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An Fe(III) wheel with a zwitterionic ligand: the structure and magnetic properties of $[Fe(OMe)_2(proline)]_{12}[ClO_4]_{12}$

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The structure and magnetic properties of a dodecanuclear iron(III) wheel are reported, featuring a bridging zwitterionic ligand.

Cyclic metal cages featuring paramagnetic ions have been heavily studied since the report by Lippard and co-workers of the first "ferric wheel".[1] The majority are either octa- or deca-nuclear; the metal···metal vectors in the former are normally bridged by one μ_2-ligand (*e.g.* fluoride) and two carboxylates,[2] in the latter the metal···metal edges are normally bridged by two μ_2-ligands (*e.g.* methoxide) and one carboxylate.[1,3] More recently dodecanuclear wheels have been reported featuring the latter bridging motif, but in both cases the wheels become slightly "buckled", *i.e.* the metal cores are no longer planar.[4,5] There are also reports of wheels where the edges are asymmetrically bridged.[6] We have been investigating complexes with a bridging L-prolinato ligand,[7] which can become zwitterionic,[8] and here demonstrate that when it features in a "ferric wheel", a planar dodecanuclear wheel results which carries a 12+ charge.

$[Fe(OMe)_2(proline)]_{12}[ClO_4]_{12}$ **1** is formed from the reaction of hydrated iron(II) perchlorate (6 mmols) with L-proline (8 mmols) in methanol (150 ml). The solution was stirred for ten minutes and crystals of **1** grew after standing for several days at room temperature. The yield was 34%.† **Caution.** Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

The structure‡ of the cation (Fig. 1) shows twelve Fe(III) centres, with each Fe···Fe contact bridged by two methoxides and one proline. The molecule has a six-fold symmetry axis, and the cage is planar making the non-crystallographic symmetry S_{12}.

Previously reported "ferric wheels" containing this bridging motif are either decanuclear and planar,[1] with the Fe···Fe···Fe angle *ca.* 144°, or dodecanuclear and slightly puckered.[4,5] Here the Fe···Fe···Fe angle is 146° at Fe(1) and 154° at Fe(2) – giving the average 150° required for a planar dodecagon. The Fe–O distances are normal: Fe–O(methoxide), 1.974 to 2.009(5); Fe–O(proline), 2.042 to 2.081(5) Å, and bond angles are not unusual. Therefore the planar dodecagon is consistent with typical Fe–O bond lengths and normal bond angles.

The high charge requires the presence of twelve perchlorate anions per wheel. These lie between the wheels, forming H-bonds from the oxygen atoms of the perchlorates to the protonated N-atoms of the proline ligands (Fig. 2). As H-bonds are formed to wheels above and below each perchlorate the result is to form a H-bonded stack of $\{Fe_{12}\}$ wheels. The O···N distances in the H-bonds vary from 2.821 to 2.867(6) Å.

The magnetic behaviour§ of **1** shows the expected antiferromagnetic exchange between the Fe(III) centres. The room temperature value of $\chi_m T$ is *ca.* 35 cm^3 K mol^{-1} (where χ_m is the molar magnetic susceptibility), which is lower than the calculated value for twelve Fe(III) centres (52.5 cm^3 K mol^{-1} for $g = 2.0$), suggesting a strong exchange interaction is operational. At low temperature there is evidence for the presence of a paramagnetic impurity; the magnetic fit was therefore restricted to data measured above 20 K.

This behaviour has been modelled for a ring of twelve $S = 5/2$ spins, derived from the method developed by Fisher for classical spins.[10] The best fit of the data (Fig. 3) for the Hamiltonian $H = -J.S_iS_{i+1}$ ($i \leq 12$, $S_{13} \equiv S_1$), gives $J = -15.8$ cm^{-1}, and $g = 1.99$. We also calculated the exchange interaction using density functional theory (DFT)¶. An exchange interaction was derived by DFT for a dimeric Fe(III) fragment containing the bridging unit found in **1**, *i.e.* two methoxides and a proline, with terminal H_2O molecules used to complete the Fe coordination spheres. This gave an exchange interaction of -13.9 cm^{-1}; this value was then used in a Monte Carlo simulation of the magnetic data with an excellent fit. It is very reassuring that the two methods of fitting the magnetic data reach a similar value.

This value of between -14 and -16 cm^{-1} is more antiferromagnetic than the exchange interaction of -9.6 cm^{-1} found for decanuclear ferric wheels,[1] or that of -10.9 cm^{-1} found in a $\{Fe_{12}\}$ ring.[4] Similarly in a $\{Fe_2\}$ complex with two bridging MeO and a O_2CMe bridge J was found to be -10.1 cm^{-1}.[13] Our value is in moderate agreement with proposed correlations between the exchange interaction and either the average[14] or smaller Fe–O–Fe angle[15] in di(alkoxo)-bridged Fe(III) complexes where there is no bridging carboxylate. Here these angles are 99.3 and 99.1° respectively, which would give values of either -12.0 or -12.4

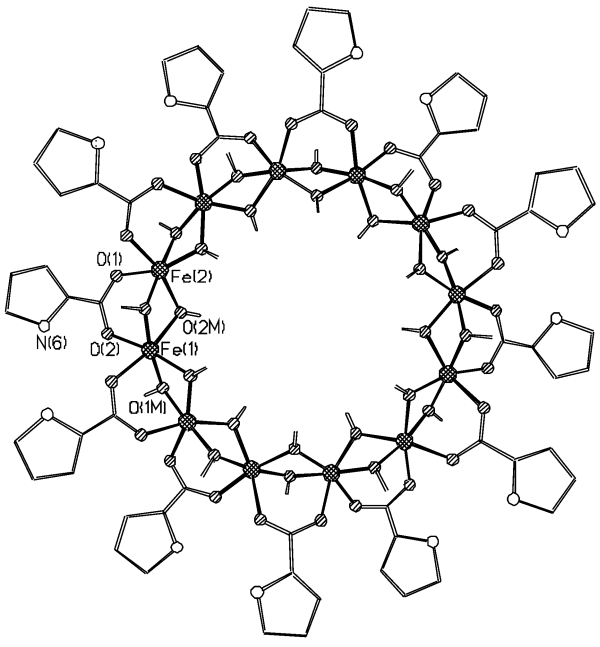

Fig. 1 The structure of the cation of **1** in the crystal. All unlabelled atoms are C-atoms.

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cm^{-1} depending on the correlation used. The electronic character of the carboxylate may be causing this slight increase in the magnitude of the exchange due to a zwitterion being involved here, rather than the more conventional carboxylates used previously. The change is very slight and the predominant superexchange path probably remains through the methoxide ligands.

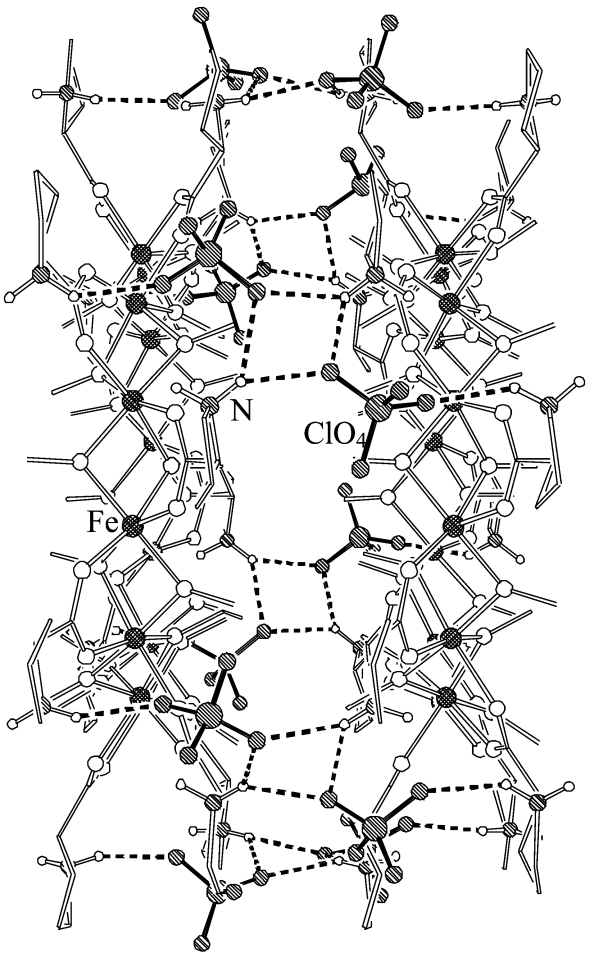

Fig. 2 The H-bonding of ClO_4 anions to $\{Fe_{12}\}$ wheels in **1** viewed perpendicular to the plane of the wheels. Fe and N atoms and atoms in ClO_4 units highlighted.

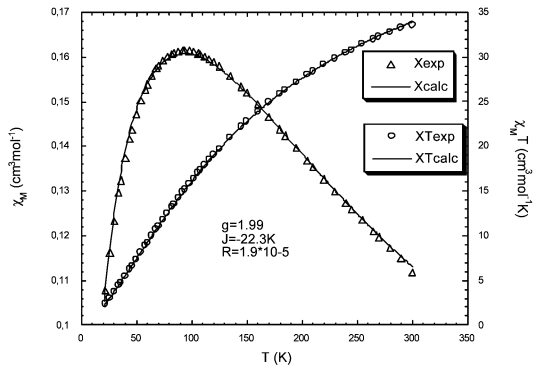

Fig. 3 The variable temperature behaviour of χ_m (△) and $\chi_m T$ (○) for **1**.

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Notes and references

† Anal. Calcd (Found) for $C_{84}H_{180}Cl_{12}Fe_{12}O_{96}$: C, 25.29(24.96); H, 4.65 (4.52); N, 4.21 (4.12)%.

‡ Crystal data for $C_{84}H_{180}Fe_{12}O_{48}$. 12 ClO_4, **1**: hexagonal, *P* 622, a = 25.0265(17), c = 7.7474(11) Å, V = 4202.3(7) Å^3, M = 3990, Z = 1 (the molecule lies on a six-fold axis and a two-fold axis), T = 150.0(2) K, $R1$ = 0.0722. Data collection, structure solution and refinement used SHELXTL.[9] Full details have been deposited and will be published later. CCDC 222686. See http://www.rsc.org/suppdata/cc/b3/b312947k/ for crystallographic data in .cif or other electronic format..

§ Variable temperature magnetic measurements on **1** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 100 G field. The data have been adjusted for the diamagnetism of the sample using Pascal's constants. The data were fitted to: $\chi_m T = \chi_{freeion} T(1+\Sigma_{n=1,11}(2u^n)+u^{12})$ where u is the Langevin function $JS(S+1)/T$ (J expressed in Kelvin).

¶ The DFT calculation used Gaussian 98,[11] with the hybrid B3LYP functional together with Ahlrich's TZV basis set. This has been found to give good numerical estimates of *J*-values in previous work.[12]

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