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Ferromagnetic Cobalt Metallocycles

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The tripodal alcohol 1,1,1-tris(hydroxymethyl)ethane (H_3thme) directs the formation of heptanuclear cobalt metallocycles in which the metal ions are coupled ferromagnetically.

In recent years, the synthesis of paramagnetic 3d transition metal clusters has given rise to a plethora of beautiful complexes—some containing more than 80 metal centers and some with spin ground states as large as $S = 51/2 \pm 1$ and $S \geq 23$.[1−3] These large spin ground states usually arise from competing antiferromagnetic exchange interactions rather than ferromagnetic exchange, especially as the nuclearity of the metal cluster increases. Despite the numerous polymetallic Co clusters characterized to date, very few have displayed ferromagnetic interactions between the metal centers. To the best of our knowledge, the only examples of ferromagnetic (homometallic) Co clusters are confined to $[Co_4]$ cubanes,[4] a $[Co_6]$ complex whose structure is based on a central cubane,[5] and a $[Co_{12}]$ wheel.[6] Further examples of ferromagnetic exchange and the coexistence of ferro- and antiferromagnetic exchange can be found in polyoxometalate chemistry in complexes with nuclearities up to nine.[7] Another interest in Co clusters that display nonzero spin ground states is their magnetic behavior at low temperature. Because of Ising-type anisotropy for Co^{2+} ions, one might expect to observe high blocking temperatures of the magnetization.

We have been exploring the reactions of tripodal alcohols such as 1,1,1-tris(hydroxymethyl)ethane (H_3thme) and its analogues in the synthesis of 3d transition metal clusters, particularly those of Mn, Fe, and Ni.[8] When fully deprotonated (tripod^{3-}), these ligands direct the formation and isolation of elaborate polymetallic arrays comprising linked or fused $[M_3]$ units that are often characterized by high-spin ground states. Here we extend this work to the synthesis of two new ferromagnetic cobalt clusters $TBA[Co^{III}Co^{II}_6(thme)_2(O_2CCMe_3)_8Br_2]\cdot MeCN$ (**1**·MeCN) and $Na_2[Co^{III}Co^{II}_6(thme)_2(O_2CMe)_{10}(OH_2)_4](O_2CMe)\cdot 4.6MeOH\cdot 3H_2O$ (**2**·4.6MeOH·3H_2O) whose structures are based on centered hexagons.

Since both clusters display essentially identical behavior, we will limit our discussion to complex **1**. Full details of complex **2** can be found in the Supporting Information.

Reaction of $CoBr_2$ with H_3thme, NaO_2CCMe_3, and TBABr in MeCN affords the complex $TBA[Co^{III}Co^{II}_6(thme)_2(O_2CCMe_3)_8Br_2]\cdot MeCN$ (**1**·MeCN, Figure 1), which crystallizes in the monoclinic space group *P*21/*n* with two crystallographically distinct molecules in the asymmetric unit and a total of four molecules per unit cell.[9] The $[Co^{III}Co^{II}_6(OR)_6]^{9+}$ core describes a centered hexagon of six edge-sharing triangles with the sole Co^{3+} ion at the center. This is directed by the presence of two $\eta^3,\eta^3,\eta^3,\mu_7$-thme^{3-} ligands that sit

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(9) Crystal data: $C_{70}H_{132}Co_7N_3O_{22}Br_2$, $M = 1940.12$, pink blocks, monoclinic, *P*21/*n*, $a = 16.2302(15)$ Å, $b = 27.2626(22)$ Å, $c = 20.8508(14)$ Å, $\beta = 107.840(7)°$, $V = 8782.38$ Å^{-3}, $Z = 4$, final *R* indices [$I > 2\sigma(I)$] R1 = 0.0487; wR2 = 0.0569, *R* indices (all data) R1 = 0.1149; wR2 = 0.0718. IR (KBr, cm^{-1}): 3436 (s), 2932 (m), 2868 (m), 1562 (s), 1425 (s), 1337 (m), 1126 (w), 1025 (s), 919 (w), 670 (m), 615 (m), 516 (w), 420 (w). Anal. Calcd (%): C 42.66, H 6.83, N 0.75, Co 22.20. Found: C 42.84, H 6.84, N 0.91, Co 22.04.

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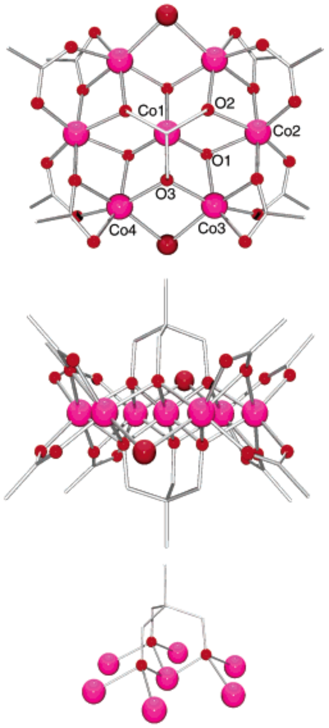

Figure 1. Molecular structure of complex **1** viewed perpendicular, (top) and parallel to the metal plane (middle). The bridging mode of the thme^{3-} ligand (bottom).

directly above and below the plane of the seven metal atoms with each O-arm forming one $[Co^{III}Co^{II}_2O]^{6+}$ triangle. This is the largest coordination mode ever seen for this ligand (Figure 1). The carboxylate ligands surround the periphery of the cluster and bridge in two ways: the common η^1,η^1,μ-mode and the less-common η^1,η^2,μ-mode. There are two Br^- ions in the complex, each of which bridge between two Co^{2+} ions along one edge of the outer $[Co^{II}_6]$ 'wheel'.

All the Co ions are in distorted octahedral geometries with the central Co displaying distinctly shorter bond lengths (1.887−1.907 Å) than those in the outer wheel (2.036−2.495 Å). The oxidation states of the Co ions were assigned on the basis of these bond length considerations, charge balance, and BVS calculations.[10] Magnetic studies were performed using a SQUID magnetometer operating in the 2−300 K temperature range with applied magnetic fields of up to 5.5 T. Upon cooling from room temperature, the $\chi_M T$ product ($H = 0.05$ T) decreases from a value of 18.8 cm^3 K mol^{-1}, corresponding to six noninteracting $S = 3/2$ with a g-value of 2.58, to a minimum at $T = 36$ K and then increases to reach a value of 28.3 cm^3 K mol^{-1} at $T = 3$ K (Figure 2, inset and Figure S3). In octahedral symmetry, high-spin $S = 3/2$ Co^{2+} complexes have an orbitally degenerate $^4T_1$ ground electronic term. The combination of a lowering of symmetry and spin−orbit coupling leads to a splitting of the 12 degenerate ground terms into six Kramers doublets. At sufficiently low temperature, only one Kramers doublet corresponding to an effective spin $S' = 1/2$ is populated. The exchange interaction can then be considered to occur between effective $S' = 1/2$ states at temperatures lower than 30 K.[11] Thus, the decrease of $\chi_M T$ upon cooling is due to the presence of such spin−orbit coupling and low-symmetry ligand field effects, while the increase below 36 K can be assigned to the presence of ferromagnetic exchange coupling between anisotropic $S' = 1/2$ local Kramers doublets. The $\chi_M T$ value at low temperature (28.3 cm^3 K mol^{-1}) corresponds well to six effective $S' = 1/2$ states, each with a g'-value of 4.34, interacting in a ferromagnetic manner.[12,13] The $M = f(H)$ plots were measured at $T = 2$ and 6 K (Figure 2). At $T = 2$ K and $H = 5.5$ T, saturation is almost reached with a value of 13 μ_B corresponding to an effective spin of the cluster $S' = 3$ with a g'-value of 4.33. This is in line with the $\chi_M T$ value at low temperature which confirms the assumption of a ferromagnetic interaction between the six Co^{2+} ions. Examination of the metallic core of **1** suggests the existence of two distinct magnetic exchange pathways that involve two carboxylates and one alkoxide between Co2 and Co3 (and symmetry equivalents) and that involving one alkoxide and one bromide between Co3 and Co4 (and symmetry equivalents). The Co−X−Co angles (X = O, Br) between all of the Co^{2+} ions fall in the ranges 88.34−88.73° (Co−O(O_2CR)−Co), 81.66° (Co−Br−Co), and 89.36−99.98° (Co−O(OR)−Co). Such values are expected to lead to ferromagnetic exchange coupling between the peripheral Co^{2+} ions.[12,13] Thus, two different exchange parameters, J and J', were considered (see Figure 2).[14] The magnetization data were calculated using the MAGPACK package assuming an axial anisotropy for the six Co^{2+} ions which leads to

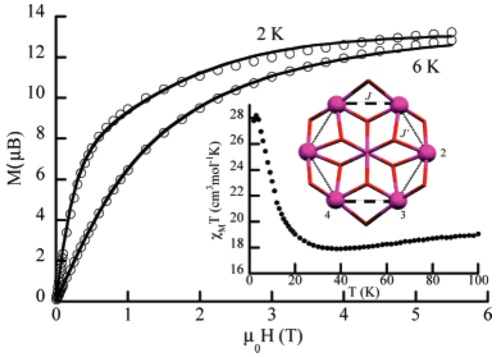

Figure 2. Top, $M = f(H)$ for $[Co_7]$ at $T = 2$ and 6 K (○) exp and (−) calculated (see text for parameters); inset: $\chi_M T = f(T)$ for an applied field $\mu_0 H = 0.05$ T. Middle, the magnetic exchange topology employed to fit the magnetization data.

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(12) At very low temperature, only one Kramers doublet is populated. The Zeeman perturbation splits this doublet into two components so that it can be treated as an effective $S' = 1/2$. In such a case the appropriate spin Hamiltonian is $\mathbf{H} = \beta\cdot S'\cdot g'\cdot H$ where g' is the tensor associated to the effective spin $S' = 1/2$. The effect of the orbital momentum is included into the values of g'. An average of the principal values of the g' tensor are in this case equal to 4.33. Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Struct. Bonding* **1982**, *52*, 37.

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(14) The spin Hamiltonian that describes the exchange interaction is the following. $\mathbf{H} = -\sum_{i=x,y,z}[J_i(S^i_1S^i_2 + S^i_4S^i_5) + J_i'(S^i_2S^i_3 + S^i_3S^i_4 + S^i_1S^i_6 + S^i_5S^i_6)]$ where J_i are the x, y, and z components. In the present case, we assumed that the exchange interaction is axial ($J_x = J_y = J_\perp$ and $J_z = J_\parallel$).

axial parameters ($J_{\|}$, $J_{\perp}$, J', $J_{\perp}'$, $g_{\|}'$ and $g'_{\perp}$) where the g'-values were assumed to be the same for each of the six Co^{2+} ions.[15] The model reproduces the $M = f(H)$ experimental data extremely well at $T = 2$ and 6 K with the following parameters: $J = 20$ cm^{-1}, $J_{\perp} = 13$ cm^{-1}, $J' = 12$ cm^{-1}, $J_{\perp}' = 7.8$ cm^{-1}, $g' = 5.2$, and $g'_{\perp} = 4.1$.[16]

To probe possible single-molecule magnetism behavior, single-crystal hysteresis loop measurements were performed using a micro-SQUID setup.[17] A transverse field method[18] allowed us to establish that the compound has an easy axis of magnetization. Figure 3 presents typical magnetization (M) vs. applied dc field (H) measurements at fields parallel to the easy or hard axis at a sweep rate of 0.014 T s^{-1} and temperatures between 0.04 and 7 K. Despite the Ising-type anisotropy, no opening of a hysteresis was observed below 7 K, indicating that no blocking of the magnetization occurs.

This is in line with the lack of out-of-phase (χ'') signals in ac susceptibility studies carried out in the 1.8−10 K temperature range at $\nu = 100$ and 1000 Hz in zero applied magnetic field (see Supporting Information, Figure S2). The absence of a blocking of the magnetization may be due to the presence of a rhombic (transverse) component of the anisotropy that induces a mixing of the low-lying sublevels and leads to a fast relaxation of the magnetization. Indeed, the complex possesses a principal 2-fold symmetry axis that lies within the plane of the molecule so that the transverse component of the anisotropy tensor will be nonzero.

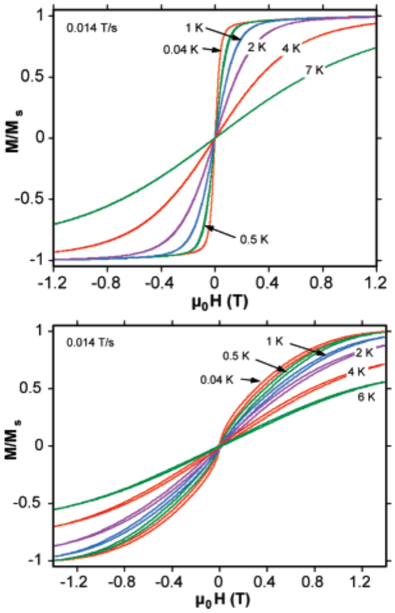

Figure 3. Single-crystal magnetization (M) of **1** vs. applied magnetic field (H); the magnetization is normalized to its saturation value and shown at different temperatures at the indicated field sweep rate. The upper picture shows the data when the field is applied parallel to the easy axis and the lower picture when the field is applied parallel to the hard axis.

The rhombic component may be canceled out only if the molecule has a symmetry axis with an order strictly larger than two. Slow relaxation of magnetization may possibly be observed by carrying out the ac studies in the presence of an applied magnetic field using larger frequencies. This may help to cast light on the relaxation mechanisms of such anisotropic complexes.

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Supporting Information Available: Crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The $M = f(H)$ data were reproduced after several calculation steps. The first consisted of fixing an average g' value and introducing different anisotropic J and J' in order to obtain close calculated data to the experimental ones. Care was taking to keep the J/J' ratio between 0.5 and 0.7, which reflects what is expected from the values of the Co−X−Co angles based on data from the literature. The second is to fix the J and J' values and do the calculations by introducing the anisotropy for g'. These two steps were carried out several times until the calculated data were as close as possible to the experimental data. The g' values obtained are reasonable for Co(II) ions and the J and J' values are in line with what is reported in the literature for similar Co−X−Co angles.

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