A phenolysis route to a new type of octanuclear iron(III) wheel: [Fe$_8$(OH)$_4$(OPh)$_8$(O$_2$CBu^t)$_{12}$]

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Alcoholysis of [Fe$_6$O$_2$(OH)$_2$(O$_2$CBu^t)$_{10}$(hep)$_2$] (**1**) affords ferric wheels of different nuclearities: methanol yields [Fe$_{10}$(OMe)$_{20}$(O$_2$CBu^t)$_{10}$], whereas phenol gives the structurally unprecedented wheel [Fe$_8$(OH)$_4$(OPh)$_8$(O$_2$CBu^t)$_{12}$], and the first to contain phenoxide.

High nuclearity iron(III) carboxylate clusters have been an active area in recent years owing to their relevance as models for protein active sites,[1] and the interesting magnetic properties that some of them possess.[2] One synthetic route to such compounds is alcoholysis, either of a ferric salt in the presence of carboxylate groups (and sometimes other chelating ligands), or of a preformed small nuclearity Fe$_x$ cluster. This type of reaction has several precedents in the literature,[3] and it has often led to the aggregation of small units into larger clusters.

In contrast, we have recently investigated the alcoholysis of the higher nuclearity compound [Fe$_6$O$_2$(OH)$_2$(O$_2$CBu^t)$_{10}$-(hep)$_2$] (**1**) (hep$^-$ = the anion of 2-(hydroxyethyl)pyridine)[4] with MeOH and PhOH. The latter has rarely been employed in Fe chemistry, and there are consequently a limited number of crystallographically characterized iron-phenoxide complexes, which include a few iron-sulfur clusters[5] and two porphyrin-based mononuclear compounds. The two alcohols were also chosen for their contrasting bulkiness and differing acidities (pK_a ≈ 10 for PhOH *vs.* pK_a ≈ 15.5 for MeOH).

Compound **1** in CHCl$_3$ was treated with an excess of MeOH, and the resulting solution filtered and left undisturbed for several weeks in a sealed flask. Green rhomboidal crystals of [Fe$_{10}$(OMe)$_{20}$(O$_2$CBu^t)$_{10}$]·CHCl$_3$ (**2**·CHCl$_3$) and a small amount of light yellow powder were obtained, and these were easily separated manually. The yield of **2**† was 13%. The crystal structure‡ (Fig. 1) reveals an Fe$_{10}$ wheel analogous to those previously observed in other compounds of formula [Fe(O-Me)$_2$(O$_2$CR)]$_{10}$ (R = Me,[6] CHPh$_2$,[7] CH$_2$Cl,[3] 3-(4-methylbenzoyl)ethyl[8]), nicknamed "ferric wheels". It contains ten octahedral Fe(III) ions in a planar ring, with each Fe bridged to its neighbours by one carboxylate and two methoxide groups. The molecule possesses idealized S_{10} symmetry. Several of the methyl groups are directed towards the center of the Fe$_{10}$ cavity, which is thus fairly crowded with distances between opposite methyl carbon atoms of *ca.* 4.5 Å. This suggested that this Fe$_{10}$ structural type could not accommodate a bulkier alkoxide, and that a different structural unit might therefore result. Complex **1** in CH$_2$Cl$_2$ was consequently treated with a large excess of PhOH. The resulting, very dark red solution was filtered and the filtrate left undisturbed. After two days, dark red crystals of [Fe$_8$(OH)$_4$(OPh)$_8$(O$_2$CBu^t)$_{12}$]·H$_2$O·CH$_2$Cl$_2$ (**3**·H$_2$O·CH$_2$Cl$_2$) were isolated in 60% yield (eqn. (1)).

$$4[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{O}_2\text{CBu}^t)_{10}(\text{hep})_2] + 24\text{PhOH} \rightarrow 8\text{hepH} +$$
$$3[\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{O}_2\text{CBu}^t)_{12}] + 4\text{H}_2\text{O} + 4\text{Bu}^t\text{CO}_2\text{H} \quad (1)$$
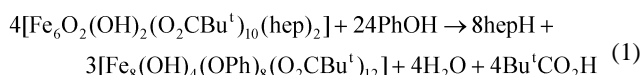
The structure§ of **3** (Fig. 2) is unprecedented in Fe chemistry, although two structures with a similar metal/oxygen backbones have been reported with V and Cr.[9] It consists of a planar ring of eight Fe(III) ions, with two types of connections between adjacent metal ions. Each Fe atom is bridged to one of its
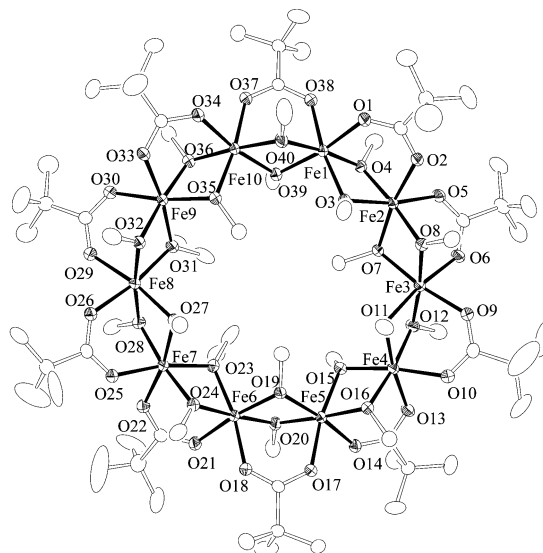
Fig. 1 ORTEP representation at the 50% probability level of complex **2**. Selected distances (Å) and angles (°): Fe(1)···Fe(2) 3.022(1), Fe(1)–O(4) 1.984(2), Fe(1)–O(39) 1.987(2), Fe(1)–O(40) 1.987(2), Fe(1)–O(3) 1.996(2), Fe(1)–O(38) 2.029(2), Fe(1)–O(1) 2.037(2); Fe2–O3–Fe1 98.78(8), Fe2–O4–Fe1 99.24(8).
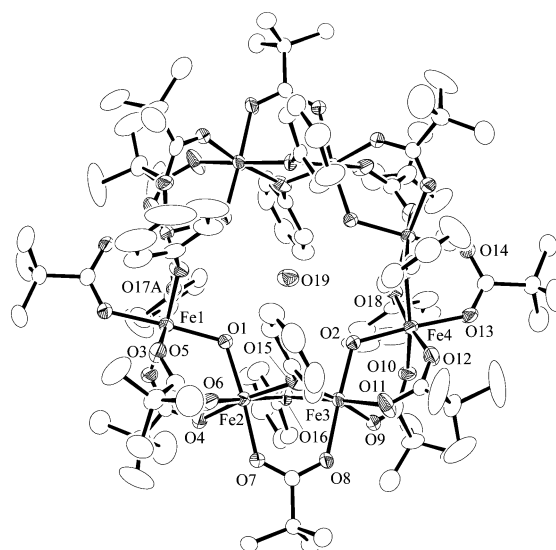

Fig. 2 ORTEP representation of centrosymmetric **3** at the 50% probability level. Selected distances (Å) and angles (°): Fe(1)···Fe(2) 3.456(1), Fe(2)···Fe(3) 3.098(1), Fe(1)–O(1) 1.982(2), Fe(1)–O(5) 1.983(2), Fe(1)–O(3) 1.991(2), Fe(1)–O(18A) 2.007(2), Fe(1)–O(17A) 2.017(2), Fe(1)–O(14A) 2.028(2), Fe(2)–O(1) 1.981(2), Fe(2)–O(6) 1.983(2), Fe(2)–O(4) 1.984(2), Fe(2)–O(15) 2.007(2), Fe(2)–O(16) 2.015(2), Fe(2)–O(7) 2.024(2), Fe(2)–O(1)–Fe(1) 121.4(1), Fe(2)–O(15)–Fe(3) 100.6(1), Fe(3)–O(16)–Fe(2) 100.55(9).

neighbours by an equatorial carboxylate and two axial μ-phenoxide ligands above and below the plane (in contrast to the methoxide groups in **2**). To the other neighbour, each Fe atom is bridged by an equatorial μ-hydroxide ion directed towards the centre of the ring, and two axial carboxylate ligands, above and below the plane. A tightly bound water molecule (O19) occupies the central cavity and is disordered with equal occupancies slightly above or below the plane (0.569 Å). In each position, it hydrogen bonds with two of the OH⁻ groups (O(19)···O(2) = 2.991 Å, O(19)···O(1) = 3.081 Å).

Complex **3** is one of the few examples of an octanuclear iron wheel.[10] The most closely related previous example is [Fe₈L₈] (LH₃ = triethanolamine) by Saalfrank and coworkers, which consists of a metallacrown encapsulating a Cs⁺ ion at its centre. The same authors report smaller nuclearity wheels when Li⁺ or Na⁺ ions are used instead of Cs⁺, thus demonstrating the effect of the guest dimensions on the size of the host ring. Attempts to introduce a bulkier guest molecule in compound **3** and thus increase the nuclearity of the ring have been unsuccessful to date.

The magnetic susceptibility of **2** and **3** was measured on microcrystalline samples in a 1 T field in the 2.00–300 K range. The experimental data for **2** and **3** are plotted as $\chi_M T$ vs. T in Fig. 3. The $\chi_M T$ value for **2** decreases gradually with decreasing temperature from 28.76 cm³ mol⁻¹ K at 300 K to 0.60 cm³ mol⁻¹ K at 2.00 K, suggesting an $S = 0$ ground state. The 300 K value is less than the spin-only ($g = 2$) value for ten non-interacting Fe(III) ions of 43.8 cm³ mol⁻¹ K, indicating antiferromagnetic interactions within the molecule and a $S = 0$ ground state. These results are in agreement with those previously observed for similar Fe₁₀ ferric wheels,[7,8] which have spin singlet ground states.

Complex **3** exhibits similar behaviour. In this case, the value of $\chi_M T$ at 300 K is 21.76 cm³ mol⁻¹ K, significantly below the 35.0 cm³ mol⁻¹ K spin-only value for eight non-interacting Fe(III) ions, consistent with antiferromagnetic exchange interactions. The $\chi_M T$ decreases steadily with decreasing temperature to 0.26 cm³ mol⁻¹ K at 2.00 K, again indicating an $S = 0$ ground state. Unlike **2**, whose virtual S_{10} symmetry makes all Fe₂ pairwise interactions equivalent, complex **3** has two different exchange interactions. Recent results with various Fe$_x$ clusters[11] have correlated an increasing strength of the exchange interaction between two oxo-bridged Fe(III) ions with shorter Fe–O distances and wider Fe–O–Fe angles. In **3**, the average Fe–O–Fe angle and Fe–O distance through the single μ-hydroxide ion are 121° and 1.97 Å, whereas those through the oxygen atom of the phenoxide groups are 100.6° and 2.01 Å, much closer to the values in the Fe₂(OMe)₂ units of complex **2**. These parameters suggest the stronger antiferromagnetic intera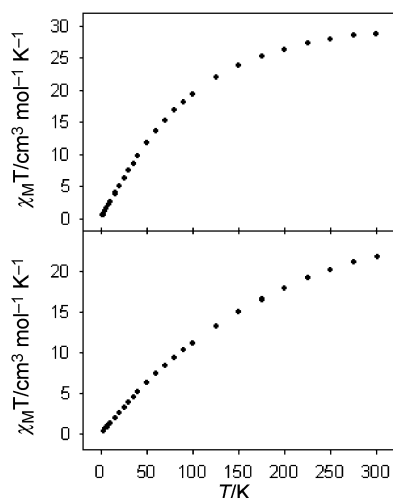ctions are within the hydroxide-bridged Fe₂ pairs. This rationalizes the faster decrease in the $\chi_M T$ value in compound **3** compared with **2**. A detailed analysis of the magnetic properties and exchange parameters of **2** and **3** will be reported in the full paper.

In conclusion, alcoholysis of high nuclearity **1** is a clean new route to other compounds. Complex **2** is a new member of a class of compounds previously obtained only from mono-nuclear or low nuclearity Fe$_x$ ($x \leq 3$) starting materials, whereas **3** is an unprecedented Fe₈ phenoxide wheel. Further alcoholysis, and particularly phenolysis, reactions of a variety of preformed Fe$_x$ ($x \geq 4$) compounds are currently in progress.

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Fig. 3 Plot of $\chi_M T$ vs. T for complexes **2** (top) and **3** (bottom).