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# A new core topology in pentanuclear complexes

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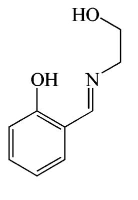
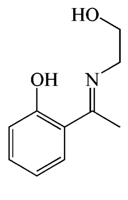
**Two members of a new family of pentanuclear $Fe^{III}$ complexes have been synthesized and found to possess competing antiferromagnetic exchange interactions that result in a spin ground state of $S = 5/2$.**

Polynuclear Fe complexes are of considerable interest from the viewpoint of both bioinorganic chemistry and molecular magnetic materials. In biological systems oxo-, hydroxo- and carboxylato-bridged Fe centers play an important role in the active sites of various non-heme Fe proteins, while the iron storage protein ferritin has a ferric oxyhydroxide core containing up to 4500 Fe centers.[1] In the field of molecular magnetism, several polynuclear $Fe^{III}$ complexes have been found to act as single-molecule magnets (SMMs).[2] These species possess an energy barrier to magnetization reversal which results from the molecular properties of a large spin ground state and a large easy-axis type magnetoanisotropy. In some of these SMMs the high spin ground state results from spin frustration associated with competing antiferromagnetic interactions. Thus complexes that display such interactions are subjects for the study of the phenomenon of spin frustration and can potentially function as SMMs. Following our initial success in the synthesis of novel $Fe_3$, $Mn_4$ and $Ni_4$ complexes with the Schiff base ligand $L^{2-}$,[3] we have turned our attention to the application of $H_2L$ and its derivative $H_2L'$ in the synthesis of new polynuclear $Fe^{III}$ complexes.



**$H_2L$**



**$H_2L'$**

Overnight reaction of a solution of $Fe(O_2CMe)_2$ in EtOH with one equivalent of ($H_2L'$) affords a precipitate which can be recrystallized from $CH_2Cl_2$/hexane as $[Fe_5O(OH)(O_2CMe)_4(L')_4]$ (**1**) in 80% yield. We have previously reported that an analogous reaction with $H_2L$ yields the trinuclear species $[Fe_3(O_2CMe)_3(L)_3]$.[3] Treatment of a solution of $[Fe_3(O_2CMe)_3(L)_3]$ in MeCN/toluene with three equivalents of $p$-$NO_2$-$C_6H_4CO_2H$, followed by repeated evaporation to dryness and re-dissolution in toluene, and finally recrystallization of the resulting residue from toluene/hexane affords $[Fe_5O(OH)(O_2CC_6H_4$-$p$-$NO_2)_4(L)_4]$ (**2**) in 25% yield.† The latter procedure is particularly noteworthy in that it involves structural rearrangement of a pre-formed polynuclear complex triggered by carboxylate substitution. The treatment of $[Fe_3(O_2CMe)_3(L)_3]$ with other carboxylic acids was also explored, however it was not possible to obtain pure materials.

The X-ray structure ‡ reveals that **1** possesses an $[Fe_5(\mu_3\text{-}O)_2(\mu_2\text{-}O)_5)]^+$ core, where the five $\mu_2$-O atoms are from the $(L')^{2-}$ ligands and are ethoxo-type (O4, O6, O14 and O16) or phenoxo-type (O5), while the $\mu_3$-bridges are oxo (O2) and hydroxo (O1) groups (Fig. 1). The core unit has a complex structure that, with some imagination, can be described as an incomplete cubane extended at one face by an incomplete adamantane unit. The four $MeCO_2^-$ ligands provide additional bridges, three binding in the typical $\mu_2$-mode, while the fourth binds in a terminal manner, displaying an intramolecular hydrogen bond to the core hydroxo group. Thus the molecule is unusual in that it contains oxo-, hydroxo-, alkoxo- and carboxylato-bridging units. The peripheral ligation is completed by the $(L')^{2-}$ ligands, each bound in a meridional bis-chelating fashion. Disregarding the differences in carboxylate and Schiff base ligands, the molecules of **1** and **2** are essentially isostructural, with only small differences in the corresponding bond distances and angles (Fig. 2). The hydroxo H atoms were located crystallographically in both structures. In addition, bond valence sum calculations are consistent with five $Fe^{III}$ centers for each complex. A search of the Cambridge Crystallographic Database reveals that the core unit evident in **1** and **2** is unprecedented for any pentanuclear complex. Moreover, only three pentanuclear $Fe^{III}$ complexes have been reported previously, all with structures very different to those of **1** and **2**.[4]

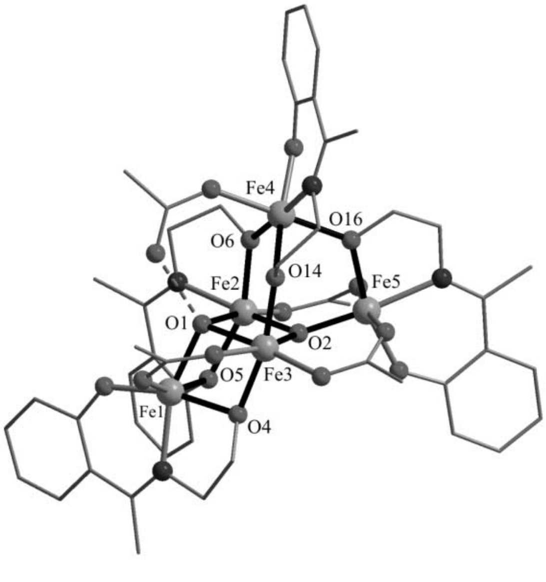


**Fig. 1** The structure of one of the independent molecules of **1**. The hydrogen bond is shown as a dashed line. Selected interatomic distances (Å) and angles (°): Fe1 ··· Fe2 3.215(2), Fe1 ··· Fe3 3.039(2), Fe2 ··· Fe3 3.003(2), Fe2 ··· Fe4 3.549(2), Fe2 ··· Fe5 3.396(2), Fe3 ··· Fe4 3.576(2), Fe3 ··· Fe5 3.357(2), Fe4 ··· Fe5 3.591(2); Fe1–O1–Fe2 105.8(2), Fe1–O5–Fe2 102.0(2), Fe1–O1–Fe3 96.9(2), Fe1–O4–Fe3 99.2(2), Fe2–O1–Fe3 93.7(2), Fe2–O2–Fe3 102.6(2), Fe2–O6–Fe4 125.3(3), Fe2–O2–Fe5 126.0(3), Fe3–O14–Fe4 127.9(2), Fe3–O2–Fe5 123.2(2), Fe4–O16–Fe5 125.6(3).

Magnetic susceptibility measurements were performed on microcrystalline samples of complexes **1** and **2** with a 1 kG field in the temperature range 1.8–300 K. For both complexes $\chi_M T$ decreases steadily from ≈ 9.5 $cm^3\ mol^{-1}$ K at 300 K to ≈ 4.3 $cm^3$

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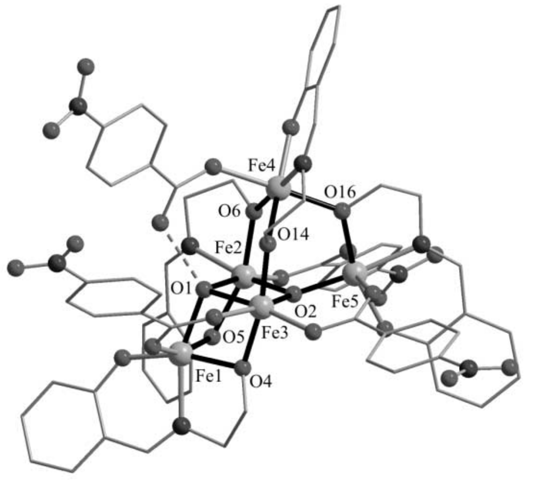

**Fig. 2** The structure of **2**. The hydrogen bond is shown as a dashed line. Selected interatomic distances (Å) and angles (°): Fe1 ··· Fe2 3.205(2), Fe1 ··· Fe3 3.084(2), Fe2 ··· Fe3 2.989(2), Fe2 ··· Fe4 3.547(2), Fe2 ··· Fe5 3.384(2), Fe3 ··· Fe4 3.555(2), Fe3 ··· Fe5 3.374(2), Fe4 ··· Fe5 3.534(2); Fe1–O1–Fe2 104.5(2), Fe1–O5–Fe2 101.3(2), Fe1–O1–Fe3 96.9(2), Fe1–O4–Fe3 101.2(2), Fe2–O1–Fe3 92.7(2), Fe2–O2–Fe3 101.9(2), Fe2–O6–Fe4 126.2(2), Fe2–O2–Fe5 125.9(2), Fe3–O14–Fe4 126.4(2), Fe3–O2–Fe5 124.7(2), Fe4–O16–Fe5 123.6(2).

mol$^{-1}$ K at 35 K, where its levels out before finally decreasing rapidly below 5 K (the data for **1** are presented in Fig. 3). This behavior is consistent with overall antiferromagnetic interactions resulting in a spin ground state of $S = 5/2$ (for an $S = 5/2$ system with $g = 2.0$, $\chi_M T = 4.4$ cm$^3$ mol$^{-1}$ K at 0 K). The low temperature decrease in $\chi_M T$ is assigned to the effects of zero-field splitting (ZFS) and/or intermolecular interactions. A consideration of the topologies of the complexes affords the coupling scheme depicted in Fig. 3. On the basis of the nature of the Fe–O–Fe bonds, the eight coupling constants that are strictly required can be reduced to three: where $J_A$ characterizes couplings with Fe–O–Fe < 106°, $J_B$ characterizes couplings through a μ-alkoxo bridge with Fe–O–Fe = 123–128°, and $J_C$ characterizes couplings through a μ-oxo bridge with Fe–O–Fe = 123–126°. The $\chi_M$ and $\chi_M T$ *vs.* $T$ data for **1** were fit§ with $g$ fixed to 2.0 to the Hamiltonian,

$$\begin{aligned} H_{ex} = -2J_A(\boldsymbol{S}_1 \times \boldsymbol{S}_2 + \boldsymbol{S}_1 \times \boldsymbol{S}_3 + \boldsymbol{S}_2 \times \boldsymbol{S}_3) - \\ 2J_B(\boldsymbol{S}_2 \times \boldsymbol{S}_4 + \boldsymbol{S}_3 \times \boldsymbol{S}_4 + \boldsymbol{S}_4 \times \boldsymbol{S}_5) - \\ 2J_C(\boldsymbol{S}_2 \times \boldsymbol{S}_5 + \boldsymbol{S}_3 \times \boldsymbol{S}_5) \end{aligned} \quad (1)$$

yielding two sets of parameters that can reproduce the data equally well: $J_A = -3.5(3)$ cm$^{-1}$, $J_B = -12.6(5)$ cm$^{-1}$ and $J_C = -53(5)$ cm$^{-1}$ or $J_A = -8.5(3)$ cm$^{-1}$, $J_B = -30(2)$cm$^{-1}$ and $J_C = -8.8(9)$ cm$^{-1}$. The former set of parameters is preferred as it has generally been observed that μ-oxo bridges mediate stronger antiferromagnetic interactions than either μ-hydroxo or μ-alkoxo bridges.[5] Moreover $J_C$ is comparable to 'body to wing' coupling constants determined for Fe$^{III}_4$ 'butterfly' complexes which involve a similar bridging mode.[6] In addition, attempts to fit the data using only two coupling constants, assuming that $J_B = J_C$, gave a significantly poorer fit. The susceptibility data for **2** were also fit to eqn. (1) to yield the similar set of parameters: $J_A = -3.0(3)$ cm$^{-1}$, $J_B = -11.4(6)$ cm$^{-1}$ and $J_C = -46(1)$ cm$^{-1}$. Finally, variable temperature magnetization measurements in the temperature range 1.8–8 K with fields up to 5 T were performed on **1** and **2** (not shown). At 1.8 K and 5 T, $M/N\mu_B$ values of 4.78 and 4.85 were obtained for **1** and **2**, respectively, consistent with $S = 5/2$. Slight deviations of the data from the appropriate Brillouin function are consistent with the effect of ZFS and/or intermolecular interactions.

In summary, two members of a new family of pentanuclear Fe$^{III}$ complexes have been synthesized and structurally characterized. One of these complexes was obtained following structural rearrangement of a pre-formed trinuclear complex triggered by carboxylate substitution, suggesting a promising route for the synthesis of new polynuclear complexes. Magnetic susceptibility measurements have revealed that competing antiferromagnetic exchange interactions afford an $S = 5/2$ spin ground state for both pentanuclear complexes, which was confirmed by magnetization saturation measurements. Further characterization of these and related complexes is in progress and will be reported in due course. In particular, EPR and inelastic neutron scattering should provide additional insight into the exchange and anisotropy parameters.

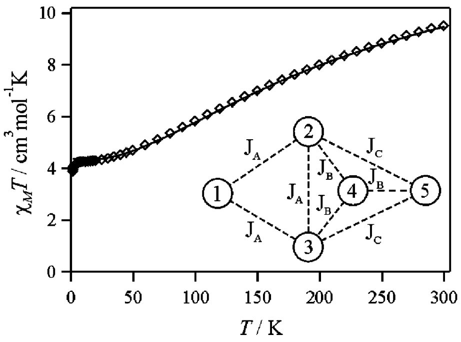

**Fig. 3** Plot of $\chi_M T$ *vs.* $T$ for **1**. The solid line is the best fit to eqn. (1).

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## Notes and references

† The proligands were synthesized as described.[3] A vacuum dried sample of complex **1** analyzed as **1**·$H_2O$. Found: C, 45.16; H, 4.86; N, 4.39. Calc for $C_{48}H_{59}N_4O_{19}Fe_5$: C, 45.21; H, 4.66; N, 4.39%. A vacuum-dried sample of complex **2** analyzed as unsolvated. Found: C, 47.13; H, 3.28; N, 6.65. Calc for $C_{64}H_{53}N_8O_{26}Fe_5$: C, 47.18; H, 3.28; N, 6.88%.

‡ The crystals were kept in contact with the mother liquor to avoid solvent loss. Crystal data for **1**·$0.25H_2O\cdot4.5CH_2Cl_2$: $C_{52.5}H_{66.5}Cl_9Fe_5N_4O_{18.25}$, $M = 1643.90$, triclinic, space group $P\bar{1}$, $a = 14.6913(12)$, $b = 23.5238(18)$, $c = 23.4482(18)$ Å, $\alpha = 62.310(8)$, $\beta = 88.319(10)$, $\gamma = 72.627(9)°$, $U = 6790.5(9)$ Å$^3$, $Z = 4$, $T = 153(2)$ K, $\mu$(Mo-Kα) = 1.465 mm$^{-1}$, 54041 reflections measured, 24746 unique ($R_{int} = 0.0969$), $R1(F) = 0.0834$, $wR2(F^2) = 0.2130$ for 13533 reflections with $I > 2\sigma(I)$. Crystal data for **2**·$H_2O\cdot C_6H_5CH_3\cdot0.5C_6H_{14}$: $C_{74}H_{70}Fe_5N_8O_{27}$, $M = 1782.63$, triclinic, space group $P\bar{1}$, $a = 15.3288(9)$, $b = 15.9751(10)$, $c = 20.0357(13)$ Å, $\alpha = 104.081(5)$, $\beta = 99.318(5)$, $\gamma = 116.649(4)$, $U = 4040.1$ Å$^3$, $Z = 2$, $T = 153(2)$ K, $\mu$(Mo-Kα) = 1.465 mm$^{-1}$, 32146 reflections measured, 13920 unique ($R_{int} = 0.0567$), $R1(F) = 0.0588$, $wR2(F^2) = 0.1597$ for 9976 reflections with $I > 2\sigma(I)$. CCDC reference numbers 213045 and 213046. See http://www.rsc.org/suppdata/dt/b3/b310500h/ for crystallographic data in CIF or other electronic format.

§ The data were fit using the Levenberg–Marquardt least-squares fitting algorithm in combination with MAGPACK.[7]

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