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Tetramanganese(II) Cluster with Centered Trigonal Topology: Structure and Magnetic Properties

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A new tetranuclear manganese(II) compound, [Mn$_4$L$_6$](ClO$_4$)$_2$ (L is the Schiff base derived from 2-pyridylaldehyde and 2-aminophenolate), has been synthesized and characterized structurally and magnetically. The compound is the first example of tetramanganese clusters with centered planar trigonal topology in which a central Mn(II) ion is connected with three peripheral Mn(II) ions by double phenoxo bridges, generating a trigonal Mn[(μ-phenoxo)$_2$Mn]$_3$ core. Magnetic studies have demonstrated a very weak ferromagnetic interaction between the central and peripheral Mn(II) ions, which leads to a high-spin ground state ($S = 10$). The ferromagnetic interaction has been tentatively related to distortion of the metal coordination environments after comparing the magnetic and structural data of the known Mn(II) complexes with similar bridging moieties.

Introduction

Polynuclear manganese clusters have received considerable interest in recent years. The interest arises, in part, from the interesting magnetochemical properties of polynuclear complexes. One of the focuses in this respect is to achieve molecular systems with high-spin ground states via intramolecular ferromagnetic coupling or ferromagnetic-like effects, which are attractive as potential precursors to molecular magnetic materials or as single-molecule magnets (SMMs).[1−4] Another important impetus for investigating polynuclear Mn clusters lies in their biological relevance. It has become accepted that the water-oxidizing complex (WOC) of Photosystem II contains a tetranuclear manganese aggregate, although the structure has not yet been fully understood.[5] Thus far, numerous Mn$_4$ clusters have been reported, the core structure varying from butterfly-like, cubane-like, adamantane-like, tetrahedral, rhomboidal, linear to "pair-of-dimer", and others.[4−7] Surprisingly, the trigonal Mn$_4$ structure with

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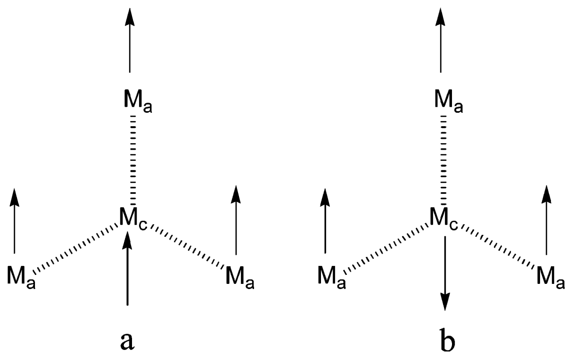
Scheme 1



a Mn atom at the center (centered trigonal cluster) has not yet been reported, although the topology is rather simple and may exhibit interesting magnetic properties: the ferromagnetic interaction between the central metal ion and the apical ones would lead to an $S = 10$ ground state with the spin structure illustrated in Scheme 1a, while the antiferromagnetic interaction would lead to an $S = 5$ ground state with the spin structure illustrated in Scheme 1b. A tetranuclear Fe(III) cluster with this simple topology and double methoxo bridges $[Fe_4(OCH_3)_6(dpm)_6$, where Hdpm = dipivaloylmethane] has been reported to behave as a single-molecule magnet[8] in which the double methoxo bridges mediate antiferromagnetic interaction to give rise to the expected $S = 5$ ground state (Scheme 1b). Herein, we reported the structural and magnetic characterization of the first Mn_4 cluster that exhibits this interesting topology. The compound, $[Mn_4L_6](ClO_4)_2$ (**1**, HL is the Schiff base derived from 2-pyridylaldehyde and 2-aminophenol), contains the trigonal $Mn(II)[(\mu_2\text{-phenoxo})_2Mn(II)]_3$ cluster core in which very weak ferromagnetic interactions are operative through the double phenoxo bridges, leading to a $S = 10$ ground state not well isolated from other low-lying states.

Experimental Section

Materials and Physical Measurements. All the starting chemicals were of A. R. grade and used as received. The L ligand was prepared by the condensation reaction of 2-pyridylaldehyde with 2-aminophenol in ethanol according to the literature procedure.[9] Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyzer. The IR spectrum was recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. The electrospray mass spectrum (ESI-MS) was obtained on a LCQ system (Finnigan MAT). Temperature-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS *XL*-7 magnetometer with an applied field of 500 Oe, and field-dependent measurements were performed on an Oxford MagLab 2000 magnetometer at 1.8 K. Diamagnetic corrections were made with Pascal's constants.[10]

Synthesis of $[Mn_4L_6](ClO_4)_2$, 1. Above an aqueous solution (10 mL) of $Mn(ClO_4)_2{\cdot}6H_2O$ (1 mmol, 0.36 g, 0.1 mol L^{-1}) and NaN_3 (2 mmol, 0.13 g, 0.2 mol L^{-1}) in a test tube was carefully added a layer of the methanol−water buffer solvent (10 mL, in 1:1 volume ratio), which was in turn layered carefully by a methanol solution (5 mL) of the HL ligand (1 mmol, 0.20 g, 0.2 mol L^{-1}). The tube was sealed and left to stand at room temperature. Mauve crystals of **1** appeared in 2 weeks. According to elemental analyses and IR spectra, the polycrystalline sample of **1** can be prepared by mixing the reactants directly in the methanol−water solution (in 1:1 volume ratio) with a yield of 56.2%. Anal. Calcd for $C_{72}H_{54}Cl_2Mn_4N_{12}O_{14}$: C, 53.98; H, 3.40; N, 10.49. Found: C, 53.69; H, 3.86; N, 10.48. IR (cm^{-1}): 1588s, 1481s, 1460s, 1299m, 1274s, 1250m, 1148m, 1095s, 865m, 778m, 751m, 622m, 588m, 529m, 517m.

Caution! Although not encountered in our experiments, perchlorate salts in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

Crystallographic Studies. Diffraction intensity data of the single crystal of **1** were collected at 293 K on a Nonius Kappa CCD diffractometer, equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Empirical absorption corrections were applied using the Sortav program.[11] All structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal for all non-hydrogen atoms.[12] Hydrogen atoms were placed at calculated positions and refined isotropically.

Crystal data: $C_{72}H_{54}Cl_2Mn_4N_{12}O_{14}$, fw = 1601.93, tetragonal, $P\bar{4}$, $a = 16.5007(4)$, $c = 14.9099(4)$ Å, $V = 4059.56(18)$ Å^3, $T = 293$ K, $Z = 2$, μ(Mo Kα) = 0.738 mm^{-1}, 50714 reflections measured, 9250 unique ($R_{int} = 0.1517$), GOF = 1.043, $R1 = 0.568$ for 4485 observed reflections, $wR2(F^2) = 0.1035$ for all data.

Results and Discussion

Synthesis. Compound **1** has been obtained by slow diffusion between the aqueous solution containing manganese perchlorate and sodium azide and the methanol solution containing the Schiff base HL. By carrying out the reaction of Mn(II) and HL in the presence of azide ions, we initially intended to synthesize Mn(II)−L complexes with azido ions as bridges, as we have done successfully with other Schiff bases.[13] However, in the present case it turned out that the azido ion is absent in the final product. Nevertheless, it seems that the azido salt plays an important role in the formation of **1**. We carried out the reaction in the same solvent system in the absence of sodium azide, but the color (yellow) and infrared spectrum of the product were inconsistent with that of **1** and the analytical data suggested a complex of composition $[Mn(L)(HL)]ClO_4$. Thus, it is likely that the azide salt acts as a base to deprotonate the phenol group of the HL ligand so that the phenolate oxygens can act as bridges. Along this line, we attempted to synthesize **1** in the presence of other bases such as NaOAc and Et_3N instead of NaN_3, but all these efforts were in vain: the color (dark-brown) and the infrared spectra of the resulting solid products

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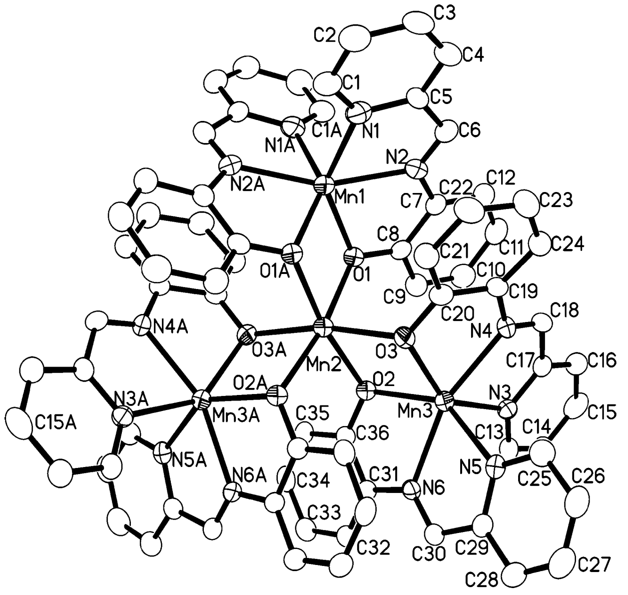

Figure 1. Perspective view of the tetramanganese cluster with the atom-labeling scheme. Thermal ellipsoids were drawn at 30% possibility.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**[a]

Mn1−O1	2.133(3)	Mn2−O1	2.159(3)
Mn1−N1	2.281(5)	Mn2−O2	2.183(3)
Mn1−N2	2.222(4)	Mn2−O3	2.166(3)
Mn3−O2	2.142(3)	Mn3−N4	2.217(4)
Mn3−O3	2.128(3)	Mn3−N5	2.272(4)
Mn3−N3	2.296(4)	Mn3−N6	2.226(4)
O1−Mn1−O1A	81.35(18)	O1−Mn2−O1A	80.18(17)
O1−Mn1−N1	139.99(15)	O1−Mn2−O2	94.30(11)
O1−Mn1−N2	73.25(15)	O1−Mn2−O3	95.46(11)
O1−Mn1−N1A	103.02(14)	O1−Mn2−O2A	171.02(11)
O1−Mn1−N2A	124.61(13)	O1−Mn2−O3A	92.93(11)
N1−Mn1−N1A	98.4(2)	O2−Mn2−O2A	92.02(15)
N1−Mn1−N2	71.87(18)	O2−Mn2−O3	80.48(11)
N1−Mn1−N2A	94.02(16)	O2−Mn2−O3A	91.87(11)
N2−Mn1-N2A	158.7(2)	O3−Mn2−O3A	169.03(16)
O2−Mn3−O3	82.30(11)	O3−Mn3−N3	142.64(12)
O2−Mn3−N3	102.11(12)	O3−Mn3−N4	73.59(13)
O2−Mn3−N4	119.92(12)	O3−Mn3−N5	105.35(13)
O2−Mn3−N5	142.25(13)	O3−Mn3−N6	125.00(13)
O2−Mn3−N6	73.97(13)	N4−Mn3−N5	97.46(14)
N3−Mn3−N4	72.22(14)	N4−Mn3−N6	159.88(14)
N3−Mn3−N5	93.63(12)	N5−Mn3−N6	71.56(14)
N3−Mn3−N6	91.28(13)	Mn1−O1−Mn2	99.24(13)
Mn3−O2−Mn2	98.13(11)	Mn3−O3−Mn2	99.09(12)
C8−O1−Mn1	116.9(3)	C8−O1−Mn2	131.7(3)
C36−O2−Mn2	129.5(3)	C36−O2−Mn3	116.6(3)
C20−O3−Mn2	128.8(3)	C20−O3−Mn3	116.0(3)

[a] Symmetry code A: $-x + 1, -y + 2, z$.

were all inconsistent with those of **1**. It seems that NaN_3 provides the most suitable basicity that induces the formation of **1**. Presumably, the other bases mentioned above, whose basicity is stronger than that of NaN_3, may lead to hydrolysis and oxidation of the Mn(II) ion. Moreover, the OAc^- ion may coordinate with manganese ions, competing with L to prevent the formation of **1**.

The IR spectrum of the complex exhibits a strong absorption at 1588 cm^{-1} due to the $\nu(C{=}N)$ vibration of the Schiff ligand. The very strong absorption centered at 1095 cm^{-1} indicates the presence of the perchlorate ion, and most of the other bands are attributable to the absorptions of the pyridyl and phenyl fragments in the L ligand. The complex is insoluble in water but soluble in ethanol, methanol, and DMF. The ESI-MS spectrum of the complex in ethanol did not exhibit any peak corresponding to the tetranuclear cluster.

Structural Characterization. The crystallographic analysis revealed that the structure of **1** consists of tetranuclear Mn(II) cluster dications, $[Mn_4L_6]^{2+}$, with perchlorate ions as counterions. A perspective view of the cluster is shown in Figure 1 with selected bond distances and angles listed in Table 1.

The cluster ion contains a $Mn(II)[(\mu_2\text{-}O)_2Mn(II)]_3$ trigonal core with a Mn atom (Mn2) at the center and three Mn atoms (Mn1, Mn3, Mn3A) at the apexes and lies on a crystallographic 2-fold axis that passes through Mn2 and Mn1. Each of the apical Mn(II) ions is ligated by two deprotonated L ligands, which are tridentate via the pyridyl nitrogen, imine nitrogen, and phenolate oxygen atoms, to complete a highly distorted octahedral $[MnN_4O_2]$ sphere. Although Mn1 and Mn3 are crystallographically independent, their bond distances and angles are similar. As expected, the Mn−N distances [2.217(4)−2.296(4) Å] are longer than the Mn−O ones [2.133(3)−2.142(3) Å]. The three donor atoms of each ligand occupy the meridional positions around the metal ion and form two five-membered chelate rings, imposing very large angular distortions upon the coordination environments: the N(pyridyl)−Mn−N(azomethine) and O(phenoxo)−Mn−N(azomethine) bite angles of the ligands are restricted to values smaller than 74°, the cis O1−Mn1−N2A, O2−Mn3−N4, and O3−Mn3−N6 angles are enlarged to 120−125°, and the trans O(phenoxo)−Mn−N(pyridyl) angles (O1−Mn1−N1, O2−Mn3−N5, and O3−Mn3−N3) vary from 140.0° to 142.6°, which deviate from the ideal angle (180°) by as much as about 40°. All six L ligands in the cluster are further coordinated to the central Mn2 atom via their phenolate oxygens, completing a pseudo-octahedral $[MnO_6]$ coordination environment around Mn2, and hence, each apical Mn(II) ion is linked to the central one through a double phenoxo bridging moiety. The distortion of the Mn2 sphere is much less significant than that of the apical Mn(II) spheres. The cis O−Mn2−O angles are in the range of 80.2−95.5°, and the trans angles are about 170°. The Mn2−O distances fall in a narrow range of 2.159(3)−2.183(3) Å and are slightly longer than the Mn(apical)−O ones. Detailed examination of the bond parameters around Mn2 shows the coordination environment approaches 3-fold symmetry very closely.

The independent double μ_2-phenoxo bridging moieties in the cluster show only minor differences. The Mn−O−Mn, O−Mn(apical)−O, and O−Mn2−O angles are in the narrow ranges of 98.1−99.2°, 81.3−82.4°, and 80.2−80.5°, respectively, while all the Mn···Mn distances spanned by the phenoxo bridges are equal within experimental error, taking the value 3.27 Å. Due to the presence of the 2-fold axis through the cluster, the four Mn atoms are strictly coplanar and form a centered isosceles triangle. The apical angle Mn3···Mn1···Mn3A is 58.8°, and the basal and side edge lengths are, respectively, 5.69 (Mn3···Mn3A) and 5.59 Å (Mn1···Mn3).

The Mn1−O1−Mn2−O1A bridging ring is strictly planar, which is imposed by the 2-fold symmetry, and the Mn2−

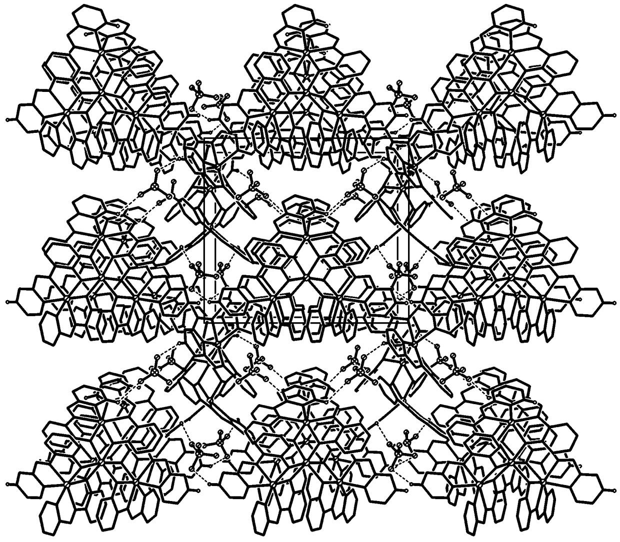

Figure 2. Stacking of the tetramanganese(II) cations and perchlorate ions in **2**, viewing down the *a* axis and showing the hydrogen bonds between the clusters and perchlorates.

O2−Mn3−O3 ring is also planar with the constituent atoms deviating from the mean plane by only ±0.001 Å, negligible within experimental error. The Mn2−O2−Mn3−O3 ring forms dihedral angles of 91.9° and 95.4° with the Mn2−O2A−Mn3A−O3A and Mn1−O1−Mn2−O1A rings, respectively. Therefore, the tetranuclear molecule has a propeller shape and is chiral. Neighboring molecules are related by $\bar{4}$ rotations to give a heterochiral but noncentrosymmetric structure. The molecules in the crystal are well separated from each other with the shortest Mn···Mn distance between neighboring clusters being 10.34 Å. The perchlorate ions reside between the tetranuclear clusters, and there are weak C−H···O hydrogen bonds between the cluster and the perchlorate ion: C15−H···O6($-x + 2$, $-y + 1$, z) and C1−H···O7(y, $-x + 2$, $-z + 1$). The H···O and C···O distances and the C−H···O angle are, respectively, 2.52 Å, 3.35 Å, and 148.7° for the former and 2.57 Å, 3.19 Å, and 124.5° for the latter. Through these hydrogen bonds each perchlorate ion bridges two clusters and each cluster interacts with four perchlorate ions, resulting in the 3D structure of **1** (Figure 2).

Magnetic Properties. The molar magnetic susceptibility (χ) of the cluster was measured at 500 Oe in the 2−300 K temperature range (Figure 3). The χT value per cluster at 300 K is 17.6 emu mol^{-1} K, corresponding to the spin-only value (17.5 emu mol^{-1} K) expected for four isolated high-spin Mn(II) ions. Upon cooling, the χT product increases monotonically and reaches 25.0 emu mol^{-1} K at 2 K. The $1/\chi$ vs T plot obeys the Curie−Weiss law with $\theta = 1.5$ K and $C = 17.8$ emu mol^{-1} K. These features suggest that a ferromagnetic interaction is operative through the double phenoxo bridges.

Taking into account that the bridging parameters (Mn−O and Mn···Mn distances and Mn−O−Mn angles) exhibit only slight differences for the Mn2−Mn1 and Mn2−Mn3 pairs, we apply the Heisenberg model to describe the exchange between the central (S_c) and apical (S_{a1}, S_{a2}, and S_{a3}) spins

$$H = -J(S_cS_{a1} + S_cS_{a2} + S_cS_{a3}) = -JS_cS_A$$

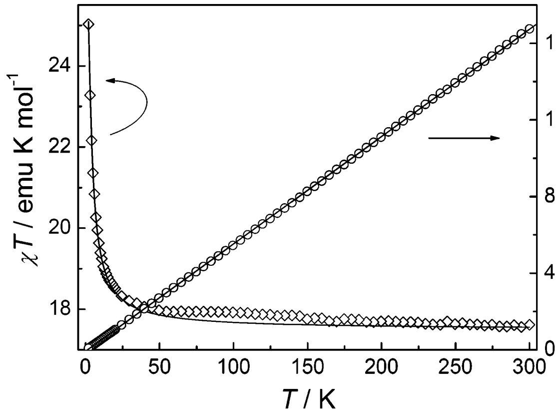

Figure 3. Temperature dependence of magnetic susceptibility shown as χT vs T (□) and $1/\chi$ vs T (○) plots. The solid lines represent the best fit by the van Vleck equation and Curie−Weiss law, respectively.

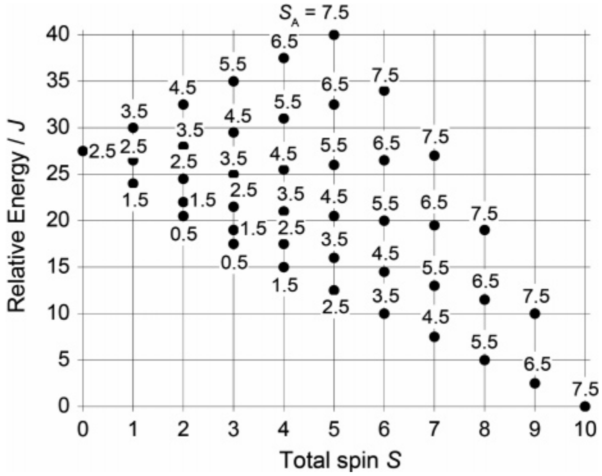

Figure 4. Relative energy levels of the $|S, S_A\rangle$ spin states, where S is the total spin of the cluster and S_A is the spin sum of the three apical Mn ions.

where $S_A = S_{a1} + S_{a2} + S_{a3}$. We neglected the interactions between apical Mn(II) ions. The eigenvalues of the above Hamiltonian, omitting the common term $JS_c(S_c + 1)/2$, are given by

$$E(S,S_A) = -(J/2)[S(S + 1) - S_A(S_A + 1)]$$

where S is the total spin of the cluster and S_A is the spin sum of the three apical Mn ions. There are a total of 42 energy levels with different S_T and S_A values (Figure 4). Applying the eigenvalues to the van Vleck equation yields a theoretical χ vs T expression

$$\chi = \frac{Ng^2\beta^2}{3k(T - \Theta)} \frac{\sum_S\sum_{S_A} S(S + 1)(2S + 1)\exp[-E(S,S_A)/kT]}{\sum_S\sum_{S_A}(2S + 1)\exp[-E(S,S_A)/kT]}$$

where the symbols have their usual meanings. The Θ parameter has been introduced to correct for secondary effects arising from zero-field splitting and intermolecular interactions. Since the clusters are well separated in the crystal lattice, the intermolecular interactions should be very small, if any. The main secondary effect should be the zero-

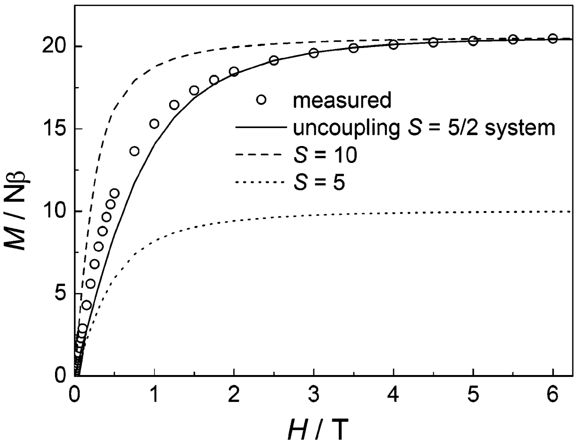

Figure 5. Field dependence of magnetization of **1** at 1.8 K (scattered open circles). The lines represent the magnetization per Mn_4 cluster calculated from the Brillouin function with different spins.

field splitting of the Mn(II) ion in the highly distorted coordination geometry. The least-squares simulation of the experimental data by this expression with g fixed at 2.00 yielded $J = 0.31$ cm^{-1} and $\Theta = -0.93$ K. The small and positive J values suggest the double phenoxo bridges in the cluster mediate a very weak ferromagnetic interaction. The ferromagnetic interaction tends to align the four Mn(II) spins in parallel, yielding a ground state with the highest spin ($S = 10$ with $S_A = 15/2$, Scheme 1a).

To further verify the weak ferromagnetic interaction, magnetization vs field measurements have been performed at 1.8 K. The molar magnetizations per Mn_4 cluster in the field range of 0−6 T are shown in Figure 5 together with the Brillouin magnetization curves for the uncoupled Mn_4 cluster and the $S = 10$ and 5 coupled states. The solid curve represents the theoretical magnetization of the Mn_4 cluster in which the four $S = 5/2$ ions are magnetically isolated ($J = 0$). When ferromagnetic coupling exists between the central and peripheral Mn(II) ions, the magnetization will saturate more rapidly than that in the uncoupled system. If the ferromagnetic coupling is increased and becomes strong enough to give a well-isolated $S = 10$ ground state, the magnetization should approach the theoretical Brillouin curve for $S = 10$ (the dashed curve in Figure 5). On the other hand, if the coupling were antiferromagnetic, the magnetization would increase less rapidly than that in the uncoupled system. The dotted Brillouin curve saturating at 10 Nβ represents the case that the antiferromagnetic interaction is strong enough to give a well-isolated $S = 5$ ground state. In the present case of **1**, the magnetization increases more rapidly than that of the uncoupled system and saturates at 20 $N\beta$, confirming the ferromagnetic interaction, but it saturates much more slowly than that in the $S = 10$ Brillouin curve, consistent with the weakness of the ferromagnetic interaction and the presence of secondary effects with $\Theta < 0$. In fact, for $J = 0.31$ cm^{-1} the spin states are poorly isolated with the first excited state ($|S, S_A\rangle = |9, 13/2\rangle$) at only 0.78 cm^{-1} above the $S = 10$ ground state. According to the Boltzmann distribution law we calculated the population distribution of the spin states at zero field and different temperatures. With $J = 0.31$ cm^{-1}, the population percentage of the $S = 10$ ground state is only about 24% at 1.8 K, and as expected, it decreases as the temperature is increased. Accordingly, the measured magnetization has more contributions from excited states of lower spins than from the ground spin. The above discussion is qualitatively valid, although we have ignored zero-field splitting effects. The negative Θ value suggests that the zero-field splitting effects should cause a decrease in magnetization, so the phenomenon that the magnetization of **1** increases more rapidly than that of the uncoupled system should be due to ferromagnetic coupling between Mn(II) ions.

Although ferromagnetic coupling between Mn(II) ions is well established for the azide bridge in the μ-1,1 mode,[13] the ferromagnetic coupling between Mn(II) ions mediated by the phenoxo bridge in **1** is rare. For dimeric Cu(II) or Ni(II) complexes it is well known that bis(μ-phenoxo), bis(μ-alkoxo), and bis(μ-hydroxo) bridges can mediate overall antiferromagnetic coupling or, in the case that accidental orthogonality is achieved, overall ferromagnetic coupling.[14,15] Good correlations between the exchange integral J and the M−O−M bridging angle have been established, and the magnetic interaction changes from antiferromagnetic to ferromagnetic at a certain angle (in most cases around 98°). However, magnetostructural analyses for coupled Mn(II) and Fe(III) complexes are far more difficult intrinsically due to complications arising from the larger numbers of magnetic orbitals and exchange pathways that have to be taken into account for high-spin d^5 ions.[16,17] Nevertheless, some semiempirical correlations between J and bridging parameters have been reported for diiron(III) complexes containing μ-phenoxo, μ-alkoxo, or μ-hydroxo bridges,[17] suggesting that J correlates strongly with Fe−O distances whereas its dependence on the M−O−M bridging angle is very weak. It is interesting to note that nearly all these diiron(III) complexes display antiferromagnetic interactions, and only one has been reported to be ferromagnetic.[18] The authors ascribed ferromagnetic coupling mainly to the distortion of the coordination geometry based on extended Hückel MO calculations.

The number of oxygen-bridged dimanganese(II) complexes is much smaller than that of the Fe(III) analogues, probably due to the tendency of Mn(II) to be oxidized. A number of dimanganese(II) complexes with a phenoxo bridge and one or two other bridges (frequently carboxylato groups) have been reported,[19,20] among which all the magnetically characterized species were found to exhibit antiferromagnetic

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intramolecular interactions with $-J < 10$ cm^{-1}. For (μ-phenoxo)bis(μ-carboxylato)dimanganese(II) complexes, Dubois et al. established recently a rough linear magnetostructural correlation between the J value and the average Mn−O(phenoxo) distance ($d_{\mathrm{Mn-O}}$), and the general trend is $-J$ decreasing as $d_{\mathrm{Mn-O}}$ increases.[20a] Some dimanganese(II) complexes with the bis(μ-phenoxo), bis(μ-alkoxo), or bis(μ-hydroxo) bridge have also been reported.[21−23] While most of them exhibit antiferromagnetic coupling ($-J < 10$ cm^{-1}) with $d_{\mathrm{Mn-O}} = 2.07-2.16$ Å,[22] only a bis(μ-alkoxo) complex and a bis(μ-phenoxo) complex, both with $d_{\mathrm{Mn-O}} = 2.15$ Å, have been found to exhibit weak ferromagnetic interactions ($J = 1.0$ and 0.8 cm^{-1}, respectively).[23,24] In the present ferromagnetic bis(μ-phenoxo)-bridged Mn_4 complex, the Mn−O distances are between 2.13 and 2.18 Å. Apparently, with these limited data it is impossible to deduce a correlation between the nature of the coupling and $d_{\mathrm{Mn-O}}$ for these complexes. We also compared these complexes in terms of the Mn−O−Mn bridging angle (87−103°) and the Mn···Mn distance (2.98−3.37 Å), and no simple magnetostructural correlation is evident concerning the nature and magnitude of the magnetic coupling. However, close inspection into structural data reveals that the metal environments in the ferromagnetic species are highly distorted from octahedral. As mentioned, in the present Mn_4 complex some cis bond angles around the apical Mn(II) ions are expanded up to 125° and some trans angles are reduced to about 140°. Similar distortion occurs for the ferromagnetic bis(μ-alkoxo)dimanganese(II) complex,[23a] while the ferromagnetic bis(μ-phenoxo)dimanganese(II) complex exhibits more significant distortion: the chelating carboxylato group dictates a very small cis angle of 55°, and the four largest angles lie in the narrow 133−140° range.[23b] It is difficult to distinguish the cis and trans angles in such a structure. On the other hand, the antiferromagnetic species exhibit relatively small distortion. The largest distortion was observed for $[\mathrm{Mn(SALPS)}]_2$ {SALPS = *N*,*N*′-[1,l′-dithiobis-(phenylene)]bis-(salicy1ideneaminato)}[22a] in which the largest cis angle and the smallest trans angle are 108° and 153°, respectively. Although the data available are limited, the above observation may suggest that the nature of magnetic coupling in this class of complexes correlates with the distortion of the coordination geometry. Perhaps the distortion, in conjunction with other factors, dictates a proper relative orientation for the interacting magnetic orbitals so that accidental orthogonality is achieved. This proposal, in accordance with the extended Hückel MO calculations for an Fe(III) species,[18] is very rough and only tentative, and theoretical calculations and more experimental data are needed to verify and revise it.

Conclusion

We presented the first example of tetramanganese clusters with centered planar trigonal topology. X-ray studies revealed that a central Mn(II) ion is connected with three peripheral Mn(II) ions by double phenoxo bridges, generating a trigonal $\mathrm{Mn}[(\mu\text{-phenoxo})_2\mathrm{Mn}]_3$ core. Detailed analyses of the temperature- and field-dependent magnetic behaviors demonstrated a very weak ferromagnetic interaction between the central and peripheral Mn(II) ions, which leads to a high-spin ground state ($S = 10$). The ferromagnetic interaction has been tentatively related to the large distortion of the metal coordination geometry after comparing the magnetic and structural data of the known Mn(II) complexes with similar bridging moieties.

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Supporting Information Available: Crystallographic data (CIF) for the compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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