The Tetranuclear Cluster $\text{Fe}^{III}[\text{Fe}^{III}(\text{salicylhydroximato})(\text{MeOH})(\text{acetate})]_3$ is an Analogue of $\text{M}^{3+} (9$-crown-3)

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The first example of transition metal co-ordination to ethereal like oxygens of a 9-metallocrown-3 ether is seen in $\text{Fe}^{III}[\text{Fe}^{III}(\text{salicylhydroximato})(\text{MeOH})(\text{acetate})]_3$ and leads to an unusual tetranuclear cluster which exhibits both inter- and intra-cluster antiferromagnetic interactions and an $S = 5$ ground state.

Organic molecules designed to bind metal cations selectively have attracted considerable attention since the first report of crown ethers. Metal ion specificity is achieved by varying cavity size, the number of ethereal oxygen donors and the basicity of these oxygen atoms. Variants of crown molecules containing other heteroatoms have been prepared. The metal complexes of these ligands exhibit interesting properties (e.g., the stabilization of low spin Co$^{II}$) and altered preferences for transition metal ions. Although analogues that substitute sulphur or nitrogen for the ring oxygen atoms are well known, comparable systems that substitute heteroatoms for the ring carbons have not been shown to bind metal ions via the ‘ethereal like’ oxygens. In this communication we present structural evidence for an inorganic analogue of 9-crown-3 (9-C-3) in which the carbon atoms have been replaced by $\text{Fe}^{3+}$ and nitrogen atoms. A single crystal X-ray analysis demonstrates that unlike 9-C-3, this complex can form a complex with a transition metal ion via the ‘ethereal like’ oxygen atoms.

The cluster $\text{Fe}^{III}[\text{Fe}^{III}(\text{salicylhydroximato})(\text{MeOH})(\text{acetate})]_3(\text{MeOH})$ (1) can be prepared by the reaction of equimolar ratios of $\text{FeSO}_4$, salicylhydroxamic acid and 3 equivalents of $\text{NaOAc}$ in methanol at room temperature with no precautions to exclude dioxygen. A red, crystalline solid that was suitable for X-ray structure analysis was recovered after slow evaporation of this methanol solution. The structure of the entire molecule is illustrated in Figure 1 and the metallocrown core is shown in Figure 2.

Crystal data for (1): $\text{Fe}^{III}[\text{Fe}^{III}(\text{salicylhydroximato})(\text{MeOH})(\text{acetate})]_3(\text{MeOH})$, $\text{Fe}_2\text{O}_2\text{N}_2\text{C}_3\text{H}_{35}$, $M = 1039$, cubic, $a = b = c = 21.861(5)$ Å, $a = b = \gamma = 90^\circ$, $U = 10447(5)$; $Z = 8$; $D_{\text{calc}} = 1.34 \text{ g cm}^{-3}$; $D_{\text{calc}} = 1.326 \text{ g cm}^{-3}$. Crystal dimensions, $0.264 \times 0.251 \times 0.338$ mm, Mo-$K_a$ ($0.7107$ Å); $T = 298$ K, Syntex $P_2_1$ four-circle diffractometer. Data were reduced using the SHELX program package and the structure was solved using SHELXS86; complex atomic scattering factors were used in refinement. Hydrogen atoms were included at calculated positions with fixed $U$ values (isotropic thermal parameters) of $0.07 \text{ Å}^2$; $\mu = 11.29 \text{ cm}^{-1}$; $0 < 20 < 20^\circ$; unique reflections = 1512; reflections with $I > 3\sigma(I) = 703$; $R = 0.064$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
linked through three high spin iron(III) ions. The SHI acts as a tetracoordinate, tetratalentate ligand with carboxyl and hydroximate oxygen atoms [O(2) and O(3), respectively] bound to one iron, and phenolate oxygen [O(1)] and hydroximate nitrogen [N(1)] atoms bound to an adjacent iron. This organization results in a [Fe-N-O]- ring system that is analogous to a 9-C-3 configuration with the carbon atoms replaced by N and FeIII.

A fourth high spin iron(III) [Fe(1)] is located on a crystallographic fourfold rotation axis. The octahedron of this iron is composed of axial co-ordination of the three ethereal like oxygens of the metalloccrown ring and three acetate oxygens that bridge the capping iron and the three ring iron atoms. The ring iron atoms are also six co-ordinate with the remaining co-ordination site being filled by methanol. The ring iron atoms are separated by 4.848 Å and the ring to capping iron distance is 3.416 Å. Other important distances and angles are provided in the caption to Figure 1.

The structure of the nine-membered ring core of (1) is similar to that recently described8 for the complex [V(VO)(salicylhydroximate)(MeOH)]2 (2). The vanadium separation (4.66 Å) is similar to that seen in the iron complex. While the cavity sizes of (1) and (2) are the same, the vanadium complex does not efficiently bind a transition ion in the capping position. This probably reflects the low affinity of the ethereal like oxygens for transition metal ions in the absence of acetate groups which provide additional stabilization of the capping iron in the tetramer. The vanadium cluster cannot form the bridging acetate mode since the terminal oxo group blocks this metal co-ordination site. The manganese complex MnIII[MnIII(salicylhydroximate)(acetato)2(DMF)]3-2DMF (3) (DMF = dimethylformamide) was the first example of transition metal binding to a metalloccrown ether core;10 however, this mixed valence cluster adopted the 12-crown-4 (12-C-4) structure. In contrast, (1) represents the initial entry into transition metal complexation using the sterically more demanding 9-C-3 configuration.

Magnetization measurements on solid samples were made at 4.2 K in fields up to 15 kOe. The data strongly suggest the presence of an S = 5 ground state. Variable temperature magnetic susceptibility data were collected at 1 kOe in a region where the magnetization varied linearly with the applied field. The data indicate both inter- and intra-cluster antiferromagnetism and were analysed using Heisenberg exchange theory. The best fit values are g = 2 (fixed), J1 = −4.92 cm−1 (capping Fe–ring Fe), J2 = −0.47 cm−1 (ring Fe–ring Fe) and J′ = −0.16 cm−1.

The structural integrity of the tetracationic iron cluster is not disturbed by dissolving the material in acetonitrile or DMF. The 1H n.m.r. spectrum of (1) in D3CCN shows resonances at +65.9, +47.0, +41.1, −26, −36, −56.6, and −62.6 p.p.m. The acetate resonance is assigned to the peak at +41.1 p.p.m. The applied field. The data indicate both inter- and intra-cluster antiferromagnetism and were analysed using Heisenberg exchange theory. The best fit values are g = 2 (fixed), J1 = −4.92 cm−1 (capping Fe–ring Fe), J2 = −0.47 cm−1 (ring Fe–ring Fe) and J′ = −0.16 cm−1.

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perpendicular to the crown core. The undistorted octahedral ions form the 9-C-3 structure. Therefore, it should be possible to form stable, aqueous soluble metalloccrown ethers through synthesis of the kinetically inert Co\textsuperscript{III} or Cr\textsuperscript{III} analogues. We expect that these exchange inert clusters will form the 9-C-3 structure since the metals should be octahedral. Thus, (1) demonstrates that future aqueous soluble metallocrowns should be capable of co-ordinating metal ions through ethereal oxygen atoms even though the organic parent is an ineffective transition ion sequestering agent.

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