

Synthesis, Structure and Preliminary Magnetic Studies of a Heptadecanuclear Iron Complex

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A novel heptadecanuclear iron complex $[\text{Fe}_{17}\text{O}_{15}(\text{OH})_6(\text{chp})_{12}(\text{phen})_8(\text{OMe})_3]$, is synthesised and structurally characterised (chp = the anion of 6-chloro-2-hydroxypyridine, phen = 1,10-phenanthroline).

Large polynuclear clusters and complexes are frequently described as adopting structures related to mineral or metal prototypes. Thus one expects that large carbonyl clusters will contain pieces of cubic close-packed metal, or large metal-oxo complexes will resemble segments of some relevant mineral. However, while certain recently characterised iron-oxo complexes¹⁻⁴ seem to support this hypothesis, structures such as the cyclic decanuclear 'ferric wheel'⁵ resemble no known archetype. This is the strength of coordination chemistry: by choice of ligand we can produce polynuclear fragments with novel metallic arrays.

Here we report a new heptadecanuclear iron complex prepared by reaction of $[\text{NEt}_4]_2[\text{Fe}_2\text{OCl}_6]$ (0.42 mmol) with Na(chp) (1.66 mmol) and 1,10-phenanthroline (1.66 mmol) in acetonitrile (30 ml). Addition of an equal volume of ethyl acetate to the filtered acetonitrile solution gives, after two weeks at 273 K, black crystals in 10% yield.† X-Ray structural analysis‡ revealed a polynuclear complex of formula $[\text{Fe}_{17}\text{O}_{15}(\text{OH})_6(\text{chp})_{12}(\text{phen})_8(\text{OMe})_3] \cdot 1.5 \text{ H}_2\text{O} \cdot 1.5 \text{ MeCN} \cdot 0.4 \text{ MeCO}_2\text{Et}$ **1**, with an iron-oxo core coated with an organic layer of phen and chp ligands. The formula is not unambiguously established; while bridging oxo- and hydroxo-groups can be assigned based on precedent, charge balance requires the postulation of one terminal OH group, which is rare in iron chemistry. The Fe-O bond length involving this group [O(1)-Fe(9) 2.050(13) Å] is longer than would be expected for a terminal hydroxide, and an alternative assignment where the terminal OH is a water molecule and where one iron atom is Fe^{II} cannot be discounted, although there is no obvious candidate for the unique iron atom. O(1) is involved in intramolecular hydrogen-bonding with close contacts (*ca.* 2.7 Å) to two chp N-atoms. The methoxide ligand present is derived from Na(chp) which was prepared in methanol. The increase in the O : Fe ratio compared with the substrate is unsurprising as no attempt was made to carry out the reaction under anhydrous conditions. The reaction to give crystals of **1** is completely reproducible, but we have yet to ascertain what products of the reaction remain in solution after two weeks.

The seventeen iron sites in **1** fall into three groups. There are eleven octahedral six-coordinate irons; two five-coordinate irons, with trigonal-bipyramidal geometry, and four four-coordinate irons which are approximately tetrahedral. The four tetrahedral irons [Fe(1)-Fe(4)] (Fig. 1), lie at four of the six vertices of a distorted trigonal prism with the final two vertices occupied by octahedral irons [Fe(5) and Fe(6)]. The face containing the two octahedral irons is capped by a further octahedral iron [Fe(7)], while the two faces which each contain only one octahedral iron are shared with further trigonal prisms. These prisms therefore contain three tetrahedral and three octahedral iron atoms [*e.g.* Fe(2), Fe(3), Fe(4), Fe(6), Fe(8) and Fe(9)]. The faces of each of these prisms which contain two tetrahedral and two octahedral irons are capped by a five-coordinate iron [Fe(12) or Fe(13)]. This capping atom, and two of the octahedral irons [either Fe(8) and Fe(9), or Fe(10) and Fe(11)] then form a tetrahedral array with one further iron [Fe(14) or Fe(15)]. The final two iron atoms are added even more irregularly to the core; Fe(16) shares two bridging oxo-atoms with Fe(12), while Fe(17) caps the face formed by Fe(2), Fe(6) and Fe(7). There are five Fe...Fe contacts of < 3 Å; all but one of these contacts involves Fe(13).

The array is held together by a mixture of μ_4 -oxo, μ_3 -oxo and μ_2 -hydroxy fragments. By comparison of Fe-O bond lengths and known geometries about bridging O fragments with those on the Cambridge Database we are confident of our assignment of μ -oxo and μ -hydroxo groups; the Fe-O(oxo) bonds are significantly shorter (mean 1.78 Å) than Fe-O(hydroxo) bonds (mean 1.98 Å). The μ_3 -O atoms are all trigonal planar, and the μ_4 -O atoms have trigonal-pyramidal geometries. The organic ligands coat the inorganic core, and there are some signs of graphitic interactions between phenanthroline moieties, *e.g.* the centroid-centroid distances between neighbouring phen ligands are *ca.* 3.7 Å (Fig. 2). It is conceivable that it is the packing of strongly bound phenanthroline ligands about the iron core that causes the irregular structure, and we might infer that this is a form of surface reconstruction occurring at a molecular level. The chp ligands are all bound only through the exocyclic oxygen atom, a form of bonding we have found frequently for this ligand with 3d metals.⁷⁻⁹ The N atoms are involved in intramolecular hydrogen bonding to other ligands such as hydroxides but there are no significant intermolecular interactions. We have been unable to relate this iron-oxygen array to any mineral prototype.

Preliminary magnetic studies of **1** appear to indicate strong antiferromagnetic coupling§ (Fig. 3). Assigning the core as all high-spin Fe^{III} would lead to a $\chi_M T$ value of *ca.* 74 emu mol⁻¹ K if the seventeen irons were non-interacting

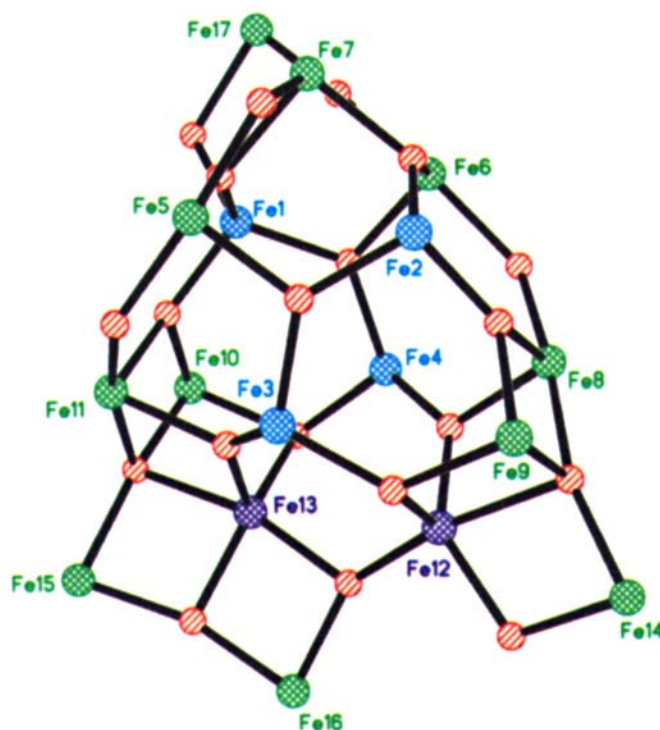


Fig. 1 The iron-oxo core of **1** showing the novel array of metal atoms. The five Fe...Fe contacts < 3 Å are: Fe(6)...Fe(7) 2.959, Fe(10)...Fe(13) 2.936, Fe(11)...Fe(13) 2.974, Fe(13)...Fe(15) 2.926, Fe(13)...Fe(16) 2.882 Å (av. e.s.ds 0.005 Å). (Tetrahedral iron sites, blue; trigonal bipyramidal iron sites, purple; octahedral iron sites, green; oxygen atoms, red.)



Fig. 2 The heptadecanuclear iron complex in **1**, showing the arrangement of organic ligands about the metallic core (Fe, green; O, red; N, blue; C, white; Cl, white)

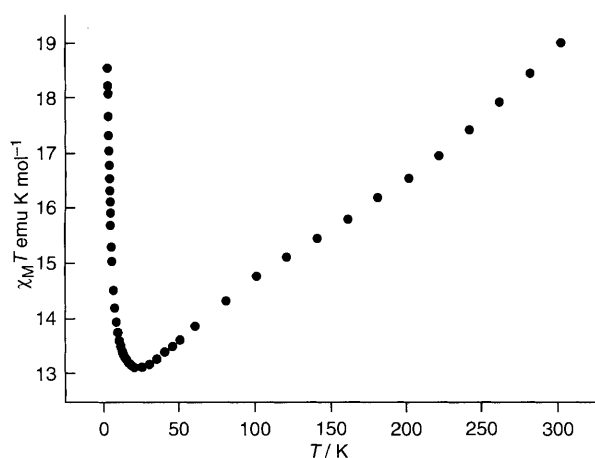


Fig. 3 Experimental temperature dependence of $\chi_M T$ per formula unit for **1**

(χ_M = molar magnetic susceptibility). Measurements indicate a much lower value for $\chi_M T$ of 19 emu mol⁻¹ K even at room temperature (corresponding to 3.00 μ_B per iron), falling to 13.1 emu mol⁻¹ K at 20 K. The $\chi_M T$ value then rises to 19 emu mol⁻¹ K at 3 K. This low temperature rise may, at least in part, be due to the presence of a paramagnetic impurity, despite the good analytical data for the compound. Other explanations of the low $\chi_M T$ values, e.g. the presence of some Fe^{II}, seem less likely given the synthetic procedures and the stoichiometric formula. Given the complexity of the structure further studies will be necessary to gain any understanding of the magnetism of this species.

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Footnotes

† Elemental analysis for **1**: Found: C, 43.9; H, 2.7; N, 8.9. Calc. for [Fe₁₇O₁₅(OH)₆(chp)₁₂(phen)₈(OMe)₃·1.5H₂O·1.5MeCN·0.4MeCO₂Et: C, 43.8; H, 2.8; N, 9.2%.

‡ Crystal data for C₁₅₉H₁₁₅Cl₁₂Fe₁₇N₂₈O₃₆·1.5CH₃CN·1.5 H₂O·0.4 C₄H₈O₂ **1**: *M* = 4483, triclinic, space group *P*1̄, *a* = 17.709(18), *b* = 18.097(21), *c* = 33.230(29) Å, α = 83.65(3), β = 82.62(4), γ = 67.19(7)°, *V* = 9708 Å³ [from 2θ values of 28 reflections measured at ±ω (25 ≤ 2θ ≤ 27°), λ = 0.71073 Å], *Z* = 2, *D_c* = 1.53 g cm⁻³, *T* = 150.0(2) K, dark brown tablet, 0.43 × 0.35 × 0.16 mm, μ = 1.47 mm⁻¹.

Data collection and processing: Stoë STADI-4 four-circle diffractometer with Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105), graphite-monochromated MoKα X-radiation, ω-scans with on-line profile-fitting (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22). All data were corrected for Lorentz and polarisation effects and for absorption (ψ-scans, *T_{min}* = 0.564, *T_{max}* = 0.610). The structure was solved for all Fe and μ-O atoms by direct methods (SIR92, A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343) and completed by iterative cycles of conjugate-gradient least squares and Δ*F* syntheses (SHELXL-93, G. M. Sheldrick, University of Göttingen, 1993). Two of the chp ligands exhibit twofold disorder about a common O-Fe vector, and an ethyl acetate molecule in the lattice is also disordered. The structure was refined against *F*² by block-matrix least squares, with the chemically reasonable condition that equivalent bond lengths and angles within the ligands were restrained to be similar. Further restraints were placed on the disordered solvate molecule. All non-H atoms within the complex were refined anisotropically with rigid body and similarity restraints for atoms within chp and phen ligands. The refinement of 2323 parameters converged to *R*₁ = 0.1023 for 9556 data with *F* > 4σ(*F*) and *wR*₂ = 0.3297 for all 18837 independent reflections (2θ ≤ 40°), and 5756 restraints.

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.

§ Variable-temperature magnetic measurements on **1** in the region 3–300 K using a 1000 G field were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules. In all cases diamagnetic corrections for the sample holders were applied to the data. Diamagnetic corrections for the samples were determined from Pascal's constants and literature values. A room-temperature field dependent study was also carried out to ensure against saturation effects.

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