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## Polyhedron

journal homepage: [www.elsevier.com/locate/poly](http://www.elsevier.com/locate/poly)Synthesis and characterisation of Fe<sub>6</sub> and Fe<sub>12</sub> clusters using bicineKristoffer Graham<sup>a</sup>, Amiera Darwish<sup>a</sup>, Alan Ferguson<sup>a</sup>, Simon Parsons<sup>b</sup>, Mark Murrie<sup>a,\*</sup><sup>a</sup> WestCHEM, Department of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ, UK<sup>b</sup> School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

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## ABSTRACT

Reaction of bicine {BicH<sub>3</sub>, *N,N*-bis(2-hydroxyethyl)glycine} with an Fe(III) oxo-centered pivalate triangle in MeCN in the presence of Et<sub>2</sub>NH yields [Et<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Fe<sub>6</sub>O<sub>2</sub>(OH)<sub>2</sub>(Bic)<sub>2</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>8</sub>], which possesses an *S* = 5 ground state. Changing the base to NaOMe produces [Fe<sub>12</sub>O<sub>4</sub>(Bic)<sub>4</sub>(HBic)<sub>4</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>8</sub>], which contains two Fe<sub>6</sub> units bridged by the carboxylate arms from the bicine ligands. The complex displays strong antiferromagnetic coupling leading to an *S* = 0 ground state.

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Polymetallic transition metal complexes continue to attract intense interest in the field of molecular magnetism [1,2]. Alongside the potential applications in high-density data storage, there are opportunities in quantum computation [3], MRI contrast agents [4], magnetic refrigeration [5], and spintronics [6]. One strand of our research focuses upon the coordination chemistry of a series of structurally related ligands with the first row transition metal ions. We are investigating the substitution of functional groups on a given ligand backbone and how this affects the topology of the clusters that crystallise from the reaction system. This approach can be illustrated by Chart 1, which shows the ligands bis-tris,<sup>1</sup> bicine {BicH<sub>3</sub>, *N,N*-bis(2-hydroxyethyl)glycine} and diethanolamine (DEA), which all share the {N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>} group. We have shown that bis-tris can assemble small fragments of iron(III) carboxylates into Fe<sub>10</sub> clusters [7]. Although the DEA ligand has not been reported as a ligand for Fe(III) complexes, replacing the NH group by an NR (R = Me, Et etc.) group leads to some interesting polynuclear Fe(III) complexes, including Fe<sub>6</sub> wheels (e.g. R = Me [8], <sup>n</sup>Bu [9]) and in the presence of carboxylate co-ligands Fe<sub>7</sub> or Fe<sub>22</sub> complexes (R = Ph [10] or Me [11]). As bicine contains a carboxylate group in addition to the {N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>} functionality this ligand should form new and interesting polynuclear Fe(III) clusters. However, the only reported polynuclear complex with the bicine ligand is a hexa-nuclear [Fe<sub>6</sub>(Bic)<sub>6</sub>] wheel [12] where each bicine ligand is tri-deprotonated. Previously, mono-deprotonated bicine has been

used to prepare mononuclear copper and lanthanide complexes [13,14] and a one-dimensional polymeric manganese chain complex [15]. Herein, we report the synthesis and characterisation of two new Fe<sub>6</sub> and Fe<sub>12</sub> complexes with bicine, which display novel core topologies.

The Fe(III) pivalate oxo-centered triangle starting material was prepared according to the literature procedure [16]. BicH<sub>3</sub> was added to [Fe<sub>3</sub>O(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>][O<sub>2</sub>CCMe<sub>3</sub>] · 2HO<sub>2</sub>CCMe<sub>3</sub> in MeCN followed by Et<sub>2</sub>NH (1:1:1). The reaction was stirred at ambient temperature for 24 h then filtered and stored in a sealed vial, yielding orange plate-like crystals of [Et<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Fe<sub>6</sub>O<sub>2</sub>(OH)<sub>2</sub>(Bic)<sub>2</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>8</sub>] · 1.5MeCN (1 · 1.5MeCN) in 16% yield after 3 weeks.<sup>2</sup> Compound **1** contains two independent dianionic hexa-nuclear Fe(III) complexes which crystallise in the triclinic space group *P*−1 (Fig. 1). The Fe<sub>6</sub> complex consists of an {Fe<sub>4</sub>O<sub>2</sub>} butterfly unit [17] (Fe2, Fe3, Fe2a, Fe3a) capped by two {Fe(Bic)} units, which sit above and below the central {Fe<sub>4</sub>O<sub>2</sub>} core. Oxidation states were confirmed as Fe(III) and oxides/hydroxides assigned by consideration of bond lengths and charge balance and using bond valence sum (BVS) analysis [18].

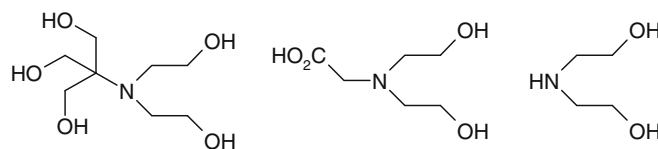
The two bicine ligands are tri-deprotonated, binding to Fe1 (and symmetry equivalent, s.e.) through N11 (and s.e.). The carboxylate arm is monodentate (O11), whereas the CH<sub>2</sub>CH<sub>2</sub>O<sup>−</sup> arms bridge Fe1 to either wing (Fe1–O41–Fe2) or body (Fe1–O61–Fe3a) centers

<sup>2</sup> Air-dried crystals analyze as 1 · 2MeCN · 4H<sub>2</sub>O, analysis (%) calc. (found): C, 42.59 (42.38); H, 7.37(7.04); N, 3.10 (3.36), selected IR data:  $\nu$  = 2961, 1667, 1556, 1482, 1421, 1347, 1220, 1069, 905, 881, 787, 651 cm<sup>−1</sup>. Crystal data for 1 · 1.5MeCN: Triclinic, *P*−1, *a* = 11.9471(15), *b* = 14.6166(19), *c* = 26.363(3) Å,  $\alpha$  = 89.775(4)°  $\beta$  = 88.84(5)°,  $\gamma$  = 66.725(4)°, *U* = 4228.0(9) Å<sup>3</sup>, *M* = 1740.27, *Z* = 2,  $\mu$ (Mo–K $\alpha$ ) = 1.077, *T* = 100 K; *R*<sub>1</sub> = 0.097, CCDC 707008.

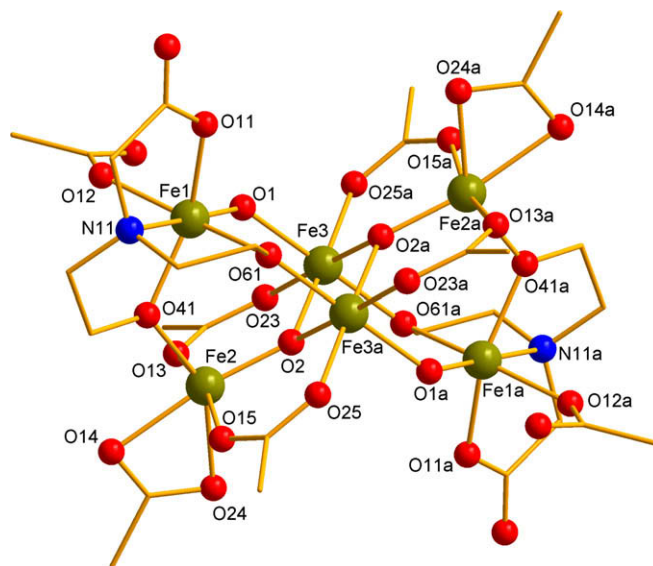
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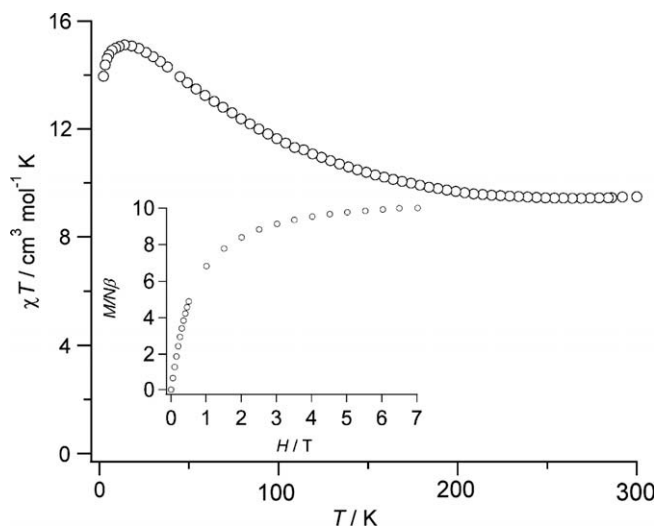
<sup>1</sup> The trivial names bis-tris and bicine are in common usage, especially when the ligands are used as biological buffers.



**Chart 1.** Ligands bis–tris, bicine and diethanolamine.



**Fig. 1.** Structure of the anion of **1** (ball and stick representation with Fe(III) gold; O, red; N, blue; C, brown; H atoms and Me groups of pivalate ligands omitted for clarity) [atom suffix a signifies the symmetry equivalent atom:  $a = 1 - x, 1 - y, 1 - z$ ]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

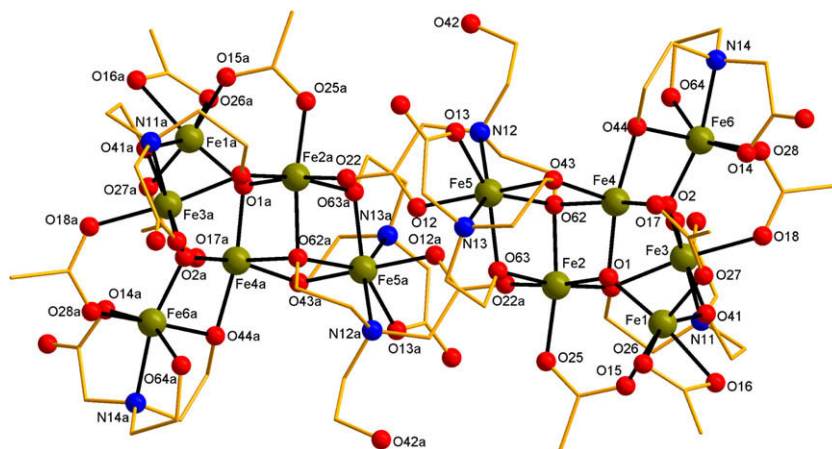


**Fig. 2.** Temperature dependence of  $\chi T$  for **1** from 300 to 1.8 K measured in a field of 1 kOe (inset, magnetisation versus field at 2 K).

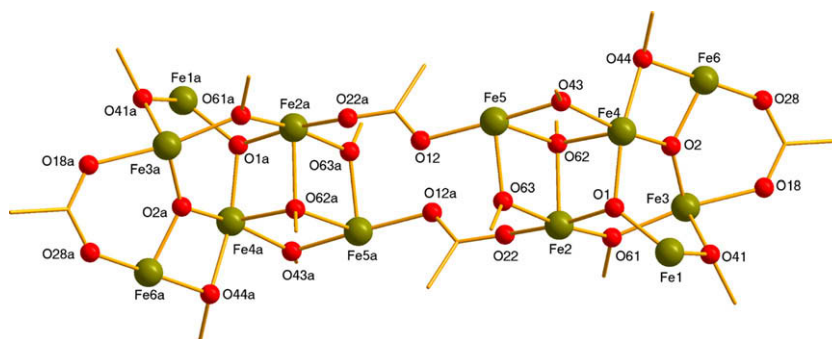
of the Fe<sub>4</sub> butterfly core. This binding mode has been observed for the [Fe<sub>6</sub>(Bic)<sub>6</sub>] wheel [12]. The hydroxide ligand (O1) also bridges Fe1 to a body iron(III) center (Fe1–O1–Fe3). Four of the eight pivalate ligands span the butterfly body-wing vectors in the typical 1,3-bridging mode. In addition, two are capping Fe2 and Fe2a in the 1,1' mode and the remaining two are monodentate bound to Fe1 and Fe1a and hydrogen-bonding to the two hydroxide groups (O1 and O1a). All Fe(III) centers are six-coordinate although the 1,1' bridging pivalate results in a rather distorted geometry at Fe2 (and s.e.). The Et<sub>2</sub>NH<sub>2</sub><sup>+</sup> cations are located above and below

the Fe<sub>6</sub> cluster, hydrogen-bonded to the bicine carboxylates (O11 and O11a) and the 1,1-bridging carboxylates (O24a and O24).<sup>3</sup> We note that in this Fe<sub>6</sub> cluster, one Fe<sub>4</sub> butterfly unit is capped by two {Fe(Bic)} units. It is interesting to compare this Fe<sub>6</sub> cluster to our Fe<sub>10</sub> clusters with bis–tris [7] where two Fe<sub>4</sub> butterfly units are bridged together by two {Fe(bis–tris)} units. Hence, we can show that clusters of different nuclearity and topology can be prepared by

<sup>3</sup> One of the crystallographically independent Et<sub>2</sub>NH<sub>2</sub><sup>+</sup> cations is disordered over two positions.



**Fig. 3.** Structure of **2** (ball and stick representation with Fe(III) gold; O, red; N, blue; C, brown; H atoms and Me groups of pivalate ligands omitted for clarity) [atom suffix *a* signifies the symmetry equivalent atom:  $a = 0.5 - x, 2.5 - y, -z$ ]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Core structure of **2**.

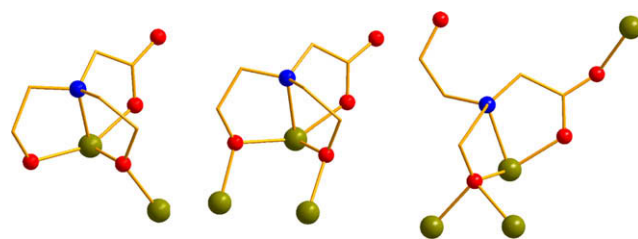
adjusting carefully the nature of the polydentate ligand, to build upon the  $\text{Fe}_4$  butterfly unit.

For **1** the value of  $\chi T$  at 300 K is  $9.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , significantly lower than for six uncoupled Fe(III) ions ( $26.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for  $g = 2$ ), indicating strong antiferromagnetic interactions between the Fe(III) centers (see Fig. 2). The value of  $\chi T$  increases steadily to a maximum of  $15.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 14.0 K, then drops sharply to  $13.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 1.8 K. This drop can be attributed to either zero-field splitting or intermolecular antiferromagnetic interactions. The magnetisation was measured as a function of applied field at 2 K, rising to a maximum value of  $M/N\beta = 10.0$  at 7 T. Both the low temperature maximum in  $\chi T$  and the magnetisation data are consistent with a spin ground state of  $S = 5$  for **1**. However, further measurements including EPR are required to determine the magnitude and size of any anisotropy. Further  $\text{Fe}_6$  clusters have been reported recently, with broadly similar topologies and  $S = 5$  ground states [19].

The change of base from  $\text{Et}_2\text{NH}$  to NaOMe produces a dodeca-nuclear complex  $[\text{Fe}_{12}\text{O}_4(\text{Bic})_4(\text{HBic})_4(\text{O}_2\text{CCMe}_3)_8] \cdot 5\text{MeCN}$  ( $2 \cdot 5\text{MeCN}$ ), in 12% yield, which crystallizes in the monoclinic space group  $C2/c$  (Fig. 3).<sup>4</sup> Compound **2** can be described as a dimer of  $\text{Fe}_6$  units, which have a different topology to the  $\text{Fe}_6$  cluster found in **1**. The two  $\text{Fe}_6$  units are separated by 6 Å, bridged by the carboxylate arms from the bicine ligands (Fig. 4). Unlike **1**, compound **2** is

not composed of  $\text{Fe}_4$  butterfly units: for **2**, more bicine is incorporated into the structure. The structure of each  $\text{Fe}_6$  unit is unusual and is formed from two corner-sharing  $\text{Fe}_3\text{O}$  triangles (Fe3, Fe6, Fe4 and Fe1, Fe2, Fe4). In addition, Fe5 bridges to Fe2 and Fe4 through three  $\text{CH}_2\text{CH}_2\text{O}^-$  arms (O62, O43, O63) from two bicine ligands, such that Fe2, Fe4 and Fe5 form an incomplete  $\{\text{Fe}_3\text{O}_4\}$  cubane.

The triply deprotonated bicine ligands (with N11 bound to Fe3 or N13 bound to Fe5) bind in the same  $\eta^2:\eta^2:\eta^1:\eta^1:\mu_3$  mode as that found in **1**. One of the doubly deprotonated ligands (with N14 bound to Fe6) caps Fe6, with one  $\text{CH}_2\text{CH}_2\text{O}^-$  arm bridging Fe6 to Fe4 and the second  $\text{CH}_2\text{CH}_2\text{OH}$  arm protonated (O64). The remaining Hbic ligand (with N12 bound to Fe5) displays a new binding mode, bridging the two halves of the cluster through the carboxylate arm. The deprotonated  $\text{CH}_2\text{CH}_2\text{O}^-$  arm (O62) is  $\mu_3$ -bridging (Fe2, Fe4, Fe5) with the second  $\text{CH}_2\text{CH}_2\text{OH}$  arm protonated and unbound (O42). Fig. 5 illustrates the different binding modes of bicine present in compounds **1** and **2**. Six of the pivalate ligands are 1,3-bridging with the remaining two 1,1'-bridging (to Fe1, Fe1a) as found in **1**. All Fe centers are six-coordinate except Fe5 (and s.e.),



**Fig. 5.** Binding modes of  $\text{BicH}_2^-$  and  $\text{Bic}^{3-}$  found in **1** and **2**.

<sup>4</sup> Air-dried crystals analyze as  $2 \cdot 2\text{MeCN} \cdot 4\text{H}_2\text{O}$ , analysis (%) calc. (found): C, 37.05 (36.77); H, 5.75 (5.67); N, 4.70 (4.95), selected IR data:  $\nu = 3397$  (broad); 2962, 1624, 1533, 1484, 1422, 1358, 1227, 1080, 1040, 889, 795,  $690 \text{ cm}^{-1}$ . Crystal data for  $2 \cdot 5\text{MeCN}$ : monoclinic,  $C2/c$ ,  $a = 29.795(5)$ ,  $b = 20.638(4)$ ,  $c = 27.218(8)$  Å,  $\beta = 120.749(7)^\circ$ ,  $U = 14384(6) \text{ \AA}^3$ ,  $M = 3033.64$ ,  $Z = 8$ ,  $\mu(\text{Mo K}\alpha) = 1.247$ ,  $T = 100 \text{ K}$ ;  $R1 = 0.0575$ . CCDC 707009.

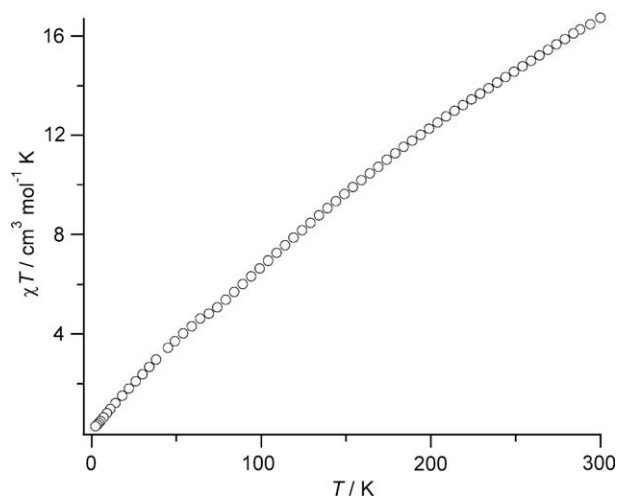


Fig. 6. Temperature dependence of  $\chi T$  for **2** from 300 to 1.8 K measured in a field of 1 kOe.

which are 7-coordinate showing a pentagonal bipyramidal geometry.

The value of  $\chi T$  for **2** at 300 K is  $16.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , significantly lower than the expected value for 12 uncoupled Fe(III) ions ( $52.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for  $g = 2$ ), indicating strong antiferromagnetic interactions between the Fe(III) centers (Fig. 6). The value of  $\chi T$  decreases steadily reaching a value of  $0.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 1.8 K consistent with an  $S = 0$  ground state.

In conclusion, we have reported two new Fe(III) complexes that incorporate the bicine ligand together with pivalate ligands. We have shown the versatility of the ligand, which can exist in different binding modes and can act as a bridging unit within the structure. The nature of the base used in the reaction has an effect on the cluster produced and this warrants further investigation. Magnetic characterisation reveals  $S = 5$  and  $S = 0$  ground states for the hexa- and dodeca-nuclear complexes, respectively.

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- [18] (a) W. Liu, H.H. Thorp, *Inorg. Chem.* 32 (1993) 4102; (b) BVS analysis of **1**: Fe1, 2.96; Fe2, 3.04; Fe3, 3.10; O1, 1.12; O2, 1.86. BVS analysis of **2**: Fe1, 2.90; Fe2, 3.03; Fe3, 2.90; Fe4, 2.97; Fe5, 2.43; Fe6, 2.96; O1, 1.77; O2, 1.85.
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