A Novel Heterotetranuclear $[Cr_2^{III}(\mu_3\text{-}O)_2Fe_2^{III}]^{8+}$ Core and Ground-state Variability due to Molecular Spin Frustration

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The reaction of LCr^{III} units with Fe^{II}(salox) units, (L = 1,4,7-trimethyl-1,4,7-triazacyclononane and H_2salox = salicylaldehyde oxime), produces *in situ* in methanol and in the presence of air, a small amount of triethylamine, $NaClO_4$ and the dark-brown complex $[L_2Cr_2(OMe)_2O_2(salox)_2Fe_2](ClO_4)_2\cdot3H_2O$, which has been characterized by X-ray crystallography and magnetic susceptibility measurements and found to have a non-diamagnetic ($S_T \neq 0$) ground state due to spin frustration.

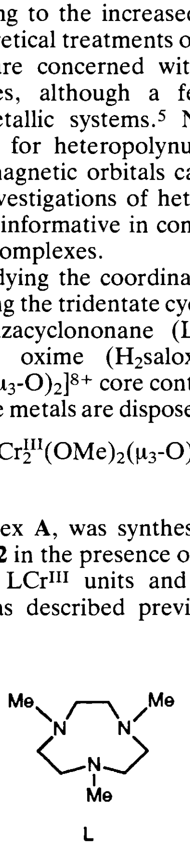
Relatively few studies dealing with magnetic tetra- and tri-nuclear systems have been reported in comparison with the number of studies dealing with dinuclear systems, primarily due to a lack of fully structurally characterized compounds and also owing to the increased complexity involved in carrying out theoretical treatments of large spin systems. Most of these studies are concerned with homotri-[1] and tetra-nuclear[2–4] complexes, although a few of them are involved with heterometallic systems.[5] New exchange pathways can be expected for heteropolynuclear complexes, where unusual sets of magnetic orbitals can be brought in close proximity; hence investigations of heteropolynuclear complexes[6] might be more informative in comparison with those of homopolynuclear complexes.

In studying the coordination chemistry of ternary systems containing the tridentate cyclic amines such as 1,4,7-trimethyl-1,4,7-triazacyclononane (L)[7] and an oxime, *viz.* salicylaldehyde oxime (H_2salox), we have isolated a novel $[Cr_2Fe_2(\mu_3\text{-}O)_2]^{8+}$ core containing tetranuclear complex, **A**, in which the metals are disposed in a butterfly-type arrangement.

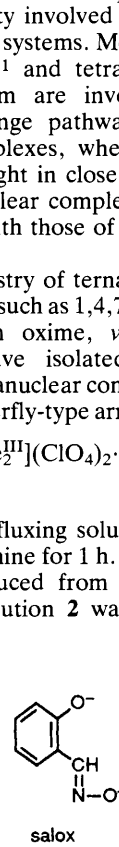
$$[L_2Cr_2^{III}(OMe)_2(\mu_3\text{-}O)_2(salox)_2Fe_2^{III}](ClO_4)_2\cdot3H_2O$$

A

Complex **A**, was synthesized by refluxing solution **1** with solution **2** in the presence of triethylamine for 1 h. [Solution **1** contains LCr^{III} units and was produced from $LCrBr_3$ (1 equiv.) as described previously.[8] Solution **2** was made by addition of solid $Fe(MeCO_2)_2$ (1 equiv.) to a methanolic solution of H_2salox (1 equiv.) under argon.] The tetranuclear complex was precipitated as the perchlorate salt† in the presence of air.



L



salox

The structure of the cation in the complex is shown in Fig. 1.‡ The geometrical centre of the cation lies on a twofold rotation axis perpendicular to the central Fe_2O_2 rhomboid. The asymmetric unit thus consists of half of the cation and well-separated ClO_4^- anions. The cation possesses a $Cr_2Fe_2(\mu_3$-

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† Yield 40–42%. Anal.calc. for $[C_{34}H_{64}N_8O_{11}Cr_2Fe_2](ClO_4)_2$: C, 34.74; H, 5.49; N, 9.53; Cr, 8.85; Fe, 9.50; ClO_4, 16.92%. Found: C, 34.1; H, 5.4; N, 9.5; Cr, 8.7; Fe, 9.2; ClO_4, 17.2%.

‡ *Crystal data* for $[C_{34}H_{58}N_8O_8Cr_2Fe_2](ClO_4)_2\cdot3H_2O$, monoclinic, space group *C*2/*c*, a = 27.249(8), b = 11.743(4), c = 18.018(6) Å, β = 121.04(2)°, V = 4940.1 Å^3, Z = 4, D_c = 1.580 g cm^{-3}, $F(000)$ = 2440, λ(Mo-Kα) = 0.71073 Å, μ = 1.17 mm^{-1}, T = 298(1) K. Brown crystal, size 0.08 × 0.15 × 0.46 mm, Siemens R3m/V diffractometer, graphite monochromator, lattice parameters refined from 28 reflections $11 \leqslant 2\theta \leqslant 25°$; ω–2θ scan, 4699 intensities collected $3 \leqslant 2\theta \leqslant 50°$, $0 \leqslant h \leqslant 32$, $0 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 21$, 3 standards every 400 showed decrease of 4%, intensities adjusted accordingly, Lp-correction, empirical absorption correction, min/max transmission 0.784/0.867, after merging (R_{int} = 0.042) 4362 unique intensities, only 1028 considered observed with $F > 4\sigma(F)$ due to very poor scattering power; structure solved by direct and Fourier methods, full-matrix least-squares refinement based on F and 150 parameters, Fe, Cr, and Cl refined anisotropically, perchlorate anion heavily disordered, H-atoms fixed at idealized positions with common isotropic displacement parameters, two significant electron densities assigned to enclosed water molecules, refinement converged at R = 0.089, max (Δ/σ) = 0.04, min/max height in final ΔF map −0.44/0.63 e Å^{-3}; scattering factors, structure solution, and refinement: SHELXTL-PLUS.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue no. 1.

$O)_2$ core.§ The metal geometry of the cluster may be described as a 'butterfly', based on two edge-sharing $CrFe_2(\mu_3\text{-}O)$ triangular units with the oxygen atoms slightly below (0.278 Å) the metal Fe_2Cr triangles. The Cr(1)···Fe(1) and Fe(1)···Fe(1a) distances are noticably short, 2.902 and 2.736 Å, respectively. The distance between Cr(1) and Cr(1a) is 5.661 Å.

The coordination geometry of the 'wing-tip' chromium ions [Cr(1) and Cr(1a)] is distorted octahedral with three nitrogen atoms, N(1), N(2) and N(3), from the facially coordinated tridentate macrocyclic amine (L) and three oxygen atoms [one from the salox O(2), one from the μ_2-bridging methoxy O(1) and one from the μ_3-bridging oxide O(3)], resulting in *fac* CrN_3O_3 cores. The 'body' iron ions [Fe(1) and Fe(1a)] are bridged by two oxides [O(3) and O(3a)]. A methoxy oxygen O(1) bridges Cr(1) and Fe(1) in an asymmetrical manner, the bond length Cr(1)–O(1) being shorter (1.974 Å) than that of Fe(1)–O(1) (2.201 Å). Each Fe^{III} ion is thus coordinated to three oxygens [O(3), O(3a) and the phenolate O(4)], an imine nitrogen N(4) from a salox ligand in the basal plane and a methoxy oxygen O(1) in the apical position, thus yielding five-coordination at Fe(1) and Fe(1a). The resulting square pyramidal geometry, $FeNO_4$, is rare for the trivalent iron with O,N based ligation; octahedral coordination is by far the most common for Fe^{III}.[9]

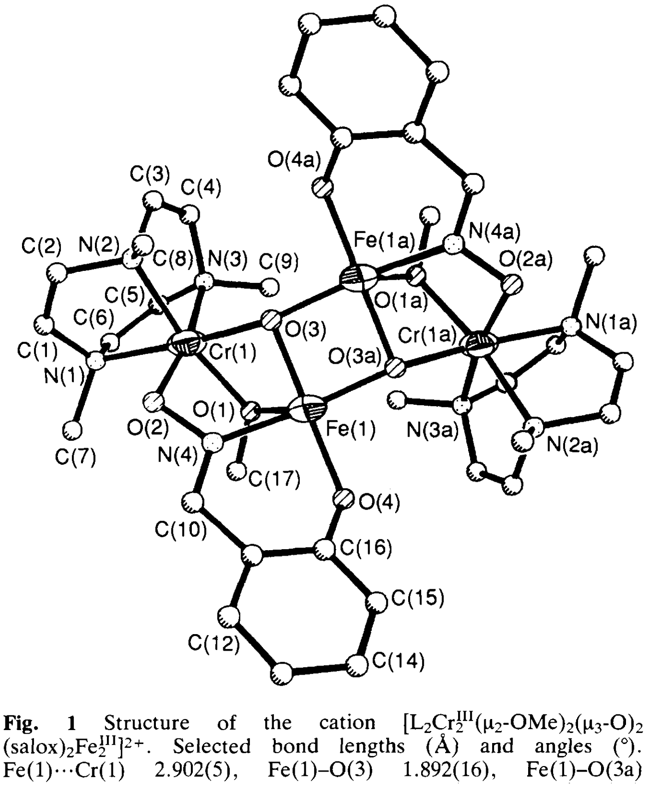


Fig. 1 Structure of the cation $[L_2Cr_2^{III}(\mu_2\text{-}OMe)_2(\mu_3\text{-}O)_2(salox)_2Fe_2^{III}]^{2+}$. Selected bond lengths (Å) and angles (°). Fe(1)···Cr(1) 2.902(5), Fe(1)–O(3) 1.892(16), Fe(1)–O(3a) 1.872(17), Fe(1)–O(4) 1.884(17), Fe(1)–O(1) 2.201(16), Fe(1)–N(4) 1.979(21), Fe(1)···Fe(1a) 2.736(10), Cr(1)–O(3) 1.938(16), Cr(1)–O(1) 1.974(15), Cr(1)–O(2) 1.954(20); O(1)–Fe(1)–O(3) 75.4(7), O(1)–Fe(1)–O(3a) 112.0(7), O(1)–Fe(1)–O(4) 106.4(7), O(3)–Fe(1)–N(4) 91.3(8), O(3)–Fe(1)–O(3a) 84.8(6), O(4)–Fe(1)–N(4) 88.5(8), O(4)–Fe(1)–O(3a) 95.0(7), N(4)–Fe(1)–O(3a) 165.1(8), O(1)–Cr(1)–O(3) 80.0(7), O(2)–Cr(1)–O(3) 90.6(7), O(3)–Cr(1)–N(1) 175.3(9), O(3)–Cr(1)–N(2) 91.3(8), O(3)–Cr(1)–N(3) 97.6(9), Fe(1)–O(1)–Cr(1) 87.9(7), Fe(1)–O(3)–Cr(1) 98.5(9), Fe(1)–O(3)–Fe(1a) 93.2(5), Cr(1)–O(3)–Fe(1a) 157.8(10).

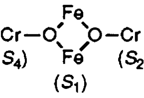
The dispositions of the μ_3-oxides are almost symmetrical and are consistent with all metals being in the trivalent oxidation level; the differences are practically insignificant within the 3σ criterion. The dihedral angle between the planes Fe(1)Fe(1a)Cr(1)O(3) and Fe(1)Fe(1a)Cr(1a)O(3a) is 135.3°. The Fe–O and Fe–N distances are consistent with a d^5 high-spin electron configuration of the Fe^{III} centres.

Magnetic measurements were made on a solid sample of the complex over the temperature range 4.1–287.5 K and are shown in Fig. 2. The molar paramagnetic susceptibility increases with decreasing temperature and reaches a maximum at 6.5 K, below which the susceptibility starts to decrease. The effective magnetic moment μ_{eff} per $Cr_2^{III}Fe_2^{III}$ cluster decreases with decreasing temperature from 8.15 μ_B at 287.5 K to 1.40 μ_B at 4.1 K. The data clearly indicate that this complex does not possess a well separated $S_T = 0$ ground state. In a qualitative sense the $S_T = 0$ state can be thought of in terms of an antiferromagnetic coupling of the two Cr^{III} ($S_{Cr} = 3/2$) and two high-spin Fe^{III} ($S_{Fe} = 5/2$) ions to produce a ground state of zero net spin.

The theoretical values of χ_M result from the Kambe vector-coupling scheme[10] combined with the van Vleck susceptibility equation,[11] which results from the spin Hamiltonian shown in eqn. (1), give an isotropic magnetic exchange

$$\hat{H} = -2J_{Cr\text{-}Fe}(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_4\cdot\hat{S}_1) - 2J_{Fe\text{-}Fe}\hat{S}_1\cdot\hat{S}_3 \quad (1)$$

with $S_1 = S_3 = 5/2$ and $S_2 = S_4 = 3/2$. In this notation $J_{Cr\text{-}Fe}$ represents the exchange interaction between adjacent chromium and iron ions and $J_{Fe\text{-}Fe}$ describes the interaction between the iron nuclei within the tetranuclear complex, shown in **1**.



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To fit particularly the low-temperature data, it was necessary to consider a constant θ. The expression used is shown in eqn. (2) where $C = Ng^2\mu_B{}^2/k$ and $f(J_{Cr\text{-}Fe}, J_{Fe\text{-}Fe}, T)$ is derived

$$\chi_{calc}^{Cr_2Fe_2} = \frac{C}{T - \theta}(J_{Cr\text{-}Fe}, J_{Fe\text{-}Fe}, T) \quad (2)$$

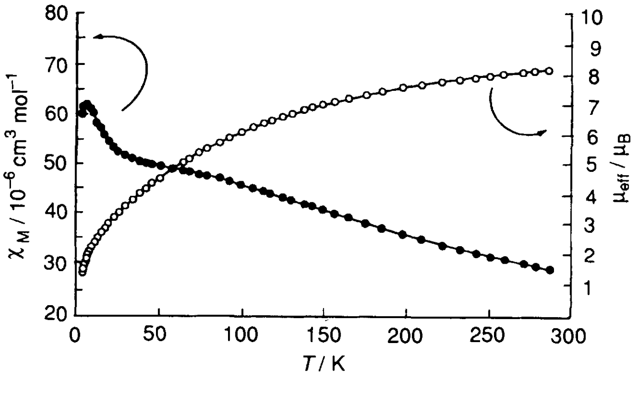

Fig. 2 Plot of χ_M and μ_{eff} *vs.* T for $[L_2Cr_2(\mu_2\text{-}OMe)_2(\mu_3\text{-}O)_2(salox)_2Fe_2](ClO_4)_2\cdot3H_2O$. The solid lines represent the best least-squares fits of the experimental data to the theoretical equation.

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§ The fact that the metal ions have remained associated with their different ligands, originating from their respective starting materials, is evidenced from an aqueous solution of the complex in 1 mol dm^{-3} $HClO_4$, which is red–violet in colour due to the presence of the $[LCr(OH_2)_3]^{3+}$ species that has an absorption maximum at 526 nm.

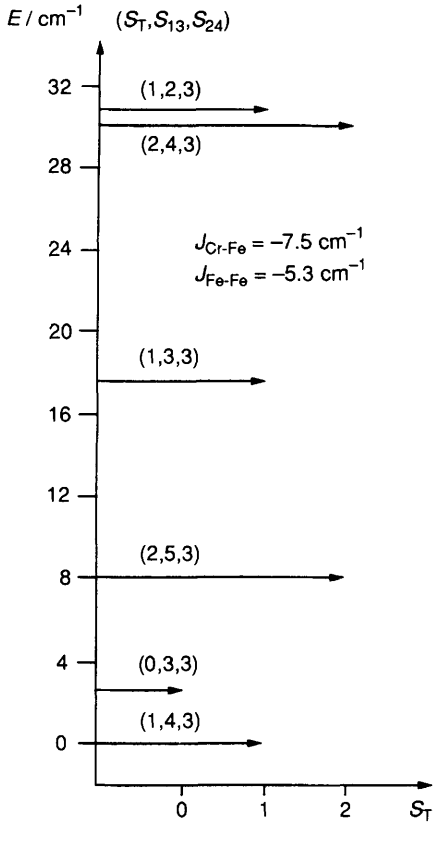
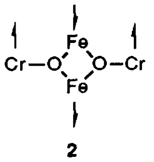


Fig. 3 Energy diagram of the low-energy states for ($Cr_2^{III}Fe_2^{III}$) complex. The energy states of the ground state S_T = 1 has arbitrarily been set at 0 cm^{-1}. The numbers in parentheses indicate the value of S for each state.

from the theoretical equation. The experimental values of χ_M have been fitted to this equation by treating $J_{\text{Cr-Fe}}$, $J_{\text{Fe-Fe}}$ and Weiss constant θ as adjustable parameters. The Zeeman interaction of high-spin iron(III) ion in a $^6A_1$ ground state and of chromium(III) ion in a $^4A_2$ ground state with practically no contribution from orbital angular momentum is isotropic; the g_{Fe} and g_{Cr} values are very close to the free-electron spin value of 2.0. Hence we have fixed molecular g to 2.0. The agreement between the calculated and observed magnetic susceptibilities is good, and the best fits are shown as solid lines in Fig. 2. The fit gave parameters $J_{\text{Cr-Fe}} = -7.5$, $J_{\text{Fe-Fe}} = -5.3$ cm^{-1}, $\theta = -14.2$ K, and mol% paramagnetic impurity = 0.13 with g fixed at 2.00. The ground state calculated with these exchange coupling parameters is a triplet (S_T = 1) state. There are three other spin states within 17 cm^{-1} of the ground state (Fig. 3).

The Cr···Fe interaction is antiferromagnetically greater than the Fe···Fe interaction and the overall favoured spin alignment is as in **2**. The Fe···Fe spin interaction is thus frustrated, and maintains the integrity of the low-lying spin states.



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To conclude, the novel heterotetranuclear [$Cr_2^{III}Fe_2^{III}$] species has an extremely complicated low-lying magnetic structure with a non-diamagnetic ($S_T \neq 0$) ground state, which is not well isolated and lies only 2.6 cm^{-1} below the first excited state due to spin frustration in the molecule. The spin frustration present in the [Cr_2Fe_2] complex represents a situation where one interaction ($J_{\text{Cr-Fe}}$) does not dominate over the other ($J_{\text{Fe-Fe}}$), thus the intrinsic character of the $J_{\text{Fe-Fe}}$ cannot be totally negated. It is interesting to note that in a homonuclear Fe_4 system the body–body interaction $J_{\text{Fe-Fe}}$ has been reported[4] to be indeterminate in contrast to our finding in this [$Cr_2^{III}Fe_2^{III}(\mu_3\text{-}O)_2$]$^{8+}$ core.

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