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Polynuclear Chromium(III) Carboxylates. 1. Synthesis, Structure, and Magnetic Properties of an Octanuclear Complex with a Ring Structure

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A novel cyclic octanuclear chromium(III) complex with hydroxo and acetato bridging ligands was isolated and its structure determined by X-ray crystallography. The complex $[Cr_8(OH)_{12}(OAc)_{12}]$ (**1**) ($OAc^- = CH_3CO_2^-$), as found in crystals of $\mathbf{1}\cdot 34H_2O$, is obtained by refluxing an aqueous solution of the trinuclear "basic" chromium acetate. $\mathbf{1}\cdot 34H_2O$ crystallizes in the tetragonal space group $I\bar{4}2d$ with the following unit cell dimensions: $a = 16.592(2)$ Å, $c = 31.557(4)$ Å, $V = 8687(1)$ Å^3, and $Z = 2$. A total of 2000 unique data with $I > 3\sigma(I)$ were used to solve and refine the structure to $R(F_o) = 0.066$ and $R_w(F_o) = 0.085$. The structure consists of eight Cr(III) ions that form a ring structure and are bridged by hydroxo and acetato ligands. Each of the two neighboring metal atoms in **1** is bridged either by two OH^- ligands and one OAc^- ligand, with a Cr···Cr distance of 2.949(2) Å, or by two OAc^- ligands and one OH^- ligand, with a Cr···Cr distance of 3.383(2) Å in an alternating fashion. The complex resides on a crystallographic $\bar{4}$ center, and the overall symmetry of **1** is S_4. The magnetic susceptibility of $\mathbf{1}\cdot 34H_2O$ was measured in the temperature range of 5−240 K. Our theoretical modeling of the susceptibility data indicates alternating antiferromagnetic exchange interactions between adjacent spin $^3/_2$ Cr^{3+} ions around the ring, of magnitude $J/k_B = 13.7$ and 8.9 K, respectively.

Introduction

Polynuclear metal complexes with ring structures have been the subject of numerous structural and spectroscopic studies. Many transition elements form highly symmetrical molecular arrays of 4−18 metal atoms, bridged by a variety of ligands in nearly planar cyclic structures.[2] Interest in these polynuclear systems stems not only from their high symmetry and the aesthetic molecular frameworks but also from the special magnetic properties associated with them. Molecules such as $[Fe_{10}(OCH_3)_2O(O_2CCH_2Cl)_{10}]$[2s] and $[Fe_{18}(OH)_6(OCH_3)_{24}(O_2CCH_3)_{12}(XDK)_6]$[2t] are only a few examples of the growing family of cyclic polymetal complexes. Compared to those of iron and manganese, structurally characterized chromium aggregates, bridged by carboxylates ligands, are few. Complexes with nuclearity >2 include cores such as $\{Cr_3O\}$,[3] $\{Cr_3(OH)_2\}$,[4] $\{Cr_4S\}$,[5] $\{Cr_4O_2\}$,[6] $\{Cr_8F_8\}$,[7a] $\{Cr_8(OH)_8\}$,[7b] $\{Cr_8O_4\}$,[7b] and $\{Cr_{12}O_{12}\}$.[8] "Basic" chromium carboxylates, in which only RCO_2^- and oxo/hydroxo/aquo ligands are present, are even fewer and include the classical trinuclear $[Cr_3O(O_2CR)_6(H_2O)_3]^+$ ion, the octanuclear $[Cr_8(OH)_8(O_2CPh)_{16}]$ and $[Cr_8O_4(O_2CPh)_{16}]$ complexes,[7b] and the ill-defined $[Cr_{12}O_{12}(O_2CCMe_3)_{15}]$ complex.[8] The structure of a cyclic octanuclear Cr(III) complex with fluoride and pivolate bridging ligands was reported by Gérbéléu et al. in 1990.[7a] The neutral complex $[Cr_8F_8(O_2CCMe_3)_{16}]$, whose eight Cr atoms form an almost planar and regular octagon, was prepared by reacting CrF_3 with pivalic acid. This complex exhibits a weak antiferromagnetic interaction between the paramagnetic Cr^{3+} ions. Recently the hydroxo analogue of this complex, namely, $[Cr_8(OH)_8(O_2CPh)_{16}]$, was reported by Atkinson et al. Magnetic measurements indicated antiferromagnetic exchange between the Cr centers with an exchange parameter $J = 12.0$ cm^{-1}.[7b]

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Table 1. Crystallographic Data for $[Cr_8(OH)_{12}(OAc)_{12}]\cdot 34H_2O$

empirical formula	$C_{24}H_{48}Cr_8O_{36}\cdot 34H_2O$	T (°C)	20 ± 2
fw	1941.08	λ (Å)	0.710 69
space group	$I\bar{4}2d$ (No. 122)	ρ_{calcd} (g cm^{-3})	1.484
a (Å)	16.592(2)	μ (cm^{-1})	10.43
c (Å)	31.557(4)	R^a	0.066
V (Å^3)	8687(1)	R_w^{b}	0.085
Z	4		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

This work is part of a project whose purpose is to synthesize high-nuclearity chromium(III) carboxylates and to elucidate their structures and magnetic properties. We were recently successful in producing a series of such new complexes, mainly with nuclearities between 6 and 8. This is a first report in a series, dedicated to this subject.

In the present report, we describe the preparation, structure, and solid-state magnetic properties of a well-defined, cyclic octanuclear chromium(III) acetate complex. The complex $[Cr_8(OH)_{12}(OAc)_{12}]$ (**1**), as found in the crystals of **1**$\cdot 34H_2O$ is neutral, water-soluble, and kinetically stable and possesses a large effective magnetic moment. These properties make it a potential candidate as a nuclear magnetic resonance imaging (MRI) contrasting agent.

Experimental Section

Synthesis. All manipulations were carried out in the open using chemicals as received.

$[Cr_8(OH)_{12}(O_2CCH_3)_{12}]\cdot 34H_2O$ (1$\cdot 34H_2O$). CrO_3 (2.0 g, 0.2 mmol) was used to produce the trinuclear basic chromium acetate according to a literature method.[9] The green solid was subsequently dissolved in 70 mL of water, and the solution was refluxed for 2 h. The resulting purple solution was kept in an open flask for slow evaporation. Dark violet prisms of **1**$\cdot 34H_2O$ were deposited after a few days. The crystals were collected, washed with cold water, and dried in vacuo (yield 17%). Anal. Calcd (found) for $C_{24}H_{116}Cr_8O_{70}$: C, 14.85 (14.88); H, 6.02 (6.06). The crystals are stable and do not lose solvent molecules on drying in vacuo. The compound is soluble in water, ethanol, acetonitrile, and acetone. Electronic spectral data obtained in H_2O, λ_{max}, nm ($\epsilon_{M/Cr}$, L mol^{-1} cm^{-1}): 411 (39), 562 (55).

X-ray Crystallography. A violet prism of approximate dimensions 0.4 × 0.3 × 0.3 mm was coated by epoxy glue, attached to the end of a glass fiber, and mounted on a Philips 1100/20 diffractometer. Mo Kα ($\lambda = 0.710\ 69$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 reflections in the range $11° < \theta < 15°$. Data were measured by using an $\omega - 2\theta$ motion. Crystallographic data and other pertinent information are given in Table 1. Data were corrected for Lorentz and polarization effects. Intensity data were corrected for absorption using the empirical absorption program DIFABS, incorporated into TEXSAN.[10] The heavy atoms were located by using the results of a SHELXS-86 direct-method analysis.[11] Structure refinement was carried out with the full-matrix least-squares program of TEXSAN. The structure was refined to convergence, using anisotropic thermal parameters for all non-hydrogen atoms.[12] All methyl hydrogen atoms were introduced in calculated positions using the riding model.

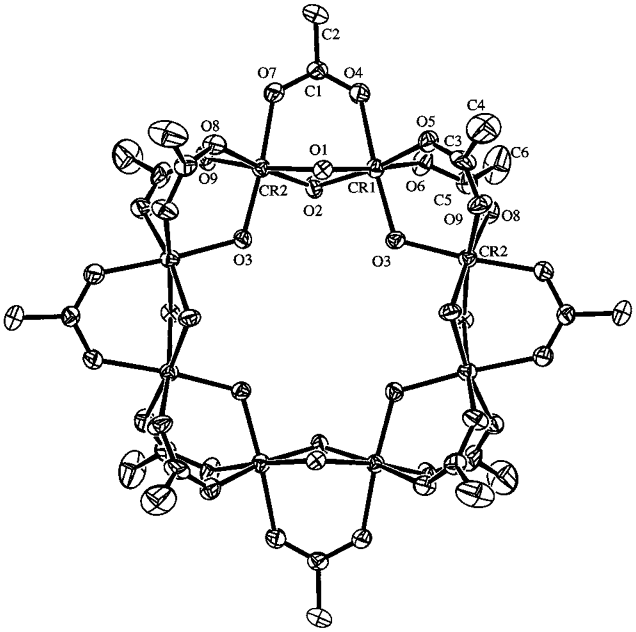

Figure 1. Structure and the numbering scheme of $[Cr_8(OH)_{12}(OAc)_{12}]$ (**1**) with 50% probability thermal ellipsoids.

Magnetic Susceptibilities. Variable-temperature magnetic susceptibility data were obtained using a Quantum Design MPMS-5S SQUID susceptometer at The Hebrew University of Jerusalem. Measurements were made with an applied magnetic field of 0.1 T (1000 G) in the temperature range 5−240 K.

Results and Discussion

Synthesis. The octanuclear complex **1** with its $\{Cr_8(OH)_{12}\}$ core is one of several products, obtained by refluxing the emerald-green aqueous solution of the trinuclear "basic" chromium acetate with the $\{Cr_3O\}$ core. In fact, **1** is produced in low yield (∼17%) relative to other cationic species which are revealed by ion-exchange chromatography and whose exact nature is under investigation in our laboratory. The complexity of this system is obvious, and we cannot comment on the mechanism of the assembly reaction in the present stages of our work.

Description of the Structure. Figure 1 shows the structure and labeling scheme of **1**, and Figure 2 presents a stereoview of the complex. The atomic positional parameters of the significant atoms are listed in Table 2, and Table 3 gives the important bond lengths and angles. As shown in Figure 1, the complex $[Cr_8(OH)_{12}(OAc)_{12}]$, **1**, consists of eight Cr(III) ions forming a ring structure which are bridged by hydroxo and acetate ligands. Each of the two neighboring metal atoms are bridged either by two hydroxo ligands and one acetate ligand, with a Cr···Cr distance of 2.949(2) Å, or by two acetate ligands and one hydroxo ligand, with a Cr···Cr distance of 3.383(2) Å, in an alternating fashion. The latter distance corresponds well with the distance previously found in the discrete $\{Cr_2(OH)(O_2CR)_2\}$ core of $[Cr_2(OH)(O_2CH)_2(H_2O)_6]^{3+}$, 3.381(1) Å.[13] A compound containing a discrete $\{Cr_2(OH)_2(O_2CR)\}$ unit with

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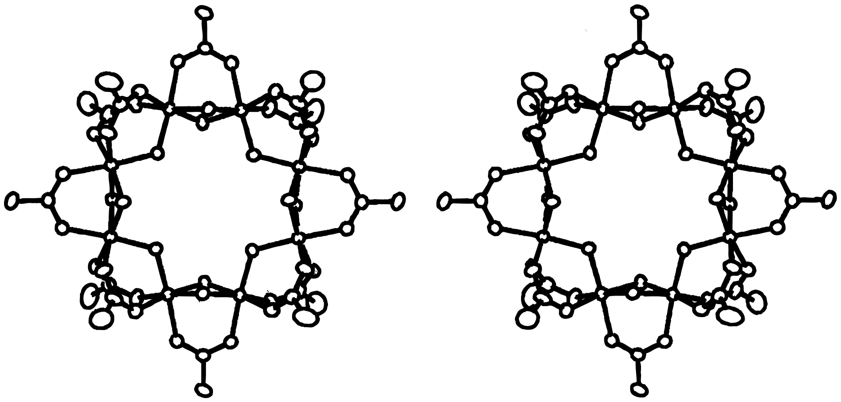

Figure 2. Stereoview of $[Cr_8(OH)_{12}(OAc)_{12}]$.

Table 2. Positional Parameters of Significant Atoms in **1**

atom	*x*	*y*	*z*
Cr(1)	0.1333(1)	0.2077(1)	0.01218(5)
Cr(2)	0.23885(9)	0.0652(1)	0.00586(5)
O(1)	0.1800(4)	0.1385(4)	−0.0321(2)
O(2)	0.1654(4)	0.1157(4)	0.0481(2)
O(3)	0.0242(3)	0.1660(4)	0.0039(2)
O(4)	0.2420(4)	0.2579(4)	0.0237(2)
O(5)	0.1193(4)	0.2968(4)	−0.0282(2)
O(6)	0.0966(4)	0.2748(5)	0.0609(2)
O(7)	0.3217(4)	0.1515(4)	0.0157(3)
O(8)	0.3115(4)	0.0266(4)	−0.0393(2)
O(9)	0.3014(5)	0.0076(4)	0.0511(3)
C(1)	0.3098(6)	0.2265(6)	0.0222(3)
C(2)	0.3823(7)	0.2766(7)	0.0294(5)
C(3)	0.0633(8)	0.3211(7)	−0.0540(4)
C(4)	0.085(1)	0.375(1)	−0.0880(5)
C(5)	0.0304(7)	0.3117(6)	0.0645(4)
C(6)	0.025(1)	0.368(1)	0.1028(5)

Table 3. Important Bond Distances (Å) and Angles (deg) in **1**

Cr(1)−Cr(2)	2.949(2)	Cr(1)−O(6)	1.993(8)
Cr(1)−Cr(2)′	3.383(2)	Cr(2)−O(1)	1.966(7)
Cr(1)−O(1)	1.967(7)	Cr(2)−O(2)	1.992(7)
Cr(1)−O(2)	1.975(7)	Cr(2)−O(3)′	1.938(6)
Cr(1)−O(3)	1.955(6)	Cr(2)−O(7)	2.008(7)
Cr(1)−O(4)	2.019(7)	Cr(2)−O(8)	1.973(8)
Cr(1)−O(5)	1.967(8)	Cr(2)−O(9)	2.007(8)
O(1)−Cr(1)−O(2)	81.4(3)	O(1)−Cr(2)−O(7)	89.6(3)
O(1)−Cr(1)−O(3)	93.6(3)	O(1)−Cr(2)−O(8)	93.7(3)
O(1)−Cr(1)−O(4)	90.9(3)	O(1)−Cr(2)−O(9)	169.9(3)
O(1)−Cr(1)−O(5)	91.4(3)	O(2)−Cr(2)−O(3)′	92.7(3)
O(1)−Cr(1)−O(6)	173.6(3)	O(2)−Cr(2)−O(7)	90.8(3)
O(2)−Cr(1)−O(3)	93.1(3)	O(2)−Cr(2)−O(8)	173.7(3)
O(2)−Cr(1)−O(4)	88.5(3)	O(2)−Cr(2)−O(9)	92.3(3)
O(2)−Cr(1)− O(5)	170.3(3)	O(3)′−Cr(2)−O(7)	175.4(3)
O(2)−Cr(1)−O(6)	94.0(3)	O(3)′−Cr(2)−O(8)	91.0(3)
O(3)−Cr(1)−O(4)	175.3(3)	O(3)′−Cr(2)−O(9)	94.0(3)
O(3)−Cr(1)−O(5)	94.0(3)	O(7)−Cr(2)−O(8)	85.7(3)
O(3)−Cr(1)−O(6)	91.0(3)	O(7)−Cr(2)−O(9)	82.8(3)
O(4)−Cr(1)−O(5)	85.0(3)	O(8)−Cr(2)−O(9)	92.5(3)
O(4)−Cr(1)−O(6)	84.5(3)	Cr(1)−O(1)−Cr(2)	97.1(3)
O(5)−Cr(1)−O(6)	92.5(3)	Cr(1)−O(2)−Cr(2)	96.0(3)
O(1)−Cr(2)−O(2)	81.0(3)	Cr(1)−O(3)−Cr(2)′	120.6(3)
O(1)−Cr(2)−O(3)′	93.9(3)		

only three bridges could not be found in the literature; the closest examples are the carbonato-bridged $[Cr_2(OH)_2(CO_3)(TACN)_2]^{2+}$ and $[Cr_2(OH)_2(O_2CCH_3)(C_{26}H_{30}N_6)]^{3+}$.[14] The latter contains four bridges rather than three, as in **1**. The Cr···Cr distances in these complexes, 2.898(2) and 2.818(2) Å, respectively, are slightly shorter than those in **1**. The octanuclear ring in **1** resides on a crystallographic $\bar{4}$ site, and the overall symmetry of the complex is therefore S_4. Each chromium atom is six-coordinated, with a nearly octahedral arrangement of six oxygen donors, three of which belong to bridging acetates and three of which belong to the hydroxo ligands. The 24+ charge of the 8 Cr(III) atoms is balanced by the negative charge of 12 hydroxo and 12 acetate ligands; therefore the overall charge of **1** is zero. The interior void of **1** has a diameter of approximately 2.1 Å, accounting for the van der Waals radii of the μ-OH groups. This value is significantly smaller than the void diameter of 3 Å found in the Cr_8F_8 system.[7] The overall geometry of complex **1** is reminiscent of the structure of the octanuclear vanadium(III) complex $[V_8(OH)_4(OC_2H_5)_8(OAc)_{12}]$, in which four of the bridging OH^- groups are replaced by ethoxide ligands.[2r] This complex is assembled by mixing $VCl_3(THF)_3$ and sodium acetate in a basic ethanolic solution. The two types of V···V distances are 3.0 Å for the $(EtO)_2(OAc)$-bridged system and 3.4 Å for the $(OH)(OAc)_2$-bridged system.

An extensive network of hydrogen bonds exists throughout the lattice of $\mathbf{1}\cdot 34H_2O$ involving all 34 water molecules of crystallization and the bridging hydroxo and acetato oxygen atoms.

Magnetic Studies. The magnetic susceptibility for a 124.2 mg sample of $[Cr_8(OH)_{12}(OAc)_{12}]\cdot 34H_2O$ vs temperature T was measured in an applied magnetic field of $H = 0.1$ T. The data, corrected for the core diamagnetism contribution, $\chi^{core} = -1.07 \times 10^{-3}$ cm^3 K/mol of FU, are shown in Figure 3a, and the inverse of these data are shown in Figure 3b. We have carried out several $\chi(T)$ measurements of smaller samples (∼20 mg) containing a few large grains. The data show the same general shape as that in Figure 3a, but the widths of the peak at ∼20 K and magnitudes are significantly different. This suggests that substantial magnetic anisotropy may be present. At low (1.8 K) temperature, we observe positive curvature in the magnetization of M vs H isotherms for $H \geq 1$ T. In the field range discussed here ($H \leq 0.1$ T), $M \propto H$ in the investigated temperature range.

At high temperatures, one expects the susceptibility of a local moment system to follow the Curie−Weiss law[15]

$$\chi(T) - \chi^{core} = \frac{C}{T - \Theta} \qquad (1)$$

where C is the Curie constant and Θ is the Weiss temperature.

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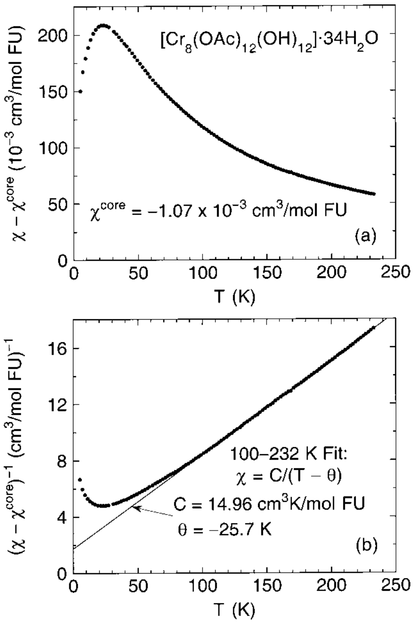

Figure 3. (a) Magnetic susceptibility χ corrected for the diamagnetic core susceptibility χ^{core} vs temperature T for $[\mathrm{Cr_8(OH)_{12}(OAc)_{12}}]\cdot 34\mathrm{H_2O}$. (b) Inverse corrected susceptibility from (a). The straight line in (b) is a fit of the data from 100 to 232 K by the Curie−Weiss law with the parameters indicated.

In terms of the spin $s = {}^3/_2$ per Cr^{3+} ion with spectroscopic splitting factor g, one has

$$C = \frac{Ng^2\mu_B{}^2 s(s+1)}{3k_B} \tag{2}$$

where N is the number of spins s, μ_B is the Bohr magneton, and k_B is Boltzmann's constant. For 1 mol of spins $s = {}^3/_2$ with $g = 2$, one obtains an expected $C = 1.875$ cm^3 K/mol of Cr, and thus for the $\mathrm{Cr_8}$ ring cluster in **1**·34H$_2$O the calculated Curie constant is

$$C^{\mathrm{calc}} = 15\ \mathrm{cm^3\ K/mol\ of\ Cr_8} \tag{3}$$

We assume that the Heisenberg spin Hamiltonian appropriately expresses the spin interactions:

$$H = \sum_{\langle ij\rangle} J_{ij} s_i \cdot s_j \tag{4}$$

where the sum is over distinct exchange bonds, J_{ij} is the exchange interaction between nearest-neighbor spins s_i and s_j, and a positive and a negative J_{ij} correspond to an antiferromagnetic (AF) and a ferromagnetic (FM) interaction, respectively. In terms of this Hamiltonian, the Weiss temperature for spins $s = {}^3/_2$ is given by[15,16]

$$\Theta = -\frac{s(s+1)}{3k_B}\sum_j J_{ij} = -\frac{5}{4k_B}\sum_j J_{ij} \tag{5}$$

At the higher temperatures, the inverse susceptibility data in Figure 3b indeed appear to be linear in T, so we fitted the data from 100 to 232 K by eq 1 and obtained the parameters

$$C = 14.96\ \mathrm{cm^3\ K/mol\ of\ FU} \tag{6a}$$

$$\Theta = -25.73\ \mathrm{K} \tag{6b}$$

as shown by the straight line in Figure 3b. The Curie constant is essentially identical with that predicted in eq 3. Equations 5 and 6b predict

$$\frac{1}{k_B}\sum_j J_{ij} = 20.6\ \mathrm{K} \tag{7}$$

Modeling of the Magnetic Susceptibility. From Figure 3, it appears that **1**·34H$_2$O may have a nonmagnetic singlet $S = 0$ ground state, where S is the spin quantum number of the entire $\mathrm{Cr_8}$ ring cluster. Additional $\chi(T)$ data down to 1.8 K (not shown) corroborate this assumption. In the following modeling, we assume a spin $S = 0$ ground state. The distance between adjacent Cr ions in the ring alternates between the two values 2.95 and 3.4 Å. We therefore expect that there are two distinct J_{ij} values in the cluster, where the magnitude of one of them is significantly greater than the other. One can in principle diagonalize the spin Hamiltonian for the 65 536 spin states of the entire cluster exactly and thereby derive the magnetic properties for comparison with the experimental data. In this paper, we choose alternative and physically more intuitive routes.

A. Coupled $s = {}^3/_2$ Dimers. In view of the expected alternating exchange along the $\mathrm{Cr_8}$ ring discussed above, in this section we will explore the applicability of a model of coupled $s = {}^3/_2$ dimers. The spin Hamiltonian (4) for the isolated dimer $H = J_1 \mathbf{s}_1 \cdot \mathbf{s}_2$ is easily diagonalized, yielding the energy levels

$$E_S = \frac{J_1}{2}S(S+1) \tag{8a}$$

$$S = 0, 1, 2, 3 \tag{8b}$$

where J_1 is the intradimer exchange interaction and we have set the zero of energy to be that for $S = 0$. Apart from the Zeeman degeneracy, the spin S states of the cluster are nondegenerate. The spin susceptibility is then calculated to be[16]

$$\chi^{\mathrm{dimer}} = \frac{Ng^2\mu_B{}^2}{k_B T}\,\frac{e^{-1/t} + 5e^{-3/t} + 14e^{-6/t}}{1 + 3e^{-1/t} + 5e^{-3/t} + 7e^{-6/t}} \tag{9}$$

where $t \equiv k_B T/J_1$. One can verify that, at sufficiently high temperatures, eq 9 yields the Curie−Weiss law (1) with C and Θ, respectively, given by eqs 3 and 5, where $\sum_j J_{ij} = J_1$. We now incorporate the coupling J_2 between each spin in a dimer and the nearest spin in the ring outside its own dimer. In the molecular field approximation, which holds accurately for weak coupling between dimers, the susceptibility in this case is simply[16]

$$\chi(T) = \frac{\chi^{\mathrm{dimer}}(T)}{1 + \chi^{\mathrm{dimer}}(T) J_2/(Ng^2\mu_B{}^2)} \tag{10}$$

We have fitted eqs 9 and 10 with $g = 2$ to the $\chi(T)$ data in Figure 3a, and the result is shown as the solid curve in Figure

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(16) Johnston, D. C. In *Handbook of Magnetic Materials*; Buschow, K. H. J., Ed.; Elsevier: Amsterdam, 1997; Vol. 10, pp 1−237.

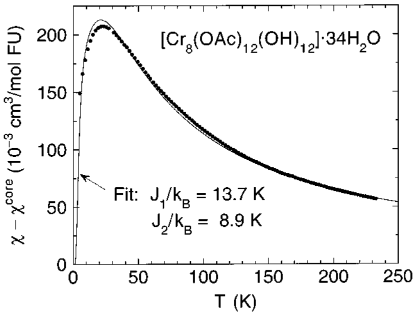

Figure 4. Fit (solid curve) of eqs 9 and 10 for coupled dimers to the magnetic susceptibility χ corrected for the diamagnetic core susceptibility χ^{core} vs temperature T for $[Cr_8(OH)_{12}(OAc)_{12}]\cdot 34H_2O$ from Figure 3a. The parameter J_1 is the AF intradimer exchange constant and J_2 is the AF interdimer interaction constant.

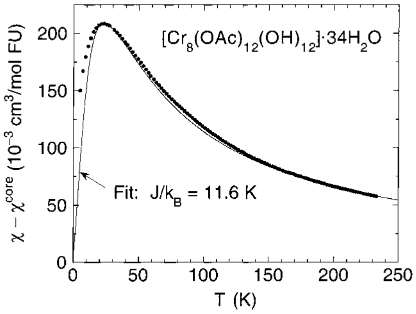

Figure 5. Fit (solid curve) of eqs 12 and 13 for a classical ring of eight spins $^3/_2$ to the magnetic susceptibility χ corrected for the diamagnetic core susceptibility χ^{core} vs temperature T for $[Cr_8(OH)_{12}(OAc)_{12}]\cdot 34H_2O$ from Figure 3a. The parameter J is the AF intradimer exchange constant, assumed to be the same for each pair of Cr spins.

4, with parameters $J_1/k_B = 13.70(14)$ K and $J_2/k_B = 8.9(6)$ K. The sum $\sum_j J_{ij} = J_1 + J_2 = 22.6$ K is close to our estimate in eq 7.

B. Classical Heisenberg Ring. An alternate approximate expression for the magnetic susceptibility can be obtained by considering the classical Heisenberg model that corresponds to the quantum spin Hamiltonian (4). In this approach, the quantum spin operators $\mathbf{S}_i$ are replaced by vectors of length $[s(s+1)]^{1/2}$ ($s = {}^3/_2$ here) that are free to point in any direction of space. To further simplify the treatment, we shall suppose that each nearest-neighbor pair of spins interacts with the same common effective exchange interaction J. One rescales J by $J \rightarrow J_c \equiv s(s+1)J$ so that the resulting classical Hamiltonian, denoted by $\mathcal{H}_c$, is given by

$$\mathcal{H}_c = J_c \sum_{i=1}^{8} \hat{e}_i \cdot \hat{e}_{i+1} \tag{11}$$

where each $\hat{e}_i$ is a unit vector and $\hat{e}_9 = \hat{e}_1$. An exact expression for the zero-field susceptibility of the classical Heisenberg ring has been derived[17] by starting from an expansion given by Joyce[18] for the correlation function $C_j(T) \equiv \langle \hat{e}_1 \cdot \hat{e}_{1+j} \rangle$, and it takes the form of an infinite series involving modified spherical Bessel functions as well as a similar, second infinite series for the partition function. Apart from the fact that numerical evaluation of the two infinite series is both highly tedious and requires some care in implementation, it turns out that a very simple yet highly accurate approximate expression for the susceptibility is available. The approximate zero-field susceptibility per spin is given by (see eqs 2.13a and 3.5 of ref 17)

$$\chi(T) = \frac{g^2 \mu_B{}^2 s(s+1)}{3k_B T} \frac{[1 - u(T)][1 - u^8(T)]}{[1 + u(T)][1 + u^8(T)]} \tag{12}$$

where $u(T)$ denotes the Langevin function

$$u(T) = \coth\left(\frac{J_c}{k_B T}\right) - \frac{k_B T}{J_c} \tag{13}$$

This result is derived in ref 17, with the primary idea being that $C_j(T)$ should display two major properties. First, this quantity should initially incorporate exponential decay with increasing j, and second, it must fulfill a cyclic boundary condition appropriate for a closed ring of N spins, namely $C_j(T) = C_{N-j}(T)$.

The solid curve shown in Figure 5 is the result of using eqs 12 and 13 and requiring (i) that the peak value of the theoretical susceptibility equal that of the experimental data and (ii) that the peak occur for $T = 23$ K. In this manner, we find that $J/k_B = 11.6$ K, in close agreement with the average value $(J_1 + J_2)/2$ determined in the preceding subsection. We emphasize that when we use the exact, cumbersome expression for the susceptibility for the eight-spin classical ring, the resulting curve cannot be distinguished from the solid curve above 23 K. Below that temperature, neither the exact classical formula nor the approximate form (12) is appropriate because a classical Heisenberg model cannot accurately describe $s = {}^3/_2$ quantum spins at sufficiently low temperatures. The exact classical susceptibility approaches a nonzero value for $T \rightarrow 0$ K, approximately 0.84 times that of the peak value, whereas the approximate formula (12) does decrease to zero, albeit linearly with T, rather than with the characteristic exponential decay, in $1/T$, associated with a singlet ground state separated by an energy gap from the excited states.

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Supporting Information Available: Tables of X-ray experimental details and complete atomic positional parameters, thermal parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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