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A Supramolecular Approach to the Crystallization of Polynuclear Aqua Ions: Structure and Magnetism of an 18-Crown-6 Adduct of Bis(μ-hydroxo)octaaquadichromium(III) Mesitylene-2-sulfonate Trihydrate

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The crystallization of polynuclear aqua ions continues to be a challenging problem. One of the more successful methods has been a supramolecular approach which uses aromatic sulfonates as counterions.[1−4] It relies on the formation of layers of the aqua cations and water molecules which are stabilized in their H-bonded network by suitably oriented layers of the sulfonate anions. The hydrophobic ends of the anions serve to separate adjacent layers of the cations and thus aid crystallization. The utility of this method has been demonstrated by the crystallization and X-ray structure elucidation of several sulfur-bridged aqua ions[5] and some oxo- and hydroxo-bridged aqua ions, including some binuclear ions[1−3,6] and a Mo(IV) trimer.[4]

Although studies of the polymerization of Cr^{3+} [1,7] and Rh^{3+} [2,8] have led to the isolation of several oligomers, attempts to crystallize oligomers with higher nuclearity than dimeric have been unsuccessful, even with sulfonate counterions. Described here is an extension of the supramolecular approach which can be widely applied in the crystallization of such ions. It relies on the introduction of noncoordinating macrocycles with donor atoms capable of H-bonding to ligated water, thus modifing the H-bonding network that surrounds the ions in solution. The cocrystallization of the Cr(III) dimer mesitylene-2-sulfonate[1] with 18-crown-6 is reported here together with the profound effect of modifying the H-bonded network on the magnetic exchange properties of the dimer in comparison to the parent system. Although supramolecular inorganic chemistry is of topical interest[9,10] and adducts of transition metal ions exist with H-bonds between the crown ethers and ligated water, e.g. $[Mn(H_2O)_6](ClO_4)_2{\cdot}$18-crown-6,[11] the Cr(III) dimer adduct is the first example of a polynuclear aqua ion incorporating such interactions.

Crystals of $[Cr_2(\mu\text{-}OH)_2(H_2O)_8][(H_3C)_3C_6H_2SO_3]_4{\cdot}C_{12}H_{24}O_6{\cdot}3H_2O$ (**1**) were obtained from aqueous solutions containing 18-crown-6 and the dimer mesitylene-2-sulfonate.[12] IR bands at 959 and 1355 cm^{-1} confirmed the presence of 18-crown-6 in the product; other bands were masked by those of the sulfonate. X-ray diffraction analysis[13] showed that dimer was present in the product, as in the parent mesitylate,[1] but had now been immobilized between sheets of 18-crown-6 molecules with the dimer cations being further separated by the sulfonates (Figures 1 and 2).

Figure 2 shows the H-bonded network of **1** including the interactions of 18-crown-6 molecules with adjacent dimer units. Additional H-bonding to water of crystallization was present in the parent mesitylate.[1] While the Cr−O distances within the dimer cation are similar to those in the parent mesitylate, there are distinct differences. In particular, the Cr_2O_2 bridging unit in the 18-crown-6 adduct is asymmetric. The Cr−O distance and Cr−O−Cr angle for O(5) {1.925(2) Å and 101.0(1)°} are different from those for O(6) {1.952(2) Å and 99.2(1)°}. The Cr···Cr distance in the 18-crown-6 adduct is slightly shorter (2.970 Å vs 3.006 Å). A small *trans* influence is evident from the $Cr-O(OH_2)$ distances *trans* to the bridging hydroxides; viz., the bond *trans* to the shorter Cr−(μ-OH) bond is slightly longer than that *trans* to other Cr−(μ-OH) bond. The interactions between the 18-crown-6 molecules and the dimer are of interest from the point of view of the general application of such molecules in the crystallization of polynuclear aqua ions. Three moderately strong H-bonds (O−H···O) are observed between each crown ether and the two ends of the dimer. These H-bonds, found between O1 and O54/O56, O3 and O52, O7 and O55, and O9 and O51/O53 (Figure 2), are in the range 2.7−2.82 Å (O···O distance) and average 2.75 Å. They are slightly weaker in strength than H-bonding interactions between the dimer and water of crystallization (average 2.67 Å) and between the dimer and sulfonate ions (average 2.66 Å). Notably, the interactions between coordinated water and 18-crown-6 are stronger in **1** than in $[Mn(H_2O)_6](ClO_4)_2{\cdot}$18-crown-6, where the corresponding O−H···O(18-crown-6) distances were 2.8−3.1 Å.[11]

The parent complex, $[Cr_2(\mu\text{-}OH)_2(H_2O)_8][(H_3C)_3C_6H_2SO_3]_4{\cdot}4H_2O$, is notable for the ferromagnetic nature of exchange

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(12) A 10 mL aqueous solution of chromium(III) dimer mesitylate[1] (0.45 g, 0.39 mmol) was added to a 5 mL aqueous solution of 18-crown-6 (0.20 g, 0.76 mmol). The final solution was mixed thoroughly and allowed to slowly evaporate at ambient temperature over 4 days. During this time, purple prismatic crystals of **1** suitable for crystallography[13] formed and were filtered off. Yield: 0.23 g, 42%. Microprobe analysis: Cr and S present. Anal. Found: C, 41.0; H, 5.8; Cr, 7.3. Calc for $C_{48}H_{92}Cr_2O_{31}S_4$: C, 41.2; H, 6.6; Cr, 7.4.

(13) Crystal data for **1**: $C_{48}H_{92}Cr_2O_{31}S_4$, $M_r = 1397.5$, crystal size 0.40 × 0.44 × 0.16 mm, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.656(2)$ Å, $b = 11.510(2)$ Å, $c = 32.042(5)$ Å, $\alpha = 95.16(1)°$, $\beta = 91.90(2)°$, $\gamma = 109.25(1)°$, $V = 3340(1)$ Å^3, $Z = 2$, $F(000) = 1540$, $D_c = 1.443$ g cm^{-3}, μ(Mo Kα) = 5.39 cm^{-1}. A total of 12 614 reflections (11 854 unique, $R_{int} = 0.021$) were collected at 296 K with $2\theta_{max} = 50.1°$ on a Rigaku AFC6S diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.710\ 69$ Å) radiation and operating in an ω-scan mode at a scan rate of 8.0° min^{-1}. Collected octants: h, 0 to +14; k, −14 to +14; l, −38 to +38. Intensity data were corrected for Lorentz−polarization and absorption effects. The structure was solved by direct methods (SAPI90) and refined by a full-matrix least-squares procedure based on F. Final refinement was based on 7106 reflections ($I > 3\sigma(I)$) and 767 parameters. Non-H atoms were refined anisotropically. Water and OH hydrogens were located from difference maps, whereas all others were calculated at chemically sensible positions. At convergence $R = 0.044$ and $R_w = 0.037$ and the maximum peak in the final difference map was 0.38 e/Å^3.

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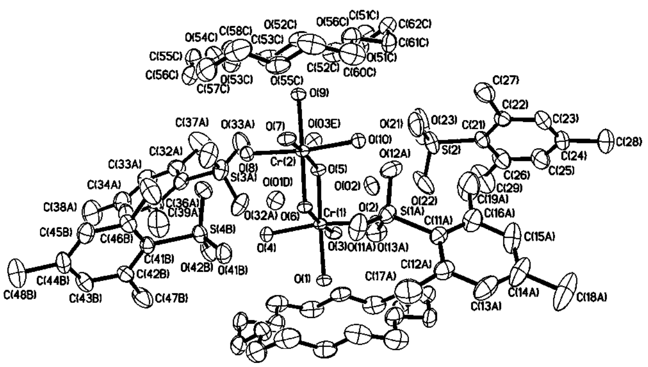

Figure 1. ORTEP diagram and atomic labeling scheme of **1** (with 20% thermal ellipsoids). Molecules labeled A−E have been transformed through the following symmetry operators: (A) 1 + *x*, *y*, *z*; (B) 1 + *x*, 1 + *y*, *z*; (C) −*x*, 2 − *y*, − *z*; (D) *x*, 1 + *y*, *z*; (E) 1 − *x*, 1 − *y*, 1 − *z*.

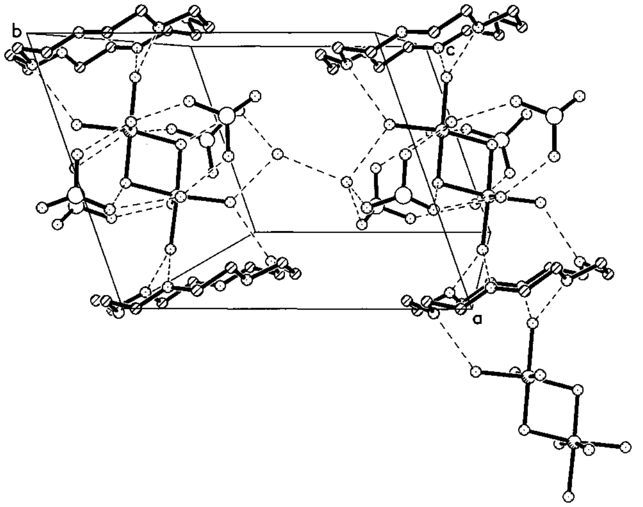

Figure 2. View of **1** showing H-bonding interactions between the dimer cation and the 18-crown-6 molecules and extending through the waters of crystallization to adjacent dimers.

coupling observed in crystalline samples, the positive *J* value being ascribed to intradimer coupling with weak interdimer coupling also proposed.[14] We recently studied the magnetism of the Rh−Cr analogue[15] and now believe that ferromagnetic coupling in this and the Cr−Cr complex is actually intermolecular in origin and transmitted between dimers *via* H-bonded water pathways. This is given further credence in the present study, where intramolecular antiferromagnetic coupling of the Cr(III) centers, within each dimer, is clearly evident in the χ vs *T* plot (Figure 3). An excellent fit of the data to the $S = {}^3/_2$ Heisenberg dimer susceptibility equation

$$\chi\ (\text{per Cr}) = \frac{N\beta^2 g^2}{kT}\,\frac{14 + 5\exp(-6J/kT) + \exp(-10J/kT)}{7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT)}$$

where the parameters have their usual meaning, gave $g = 1.99$ and $J = -5.7$ cm^{-1}. The value of *J* (the isotropic exchange parameter equals half the separation between the $S = 0$ and $S = 1$ levels) is typical for hydroxo-bridged Cr(III) systems.[16] Calculations of *J* based on the Glerup, Hodgson, and Pedersen model[16] gave $J = -2$ cm^{-1} for a Cr−O distance of 1.925 Å, bridging angle (θ) of 101°, and tilt angle (ϕ) of 53° and $J = -1$ cm^{-1} for a Cr−O distance of 1.953 Å, $\theta = 99.2(1)°$, and $\phi = 62°$. These values are in fair agreement with the measured values (further comparisons of calculated and measured *J* values for hydroxo-bridged Cr(III) systems are given in ref 16). A comparison of the magnetic behaviors of the two forms of dimer indicates that individual dimer units in the 18-crown-6 adduct are magnetically isolated and that interdimer H-bonded water pathways, responsible for ferromagnetic coupling in the parent complex, have been "closed off". Although in the 18-crown-6 adduct a H-bonded pathway exists for potential intermolecular interactions along the *b* axis (parallel to the crown ethers; Figure 2), pathways involving the ends of each dimer and water of crystallization, present in the parent complex, have been replaced by interactions with the 18-crown-6 molecules. Fine details of this novel effect are being elucidated, but it appears that H-bonded pathways emerging from the ends of the dimer, rather than from the "bridging groups", are responsible for the ferromagnetic behavior of the parent complex and, by inference, the isostructural complex, $[\mathrm{CrRh}(\mu\text{-OH})_2(\mathrm{H_2O})_8][(\mathrm{H_3C})_3\mathrm{C_6H_2SO_3}]_4\cdot 4\mathrm{H_2O}$.[3]

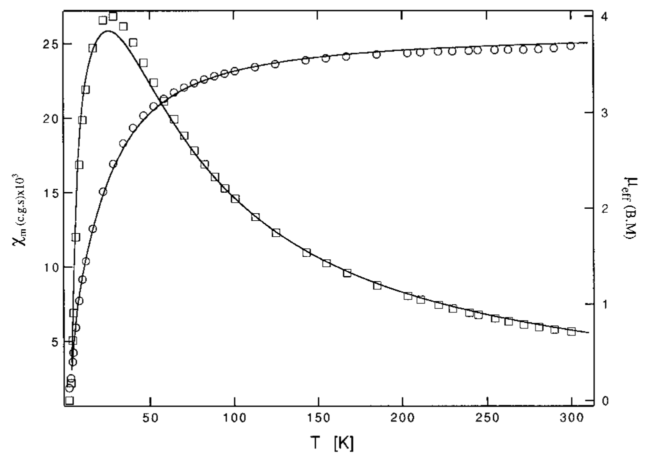

Figure 3. Experimental and fitted (solid line; parameters in text) temperature dependence of the molar magnetic susceptibility (□) and magnetic moment (○) of **1**.

In recent years, there have been a number of reports of antiferromagnetic exchange interactions in Cr(III) complexes which are mediated through H-bonding interactions.[17] The contrasting behaviors of the Cr(III) dimer mesitylate[14] and its 18-crown-6 adduct provide strong evidence for the proposal that ferromagnetic interactions can also be mediated through H-bonded networks. In view of this finding, the weak ferromagnetism in $\mathrm{Na_4[Cr_2(\mu\text{-OH})_2(malonato)_4]\cdot 5H_2O}$[18] could also arise through H-bonding interactions involving water of crystallization.

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Supporting Information Available: A description of the structure determination and tables of crystal data, atomic coordinates, isotropic and anisotropic displacement parameters, interatomic distances and angles, torsion angles, and nonbonded contacts (35 pages). Ordering information is given on any current masthead page.

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