A discrete Fe_{18} 'molecular chain'

Rashmi Bagai, Khalil A. Abboud and George Christou*

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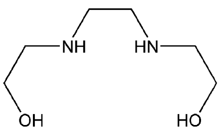
The use of a new O,N,N,O chelate has led to two new Fe_6 and Fe_{18} molecular compounds, the latter with an unusual double-headed serpentine chain structure.

The synthesis and study of molecular clusters of paramagnetic transition metal ions continue to be a major research thrust of groups around the world. This is driven by a variety of reasons, from bioinorganic modelling efforts[1] to the application of a molecular, 'bottom-up' approach to nanoscale magnetic materials.[2] This is particularly true for oxo-bridged Fe(III) clusters of various nuclearities, which have been studied as models of Fe sites in proteins and enzymes, as well as models of intermediate stages of the growth of the giant Fe/O core of the Fe storage protein ferritin. In addition, there are now several Fe-containing single-molecule magnets, species that behave as molecular superparamagnets.[3] In fact, the biological and magnetic areas involve the same Fe/O chemistry, as emphasized by the fact that the Fe/O core of ferritin can be considered a nanoscale magnetic particle.[4]



$heenH_2$

The above considerations and others continue to stimulate groups around the world to develop new synthetic methods that can yield new polynuclear Fe/O clusters. One successful strategy has been the use of alkoxide-based ligands,[5] since this functionality is an excellent bridging group that fosters higher nuclearity product formation. In the present work, we have been investigating the use of a new O,N,N,O-based chelate for transition metal cluster chemistry, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine ($heenH_2$). There were no literature reports of any cluster compounds with deprotonated $heenH_2$, but its two alcohol arms suggested a rich potential for polynuclear product formation. Thus, a variety of reactions have been systematically explored with various Fe(III) reagents and ratios. The reaction of $Fe(ClO_4)_3$, NaO_2CPh and $heenH_2$ in a 1 : 2 : 1 molar ratio in EtOH gave $[Fe_6O_2(O_2CPh)_5(heen)_3(heenH)](ClO_4)_2\cdot 2EtOH\cdot 1.5H_2O$ (**1**$\cdot 2EtOH\cdot 1.5H_2O$) in 30% yield.†‡ The structure of the centrosymmetric cation of **1** (Fig. 1) can be described as a central $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ butterfly-like unit (Fe1, Fe1′, Fe2 and Fe2′) connected through both its body (Fe1, Fe1′) and wingtip atoms (Fe2, Fe2′) to two additional Fe atoms Fe3 and Fe3′ by $heen^{2-}$ (O8, O9, O10) alkoxide arms. At one end of the molecule (Fe3) the remaining $heen^{2-}$ alkoxide arm (O11) binds terminally; at the other end (Fe3′), this arm (O20) is protonated and unbound (*i.e.* a $heenH^{-}$ group) and there is instead a $PhCO_2^{-}$ bound terminally (Fig. 1; only benzoate *ipso* C atoms shown). These two situations at the two ends are, of course, disordered by the centre of symmetry, which makes Fe3 and Fe3′ equivalent; only one of the disorder components is shown in Fig. 1. Ligation is completed by four benzoate groups in the common η^1:η^1:μ-mode bridging the body and wingtip iron atoms of the central butterfly unit. A number of Fe_6 complexes have been reported previously, possessing a variety of metal topologies such as planar, twisted boat, chair, parallel triangles, octahedral, ladder-like, cyclic *etc.*, but the Fe_6 core of **1** is unprecedented.[6]

The reaction between $[Fe_3O(O_2CBu^t)_6(H_2O)_3](NO_3)$ and $heenH_2$ in a 2 : 3 molar ratio in CH_2Cl_2, followed by layering with pentanes, gave orange crystals of $[Fe_{18}O_8(OH)_2(O_2CBu^t)_{28}(heen)_4]\cdot 4C_5H_{12}\cdot 4CH_2Cl_2$ (**2**$\cdot 4C_5H_{12}\cdot 4CH_2Cl_2$) in 15% yield.‡§ The structure of centrosymmetric **2** (Fig. 2) comprises a remarkable Fe_{18} cluster that can be described as seven $[Fe_2O_2]$ rhombs linked into a chain, and attached to four end Fe atoms (Fe8, Fe8′, Fe9, Fe9′). Alternatively, it can be better described as the linkage by $heen^{2-}$ alkoxide arms O5 and O5′ of two central $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ butterfly units (Fe1, Fe2, Fe3 and Fe4, and its symmetry partner), like that in **1**, and then connected to additional $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ butterfly units at each end *via* intermediate Fe atoms Fe5 and Fe5′, the bridges being $heen^{2-}$ alkoxide arms O16 and O17 on one side of Fe5, and $heen^{2-}$ alkoxide arm O18 and a hydroxide ion O19 on the other side. Peripheral ligation is provided by four chelating $heen^{2-}$ and twenty-eight pivalate groups, twenty-two of the latter

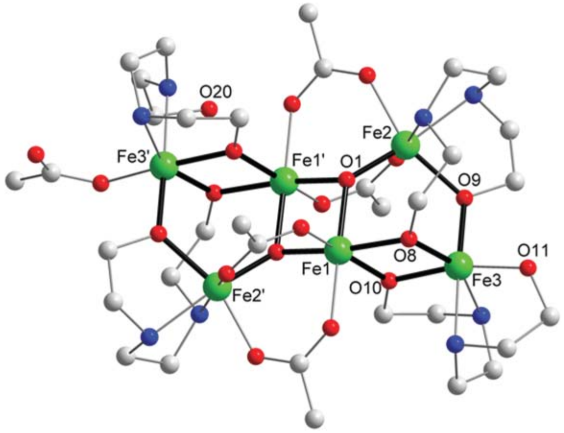


Fig. 1 Labelled representation of the cation of **1** with core Fe–O bonds as thick black lines; only the *ipso* benzoate C atoms are shown. Colour code: Fe, green; O, red; N, blue; C, grey.

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA. E-mail: christou@chem.ufl.edu; Fax: +1 352-392-8757; Tel: +1 352-392-8314

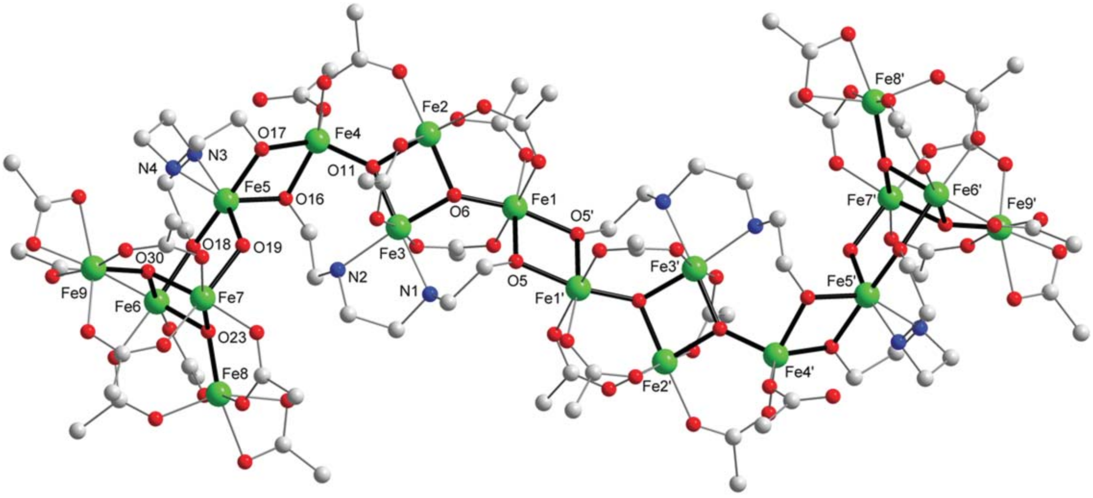


Fig. 2 Labelled structure of **2**, with core Fe–O bonds as thick black lines and pivalate Me groups omitted. Fe, green; O, red; N, blue; C, grey.

in the common η^1:η^1:μ-mode, four in an η^2 chelating mode (Fe8, Fe8′, Fe9, Fe9′), and two in an η^1 terminal mode on Fe4 and Fe4′. Two of the four heen^{2-} groups are in an η^2:η^1:η^1:η^2:μ_3-mode (N3 and N4 chelate Fe5, O17 bridges Fe4 and Fe5, and O18 bridges Fe5 and Fe6) and the other two are in an η^2:η^1:η^1:η^2:μ_5-mode (N1 and N2 chelate Fe3, O5 bridges Fe1 and Fe1′, and O16 bridges Fe4 and Fe5).

The overall topology of **2** is chain-like and resembles a double-headed serpent (or Florida alligator) with both sets of jaws wide open. Such a molecule is not only unprecedented in Fe chemistry, it represents the highest-nuclearity, chain-like metal-containing molecule to be yet discovered, and can reasonably be called a 'molecular chain'. The next longest such molecular chain is a $Cr_{12}Ni_3$ species.[7] There are only two previous Fe_{18} clusters known, and they are both wheel complexes, *i.e.* closed molecular chains.[8]

The dc magnetic susceptibilities (χ_M) of dried **1**·H_2O and **2** (Fig. 3) were measured on powdered samples restrained in eicosane in a 0.1 T field and in the 5.0–300 K temperature range. For **1**·H_2O, the value of $\chi_M T$ steadily decreases from 10.05 cm^3 K mol^{-1} at 300 K to 8.13 cm^3 K mol^{-1} at 70 K and then rises to 10.32 cm^3 K mol^{-1} at 5.0 K (Fig. 3), which suggests an S = 4 ground state. This was confirmed by the fit of dc magnetization (M) *vs.* field (H) and temperature (T) data collected in the 1.8–10 K and 0.1–4 T ranges (Fig. 4). Two fits were obtained, depending on the sign of D (axial anisotropy); S = 4, g = 2.06, D = −0.29 cm^{-1}; S = 4, g = 2.05, D = 0.35 cm^{-1}. A root-mean-square (rms) error analysis shows that the one with $D < 0$ is superior, suggesting this to be the true sign of D (Fig. 5),

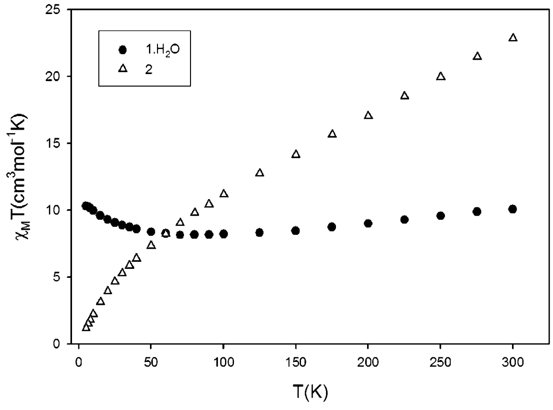


Fig. 3 Plot of $\chi_M T$ *vs.* T for complexes **1**·H_2O and **2**.

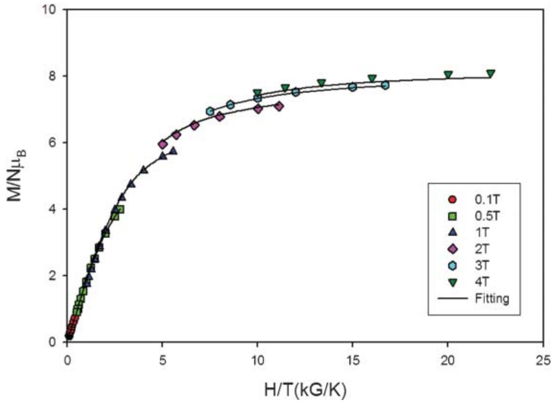


Fig. 4 Plot of reduced magnetization ($M/N\mu_B$) *vs.* H/T for **1**·H_2O.

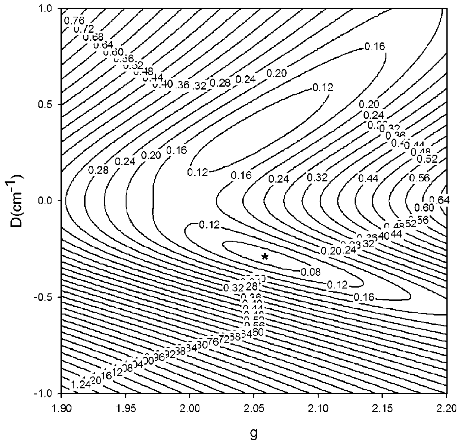
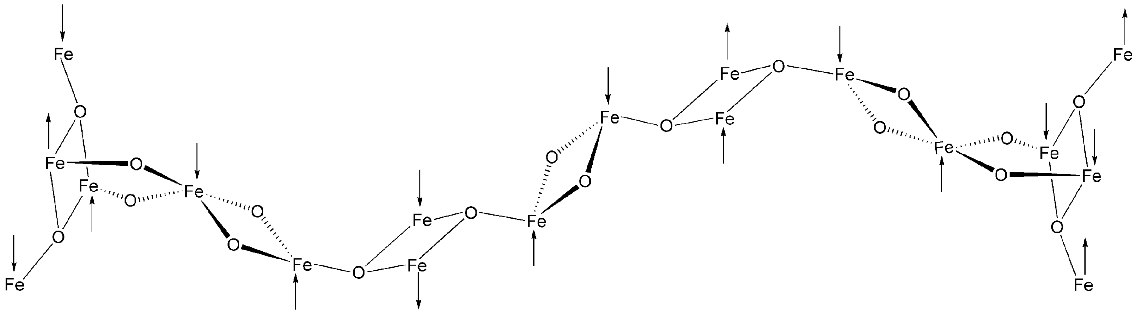


Fig. 5 Two-dimensional contour plot of the rms error *vs.* D and g for the fit for **1**·H_2O. The asterisk marks the best-fit position (error minimum).



Scheme 1

but confirmation must await EPR studies. When data collected at fields >4 T were used, the fits were poor, suggesting that excited states with $S > 4$ are stabilized by the field and become populated. In order to confirm the ground state, the dc field was removed by carrying out ac susceptibility measurements in the 1.8–10 K range with a 3.5 G ac field oscillating at frequencies in the 50–1000 Hz range. The in-phase ac signal also indicates an $S = 4$ ground state.

For **2**, $\chi_M T$ steadily decreases from 22.83 cm^3 K mol^{-1} at 300 K to 1.16 cm^3 K mol^{-1} at 5.0 K (Fig. 3). The behavior with decreasing temperature and the low value of $\chi_M T$ at 5 K are indicative of an $S = 0$ ground state. This is not unexpected given that this is the most common ground state for Fe^{III}_x clusters where x is even. There are common exceptions to this rule, however, when the topology is such as to introduce competing antiferromagnetic exchange interactions and spin frustration effects that result in often significant ground state S values. In fact, the $S = 4$ ground state of **1** must be due to such an effect, since all interactions are expected to be antiferromagnetic, as is essentially always the case for high-spin Fe(III), and a detailed experimental and theoretical analysis of the exchange interactions within this complex is planned. For complex **2**, the $S = 0$ ground state can be rationalized as shown in Scheme 1: the central Fe_4 butterfly units are known to exhibit spin frustration effects within their triangular subunits and to possess an $S = 0$ ground state as a result of the four 'wingtip-body' interactions of the four edges overcoming (frustrating) the 'body–body' interaction.[9] The antiferromagnetic interactions between separate butterfly units and between them and Fe5/Fe5′ then lead to an expected $S = 0$ ground state, as found experimentally. Of course, since **2** has an $S = 0$ ground state, the depicted spin alignments in Scheme 1 represent only one of the component wavefunctions of the ground state eigenstate.

In conclusion, the initial use of heenH_2 in transition metal chemistry has provided an entry into new cluster types, including a most unusual discrete chain-like structure with a double-headed serpentine or alligator topology. We like to think of this complex as a 'molecular chain', emphasizing both its discrete size and extended topology. Such molecular chains represent an intermediate situation between small molecular units and true 1-D chains, and should prove useful as such for study of the physical properties of this intermediate size regime. They also provide an important potential comparison of 'open' (molecular chain) *vs.* 'closed' (molecular wheel) forms of extended molecular species. For this reason, and with complex **2** as the stimulus, we are currently exploring more directed and targeted synthetic methods for obtaining extended single-strand molecular chains of different lengths for a more systematic study of this new area, as well as a more precise comparison with the growing number of molecular wheel complexes that are available.

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Notes and references

† Crystal data for **1**·2EtOH·1.5H_2O: $C_{63}H_{97}N_8Fe_6O_{31.5}Cl_2$, $M = 1876.49$, triclinic, $P\bar{1}$, $a = 11.7319(8)$ Å, $b = 13.5034(9)$ Å, $c = 13.8033(10)$ Å, $\alpha = 113.332(1)°$, $\beta = 92.028(1)°$, $\gamma = 99.130(1)°$, $V = 1970.8(2)$ Å^3, $Z = 1$, $T = 173(2)$ K, $R_1 = 0.0622$, w$R_2 = 0.1551$ ($I > 2\sigma(I)$). CCDC 650229. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708783g

‡ Calcd (found) for **1**·H_2O ($C_{59}H_{84}N_8Fe_6O_{29}Cl_2$): C, 39.92 (39.84); H, 4.77 (4.62); N, 6.31 (6.19%). Calcd (found) for **2** ($C_{164}H_{308}N_8Fe_{18}O_{74}$): C, 42.98 (43.25); H, 6.82 (6.99); N, 2.44 (2.43%).

§ Crystal data for **2**·4C_5H_{12}·4CH_2Cl_2: $C_{188}H_{364}Cl_8N_8Fe_{18}O_{74}$, $M = 5209.77$, triclinic, $P\bar{1}$, $a = 15.7923(12)$ Å, $b = 17.9984(13)$ Å, $c = 24.8805(19)$ Å, $\alpha = 106.938(2)°$, $\beta = 104.711(2)°$, $\gamma = 90.867(2)°$, $V = 6513.0(8)$ Å^3, $Z = 1$, $T = 173(2)$ K, $R_1 = 0.0467$, w$R_2 = 0.01252$ ($I > 2\sigma(I)$). CCDC 650230. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708783g

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