The Tetranuclear Cluster $Fe^{III}[Fe^{III}(salicylhydroximato)(MeOH)(acetate)]_3$ is an Analogue of 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 Fe^{III} $[Fe^{III}(salicylhydroximato)(MeOH)(acetate)]_3$ 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.[1] Metal ion specificity is achieved by varying cavity size, the number of ethereal oxygen donors and the basicity of these oxygen atoms.[2,3] Variants of crown molecules containing other heteroatoms have been prepared.[4—6] The metal complexes of these ligands exhibit interesting properties (*e.g.*, the stabilization of low spin Co^{II}[7]) 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we present structural evidence for an inorganic analogue of 9-crown-3 (9-C-3) in which the carbon atoms have been replaced by Fe^{3+} and nitrogen atoms.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 $Fe^{III}[Fe^{III}(salicylhydroximato)(MeOH)(acetate)]_3 \cdot 3MeOH$ (**1**) can be prepared by the reaction of equimolar ratios of $FeSO_4$, salicylhydroxamic acid and 3 equivalents of 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. The core is constructed with three salicylhydroximato (SHI) ligands

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† *Crystal data* for (**1**): $Fe^{III}[Fe^{III}(salicylhydroximato)(MeOH)(acetate)]_3 \cdot 3MeOH$, $Fe_4O_{21}N_3C_{33}H_{45}$, $M = 1039$; cubic, $Pa\bar{3}$, $a = b = c = 21.861(5)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 10447(5)$; $Z = 8$; $D_{obs} = 1.34$ g cm^{-3}; $D_{calc} = 1.326$ g cm^{-3}. Crystal dimensions, $0.264 \times 0.251 \times 0.338$ mm, Mo-K_α (0.7107 Å); $T = 298$ K, Syntex $P2_1$ four-circle diffractometer. Data were reduced using the SHELX program package and the structure was solved using SHELXS86; complex atomic scattering factors[8] were used in refinement. Hydrogen atoms were included at calculated positions with fixed U values (isotropic thermal parameters) of 0.07 $Å^2$; $\mu = 11.29$ cm^{-1}; $0 < 2\theta < 50°$; 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.

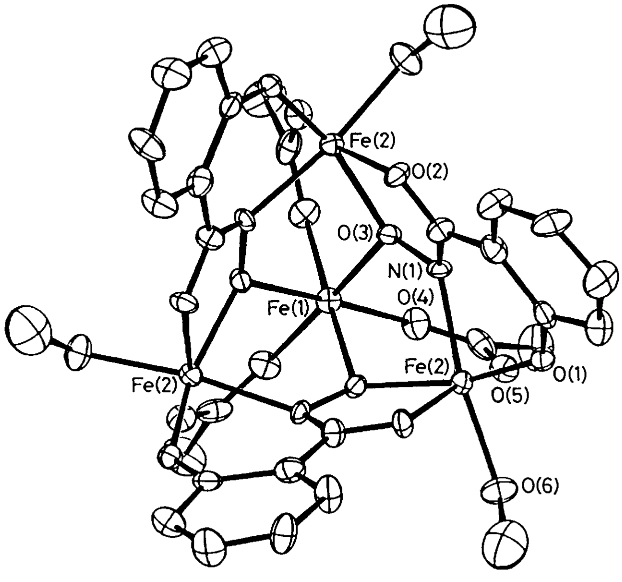

Figure 1. An ORTEP diagram of Fe^{III}[Fe^{III}(SHI)(MeOH)(acetate)]$_3$ with numbering scheme. Important bond lengths (Å) and angles (°). Fe(1)–Fe(2) 3.416(4), Fe(2)–Fe(2′) 4.848(4), Fe(1)–O(3) 2.00(1), Fe(1)–O(4) 2.01(1), Fe(2)–O(3) 2.06(1), Fe(2)–O(1) 1.91(1), Fe(2)–O(2) 2.00(1), Fe(2)–O(5) 1.99(1), Fe(2)–O(6) 2.08(1), Fe(2)–N 2.08(1); O(3)–Fe(1)–O(3′) 88.2(5), O(3)–Fe(1)–O(4) 93.4(5), O(4)–Fe(1)–O(4′) 87.6(5), O(1)–Fe(2)–O(2) 92.6(5), O(1)–Fe(2)–O(3) 161.5(5), O(1)–Fe(2)–O(5) 102.6(6), O(1)–Fe(2)–O(6) 93.2(6), O(1)–Fe(2)–N 83.9(5), O(2)–Fe(2)–O(3) 77.2(5), O(2)–Fe(2)–O(5) 160.7(5), O(2)–Fe(2)–O(6) 86.9(5), O(2)–Fe(2)–N 102.2(6), O(3)–Fe(2)–O(5) 90.9(5), O(3)–Fe(2)–O(6) 101.5(5), O(3)–Fe(2)–N 83.3(5), O(5)–Fe(2)–O(6) 80.5(6), O(5)–Fe(2)–N 91.3(6), O(6)–Fe(2)–N 170.5(6), Fe(1)–O(3)–Fe(2) 114.7, Fe(1)–O(3)–N 118.3(8), Fe(2)–O(3)–N 114.1(6), Fe(2)–N–O(3) 119.6(8):

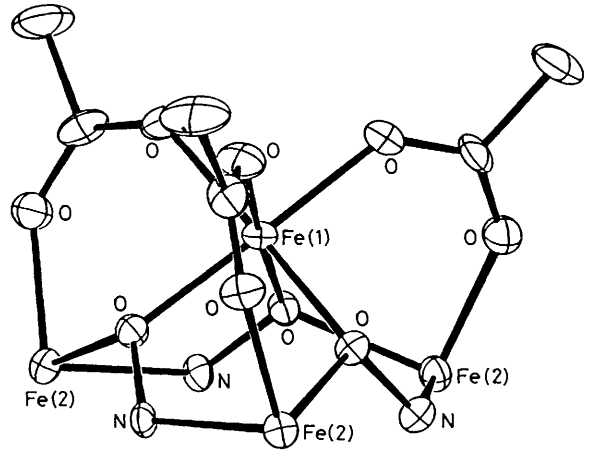

Figure 2. Core of the molecule illustrating the relationship of the [Fe^{3+}(SHI)(MeOH)(acetate)]$_3$ unit to 9-C-3. The capping Fe^{3+} is 1.18 Å above the plane of the three oxygen atoms and 1.89 Å above the plane of the three iron atoms.

linked through three high spin iron(III) ions. The SHI acts as a trianionic, tetradentate ligand with carbonyl 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 an [Fe–N–O–]$_3$ ring system that is analogous to a 9-C-3 with the carbon atoms replaced by N and Fe^{III}. A fourth high spin iron(III) [Fe(1)] is located on a crystallographic three-fold axis. The octahedron of this iron is composed of facial co-ordination of the three ethereal like oxygens of the metallocrown ring and three acetate oxygens that bridge the capping iron and the three ring irons. The ring irons 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 described[9] for the complex [V(V)O-(salicylhydroximato)(MeOH)]$_3$ (**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 Mn^{II}[Mn^{III}-(salicylhydroximato)(acetato)$_{0.5}$(DMF)$_{1.5}$]$_4$·2DMF (**3**) (DMF = dimethylformamide) was the first example of transition metal binding to a metallocrown 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), $J_1 = -4.92$ cm^{-1} (capping Fe–ring Fe), $J_2 = -0.47$ cm^{-1} (ring Fe–ring Fe) and $zJ' = -0.16$ cm^{-1}.

The structural integrity of the tetranuclear iron cluster is not disturbed by dissolving the material in acetonitrile or DMF. The ^{1}H n.m.r. spectrum of (**1**) in D$_3$CCN 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. using the [^{2}H$_3$]acetate substituted cluster. The cluster is e.p.r. silent in DMF at 100 K, also suggesting that Fe^{III} does not dissociate from either the ring or capping positions. A quasi-reversible one electron wave is centred at −330 mV *vs.* standard calomel electrode (SCE) in DMF. Rotating platinum electrode voltammetry indicates that this is a reductive process and is tentatively assigned to the conversion of the capping metal to Fe^{II}.

Complexes (**1**), (**2**), and (**3**) are stable in DMF, dichloromethane or acetonitrile, making practical applications with these compounds promising in poorly donating organic solvents. In contrast, ^{1}H n.m.r. and e.p.r. show that (**1**), (**2**), and (**3**) rapidly dissociate in methanol or water. Although both 9-C-3 and 12-C-4 analogues are now known for these clusters, in every example the ring metals of the metallocrowns are trivalent ions [Fe^{III} in (**1**), V(V)O^{3+} in (**2**), and Mn^{III} in (**3**)]. The conversion of the manganese cluster to the 12-C-4 form was a result of the destabilization of the 9-C-3 structure by Jahn–Teller elongation about the z axis. By adopting the twelve-membered ring in (**3**), this distortion can be oriented 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 metallocrown ethers through synthesis of the kinetically inert Co^{III} or Cr^{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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