A novel pentanuclear iron(III) complex with a defective double-cubane core

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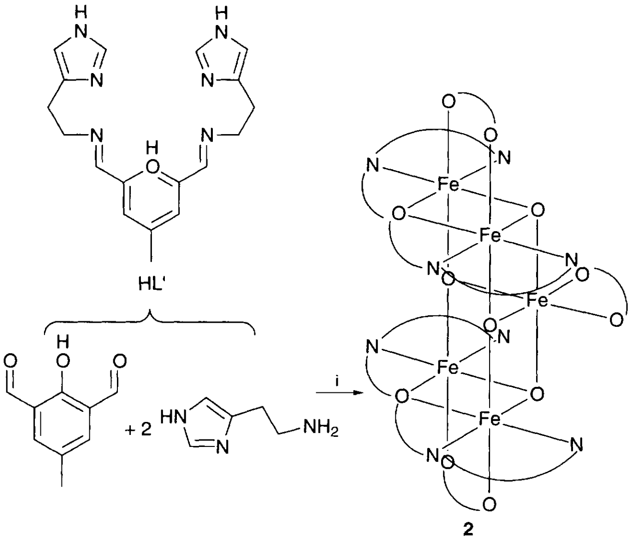
A novel pentanuclear iron(III) complex with 2,6-bis[*N*-(4-imidazolylethyl)iminomethyl]-4-methylphenol (HL′), $[Fe_5(L')_2(O)_4(MeCO_2)_3][ClO_4]_2\cdot 2EtOH\cdot H_2O$, is synthesized and characterized by X-ray crystallography, Mössbauer spectroscopy and magnetic susceptibility.

There is considerable current interest in the synthesis of multinuclear metal complexes, since these molecules might be useful as building blocks for 'magnetic molecular materials'[1] and model compounds for understanding the properties of metalloproteins.[2] In order to achieve syntheses of multinuclear metal complexes, we are pursuing a method using dinucleating ligands.[3–8] Our dinucleating ligands are Schiff-base type pentadentate ligands containing a central bridging donor atom. These ligands have compartments providing three donor atoms for each metal ion and bridge two metal ions to form dinuclear metal complexes. To date, mononuclear (Fe, Mn), dinuclear (Mn_2), trinuclear (Mn_3) and tetranuclear (Mn_4, Ni_4) complexes have been characterised.[3–7] In the course of this study, we successfully isolated a novel pentanuclear (Fe_5) complex, $[Fe_5(L)_2(O)(OH)_2(MeCO_2)_5(dmf)]\cdot C_6H_6\cdot 2H_2O$ **1**, by the application of our method to the iron system.[8] The structure revealed by X-ray crystallography shows that a square-pyramidal Fe_5 framework is formed by association of the two dinuclear units by virtue of linking to the fifth iron moiety. Concerning this complex, we have also isolated another interesting pentanuclear iron(III) complex by the use of a related pentadentate Schiff-base ligand, 2,6-bis[*N*-(4-imidazolylethyl)iminomethyl]-4-methylphenol (HL′). Herein we report the synthesis and X-ray crystal structure of the novel pentanuclear iron(III) complex, $[Fe_5(L')_2(O)_4(MeCO_2)_3][ClO_4]_2\cdot 2EtOH\cdot H_2O$ **2**.

Complex **2** was prepared as follows (Scheme 1). 2,6-Diformyl-4-methylphenol (7 mg) and histamine (11 mg) were dissolved in ethanol. Then iron(II) chloride tetrahydrate (20 mg), sodium acetate (33 mg) and sodium perchlorate (24 mg) were successively added and the solution was filtered. To the filtrate was added 10 mg of triethylamine to give dark brown crystals of **2**. The molecular structure of **2** was determined by X-ray crystallography.† A perspective view of **2** is shown in Fig. 1. In contrast to the case for **1**,[8] the five Fe atoms of **2** are located at the corners of a defective double cubane. The shorter Fe···Fe distances within the cubanes range from 2.888(2) [Fe(1)···Fe(3)] to 3.002(3) Å [Fe(4)···Fe(5)]. In one dinuclear unit, the Fe(1) and Fe(2) atoms are bridged by a phenoxo-oxygen atom, O(1) of the dinucleating ligand, oxo ion, O(3) and one acetate ion. Similarly, in the other dinuclear unit, the Fe(4) and Fe(5) atoms are bridged by a phenoxo-oxygen atom, O(2), of the dinucleating ligand, oxo ion, O(6), and one acetate ion. These dinuclear units are stacked upon each other by oxo [O(4) and O(5)] bridges which are connected to the Fe(3) atom. The coordination environments of the five Fe atoms are not



Scheme 1 *Reagents and conditions*: i, $FeCl_2\cdot 4H_2O$, $MeCO_2Na$, $NaClO_4$, EtOH, then NEt_3

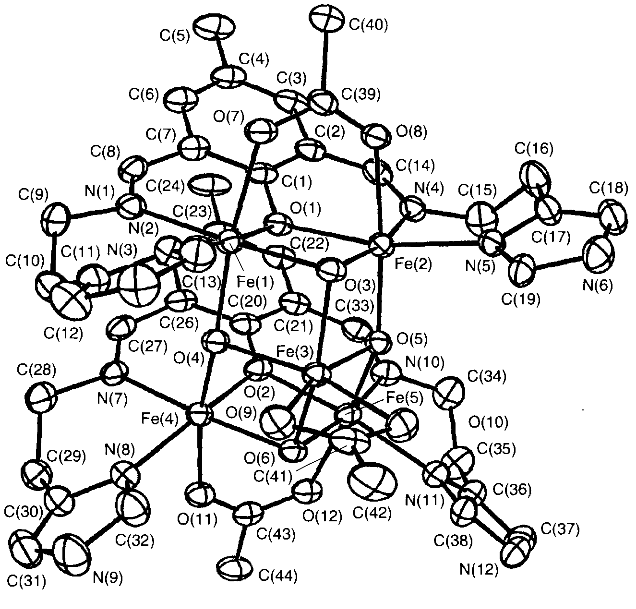


Fig. 1 Structure of the pentanuclear iron molecule in **2**. Selected interatomic distances (Å) and angles (°): Fe(1)···Fe(2) 2.983(3), Fe(1)···Fe(3) 2.888(2), Fe(1)···(4) 3.742(2), Fe(2)···Fe(3) 2.922(3), Fe(2)···Fe(5) 3.693(2), Fe(3)···Fe(4) 2.929(2), Fe(3)···(5) 2.933(2), Fe(4)···Fe(5) 3.002(3), Fe(1)–O(1) 2.089(8), Fe(1)–O(3) 1.954(7), Fe(1)–O(4) 1.918(8), Fe(1)–O(7) 2.102(9), Fe(1)–N(1) 2.115(9), Fe(1)–N(2) 2.07(1), Fe(2)–O(1) 2.115(7), Fe(2)–O(3) 1.955(8), Fe(2)–O(5) 1.900(8), Fe(2)–O(8) 2.100(8), Fe(2)–N(4) 2.107(9), Fe(2)–N(5) 2.096(9), Fe(3)–O(3) 1.970(8), Fe(3)–O(4) 2.009(7), Fe(3)–O(5) 2.040(8), Fe(3)–O(6) 1.962(7), Fe(3)–O(9) 2.136(8), Fe(3)–O(10) 2.145(7), Fe(4)–O(2) 2.048(8), Fe(4)–O(4) 1.906(7), Fe(4)–O(6) 1.974(7), Fe(4)–O(11) 2.103(8), Fe(4)–N(7) 2.142(8), Fe(4)–N(8) 2.05(1), Fe(5)–O(2) 2.064(7), Fe(5)–O(5) 1.917(7), Fe(5)–O(6) 1.965(8), Fe(5)–O(12) 2.112(8), Fe(5)–N(10) 2.13(1), Fe(5)–N(11) 2.08(1); Fe(1)–O(2)–Fe(2) 90.4(2), Fe(4)–O(2)–Fe(5) 93.8(3), Fe(1)–O(3)–Fe(2) 99.5(3), Fe(1)–O(3)–Fe(3) 94.8(3), Fe(2)–O(3)–Fe(3) 96.2(3), Fe(1)–O(4)–Fe(3) 94.7(3), Fe(1)–O(4)–Fe(4) 156.3(4), Fe(3)–O(4)–Fe(4) 96.9(3), Fe(2)–O(5)–Fe(3) 95.7(3), Fe(2)–O(5)–Fe(5) 150.7(3), Fe(3)–O(5)–Fe(5) 95.6(4), Fe(3)–O(6)–Fe(4) 96.2(3), Fe(3)–O(6)–Fe(5) 96.7(4), Fe(4)–O(6)–Fe(5) 99.3(3).

equivalent. The Fe(1), Fe(2), Fe(4) and Fe(5) atoms have an N_2O_4 donor set in a distorted octahedron, while the Fe(3) atom is coordinated to the four μ_3-O ions [O(3), O(4), O(5) and O(6)] and bidentate acetate ion forming a distorted octahedron. The Fe–O and Fe–N distances are typical of high-spin iron(III) complexes.[9] This is the first example of a structurally characterized pentanuclear iron complex with a defective double-cubane core.

Mössbauer spectra were measured for a polycrystalline sample of **2** at 300 and 80 K and the room temperature spectrum is shown in Fig. 2. The Mössbauer parameters (δ = 0.38 mm s^{-1} and ΔE_q = 0.85 mm s^{-1} at 300 K; δ = 0.48 mm s^{-1} and ΔE_q = 0.86 mm s^{-1} at 80 K) are characteristic of high-spin iron(III) complexes.[10] These spectra are slightly broadened, which might indicate the existence of two differing sites; one for Fe(1), Fe(2), Fe(4) and Fe(5) atoms which have $Fe^{III}N_2O_4$ environments and the other for the Fe(3) atom which has a $Fe^{III}O_6$ environment.

At 297 K the effective magnetic moment of **2** is 7.75 μ_B which is smaller than the expected value (13.23 μ_B) for five uncoupled S = 5/2 spins; μ_B steadily decreases on lowering the temperature, reaching 6.22 μ_B at 80 K, indicative of antiferromagnetic coupling between the five high-spin iron(III) centres. This is in contrast to the magnetic behaviour of **1** which shows a high-spin multiplicity in the ground state.[8]

A variety of multinuclear iron compounds containing 2, 3, 4, 6, 8, 10, 11, 12, 16, 17 or 19 iron atoms have been reported.[2,11–14] Most often, the synthetic route to the multinuclear units has been done by a self-assembly reaction. The present complex **2** as well as complex **1** is distinguished from these compounds by their novel structures and nuclearity. Our approach using dinucleating ligands has led to the discovery of remarkable Fe_5 species.

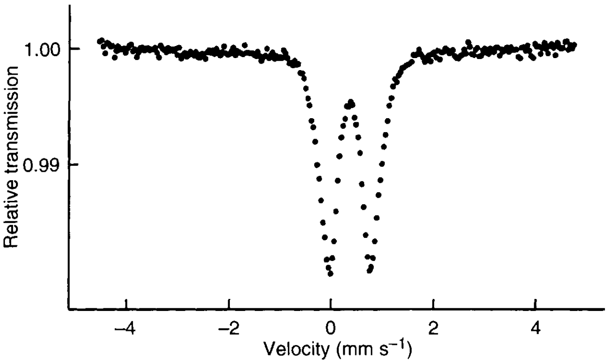


Fig 2 Mössbauer spectrum of **2** at room temperature

Footnote

† *Crystal data* for **2**: $C_{48}H_{65}Cl_2Fe_5N_{12}O_{23}$, M = 1528.2, triclinic, space group $P\bar{1}$, a = 16.013(8), b = 18.188(9), c = 13.841(7) Å, α = 98.79(3), β = 108.65(3), γ = 103.44(3)°, U = 3600(3) Å^3, Z = 2, D_m = 1.41, D_c = 1.41 g cm^{-3}, μ(Mo-Kα) = 11.30 cm^{-1}. A total of 11277 reflections ($2 < 2\theta < 48°$) were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation; 6801 with $I > 3\sigma(I)$ were assumed as observed. The structure was solved by the direct method and refined by full-matrix least-squares. The refinement converged at R = 0.069, R_w = 0.099.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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Received, 17th August 1995; Com. 5/05488E