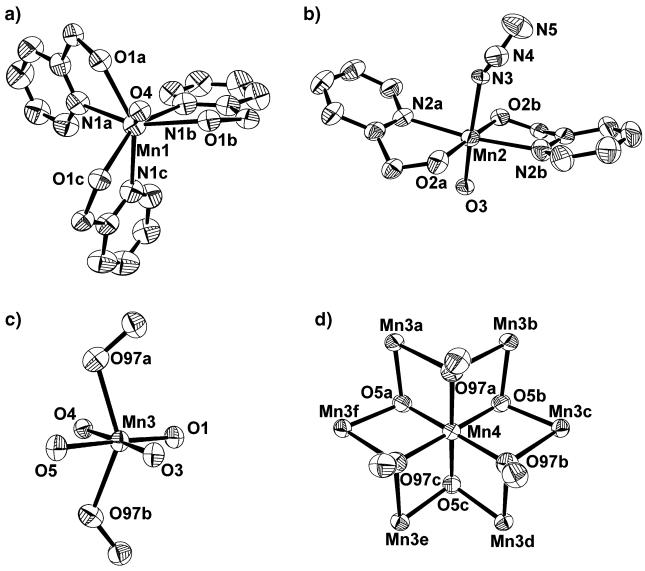

Figure 5. The first coordination sphere of each crystallographically unique manganese center is shown as an ORTEP diagram with thermal ellipsoids at 50% probability. a) Mn1, b) Mn2, c) Mn3, d) Mn4.

have an average separation of 2.13 Å.[18] The six Mn2 centers (on twofold axes) are six-coordinate, through interactions with two pyridyl nitrogen atoms (N2) and two oxygen atoms (O2) from the $pdol^{2-}$ ligand, a nitrogen atom from a disordered azide ligand (N3–N5), and a μ_3 oxygen atom (O3) that is part of the core (Figure 5b). The average bond length between Mn2 centers (2.05 Å) and the Jahn–Teller elongation along the N_{pyr}-Mn2-N_{pyr} axis (Mn2–N_{pyr} = 2.28 Å) support a +3 oxidation state.

The core of **1** also consists of two manganese species. The twelve Mn3 centers are six-coordinate, with one μ-oxygen atom from the $pdol^{2-}$ ligand (O1), two μ_3-oxide (O4 and O3), two μ_3-methoxide (O97), and a μ_4-oxide oxygen atoms (O5; Figure 2, 4, and 5c). The Mn3 ions are in the +3 oxidation state, as suggested by the average manganese separation of 2.05 Å, and the Jahn–Teller elongation along the O_{MeO}-Mn3-O_{MeO} axis (Mn3–O_{MeO} 2.31 Å). The four Mn4 centers (on a threefold axis) have an average manganese-to-ligand bond length of 2.02 Å. They are six-coordinated, with three μ_3-methoxide (O97) and three μ_4-oxide oxygen atoms (O5) (Figure 2, 4, and 5c).

Variable-temperature dc magnetic susceptibility data were collected on a powder sample mulled with eicosane over a 1.8–300 K temperature range at 2500 G under zero-field cooled conditions using a SQUID magnetometer. The effective magnetic moment (μ_{eff}) steadily decreased as the temperature was lowered from 300 K (μ_{eff} = 10.82) to 4.25 K (μ_{eff} = 3.02) indicating an overall antiferromagnetic interaction (Figure S1). Plots of the magnetization curves at 4.25 K and 10 K over the range of 200 G to 55000 G in an eicosane matrix (Figure S2) show no evidence for saturation, which precludes the determination of the ground-state spin.

We collected ac susceptibility data to probe the magnetization relaxation of the sample. Variable-temperature ac SQUID experiments were performed over the temperature range of 1.9–10 K at frequencies of 1–1000 Hz, with zero applied dc magnetic field and a 3.5 G oscillating ac magnetic field. The in-phase susceptibility (χ') begins to decrease and the out-of-phase susceptibility (χ'') begins to increase drastically near 2.5 K at all tested frequencies (Figure 6); this trend continues as the temperature is decreased. In addition, the out-of-phase susceptibility is frequency dependent as the onset temperature is slightly increased at higher frequencies. These observations provide strong evidence that **1** behaves as a single-molecule magnet. Unfortunately, the blocking temperature of the compound could not be determined and studies at lower temperatures are in progress.

In conclusion, we have synthesized a new member of the metallacrown family that structurally resembles a metallacryptate. The high nuclearity of the system coupled with

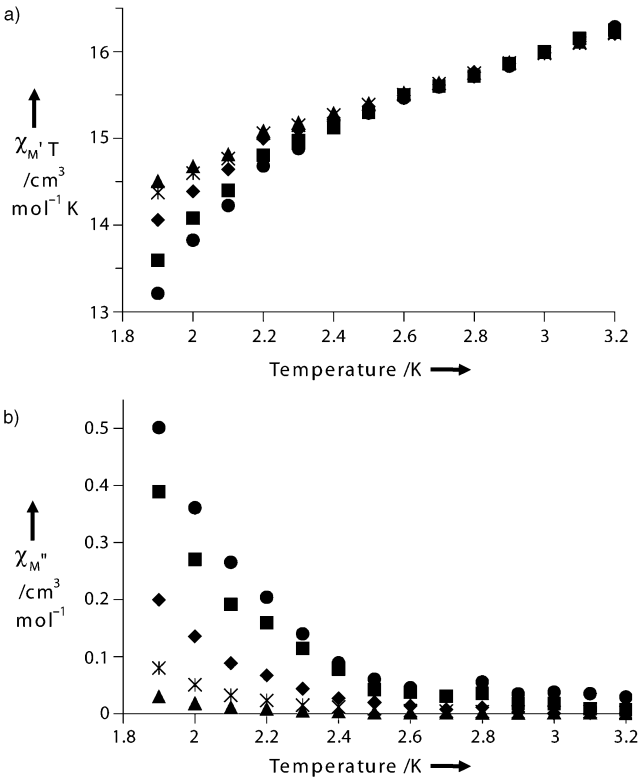

Figure 6. Temperature-dependent ac susceptibility measurements of **1**. a) In-phase susceptibility; b) out-of-phase susceptibility (■ 1 Hz; * 10 Hz; ◆ 100 Hz; ■ 500 Hz; ▲ 1000 Hz).

significant magnetic exchange interactions between Mn ions results in the observation of single-molecule-magnet behavior. These observations suggest that metallacrown topologies may represent a novel class of molecular magnets.

Experimental Section

Complex **1** was synthesized by adding sodium hydroxide (10 mmol) and di-(2-pyridyl)-ketonoxime ligand (dpk; 10 mmol) to $MnCl_2 \cdot 4H_2O$ (15 mmol) in methanol (40 mL). NaN_3 (10 mmol) dissolved in methanol (10 mL) was then added. The resulting dark red-brown solution was reduced to a volume of 20 mL after stirring for 5 h. After 4 days, red-black octahedral crystals were deposited from the mother liquor.

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[17] Crystals of **1** have been structurally characterized with the formula $Mn_{26}O_{16}(pdol)_{12}(N_3)_6(CH_3O)_{12}$. Elemental analysis (%) calcd for $C_{144}H_{132}N_{42}O_{52}Mn_{26}$: C 36.68, H 2.80, N 12.48; found: C 36.20, H 3.00, N 12.10; yield 20%. Crystal data for **1**: $M_W = 4711.36$, cubic, space group $Fd\bar{3}$ (no. 203), $a = 34.6619(13)$, $b = 34.6619(13)$, $c = 34.6619(13)$ Å, $V = 41644(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.503$ mg m^{-3}, $2.88° < \theta < 28.30°$, crystal dimensions $0.34 \times 0.34 \times 0.34$ mm, $\mu = 1.590$ mm^{-1}, $T = 150(2)$ K; 4343 unique of 110229 reflections collected. 4343 reflections and 228 parameters were used for the full-matrix, least-squares refinement on F^2, $R1 = 0.0479$ ($I > 2\sigma(I)$), $R1 = 0.0709$ (all data); $wR2 = 0.1310$ ($I > 2\sigma(I)$), $wR2 = 0.1697$ (all data). Further details are given in the Supporting Information. CCDC-201416 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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