Alkali Metal Templated Assembly of an Iron Trigonal Prism

Jeremy C. Goodwin,[a] Daniel J. Price,[b] Annie K. Powell,*[c] and Sarah L. Heath*[a]

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A novel hexanuclear iron(III) complex $[Fe_6(C_7H_{11}NO_5)_6(\mu_2\text{-}O)_3Na][NO_3]\cdot18H_2O$ has been synthesised from *N*-(2-hydroxypropyl)iminodiacetic acid and has been shown by X-ray crystallography to possess a prismatic structure containing a sodium ion in the core.

Introduction

Metal-directed spontaneous self-assembly has been shown to be a versatile tool in the construction of some spectacular three dimensional polymetallic architectures.[1−6] In recent years there have been several examples of the use of alkali metals to template the assembly of two dimensional metallomacrocycles[7−10] and, more recently, a three dimensional cobalt/rhenium box.[11] In the case of the metallomacrocycles, the size of the macrocycle is controlled by the radii of the templating cation. For example, with sodium Fe_6,[8,9] Cu_6[7] and Mn_6[10] wheels have been synthesised, whereas caesium promotes the synthesis of an Fe_8 wheel.[9] The metallobox formed with cobalt and rhenium is also cation selective, preferentially binding caesium over potassium. The organisation of transition metal based motifs around templating cations offers prospects for the production of tailored molecular materials and the creation of size selective host species. We have been investigating the reactions of transition metals with molecules based on the ligand heidi [H_3heidi = $N(CH_2COOH)_2(CH_2CH_2OH)$] which we have reported previously in the synthesis of polyiron(III) oxyhydroxide clusters.[12] Here we report the alkali metal templated synthesis of a new, three dimensional architecture formed with the related ligand pida [H_3pida = *N*-(2-hydroxypropyl)iminodiacetic acid], which produces an arrangement where the iron atoms form a twisted trigonal prism.

Results and Discussion

The reaction of equimolar amounts of H_3pida [*N*-(2-hydroxypropyl)iminodiacetic acid] with hydrated iron(III) nitrate and sodium hydroxide in a threefold molar excess results in the formation of **1**. An X-ray analysis of **1** reveals the formation of a beautiful three dimensional Fe_6 cage structure assembled around a central sodium cation, $[Fe_6(C_7H_{11}NO_5)_6(\mu_2\text{-}O)_3Na][NO_3]\cdot18H_2O$, the cation of which is shown in Figure 1. The cage is formed through the interaction of three μ_2-oxide-bridged iron dimer units $\{LFe\}_2O$, linked by carboxylate bridges and templated about the central Na^+ through further carboxylate interactions. Each iron centre is in a distorted octahedral geometry consisting of a nitrogen, two carboxylate oxygens and a protonated alcohol oxygen from the ligand, a bridging μ_2-oxide and a bridging carboxylate from a symmetry related ligand. The iron-oxy core of **1** is shown in Figure 2a. The central sodium ion lies on a three fold rotation axis and is surrounded by a slightly distorted trigonal prism of oxygen atoms (Figure 2b) formed from the coordinating carboxylate oxygens of the ligand (O2, O2A, O2B, O7, O7A, O7B) with sodium to oxygen bond lengths of 2.444(3) and

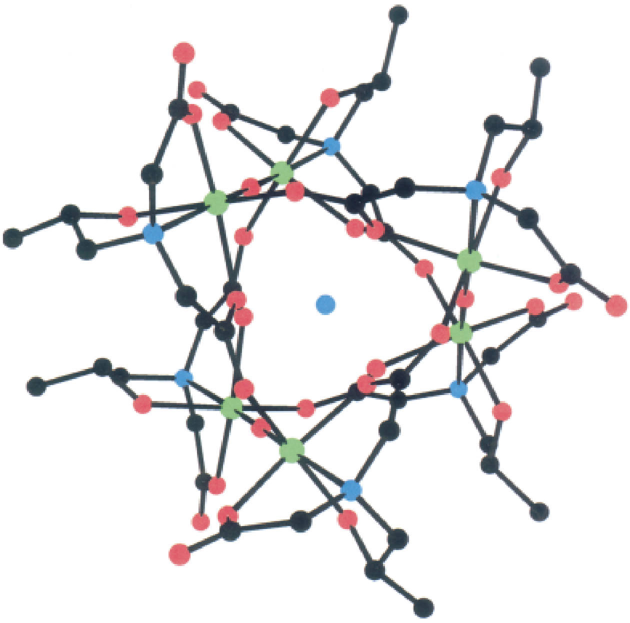

Figure 1. The cation of $[Fe_6(C_7H_{11}NO_5)_6(\mu_2\text{-}O)_3Na]^+$ **(1)** viewed down the *a* axis

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[a] Department of Chemistry, University of York,
Heslington, York, YO10 5DD, U.K.
Fax: (internat.) + 44-1904/432-516
E-mail: slh11@york.ac.uk, jcg105@york.ac.uk
[b] Department of Chemistry, University of Edinburgh,
West Mains Road, Edinburgh, EH9 3JJ, UK
Fax: (internat.) + 44-131/650-4743
E-mail: djp01@holyrood.ed.ac.uk
[c] Institut für Anorganische Chemie, Universität Karlsruhe,
Engesserstr. Geb. 30.45, D-76128 Karlsruhe, Germany
Fax: (internat.) + 49-721/608-8142
E-mail: powell@achibm6.chemie.uni-karlsruhe.de

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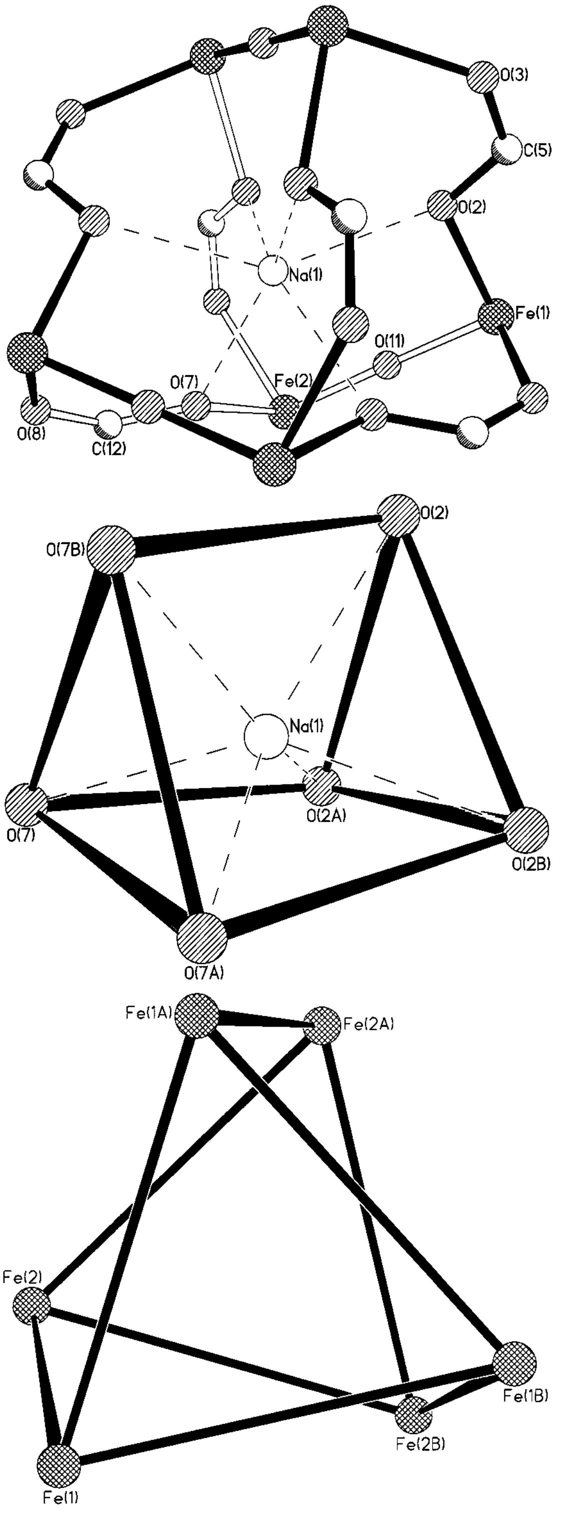

Figure 2. a) The central core of **1**; b) the coordination environment of the Na^+ cation; c) the distorted trigonal prismatic arrangement of the iron atoms

2.446(3) Å. The bridging μ_2-oxide oxygen (O11) is further away from the sodium at a distance of 2.986(3) Å. The volume of the oxygen prism, as calculated using the area of the smaller triangular face defined by O2, O2A, O2B, O7, is 14.11 Å^3.

The iron atoms are arranged in a much more distorted trigonal prism with the trigonal faces rotated at an angle of 27.3° to each other, as illustrated in Figure 2c. The iron atoms that form the trigonal faces of the prism are bridged by the carboxylate oxygens and are separated by distances of 5.362 Å (Fe2, Fe2A, Fe2B) and 5.365 Å (Fe1, Fe1A, Fe1B). The intra-trigonal interactions are afforded by an almost linear μ_2-oxide bridge [Fe1−O11−Fe2 = 179.1(2)°] and, consequently, the iron atoms have a much shorter separation, Fe1−Fe2 = 3.548 Å.

Reactions of equimolar equivalents of iron(III) nitrate and the barium salt of *N*-(2-hydroxypropyl)iminodiacetic acid with two equivalents of sodium hydroxide, results in the formation of the alkoxo bridged dimer $[Fe_2(C_7H_{10}NO_5)_2(H_2O)_2]$ **(2)**. The product is isostructural with the iron/heidi alkoxo bridged dimer synthesised by us previously.[12]

Preliminary magnetic studies have been performed on a powdered sample of **1** between 2 and 300 K in an applied field of 50 G. The susceptibility versus temperature is shown in Figure 3. It is clear from the product $\chi T(T)$ and the effective moment $\mu_{eff}(T)$ that **1** shows a very strong anti-ferromagnetic character, although the system does not follow a Curie-Weiss law. The room temperature net moment per iron ion is 1.83 μ_B which is much smaller than the expected value of 5.92 μ_B for isolated spin 5/2 ions implying a strong exchange coupling even at this temperature.

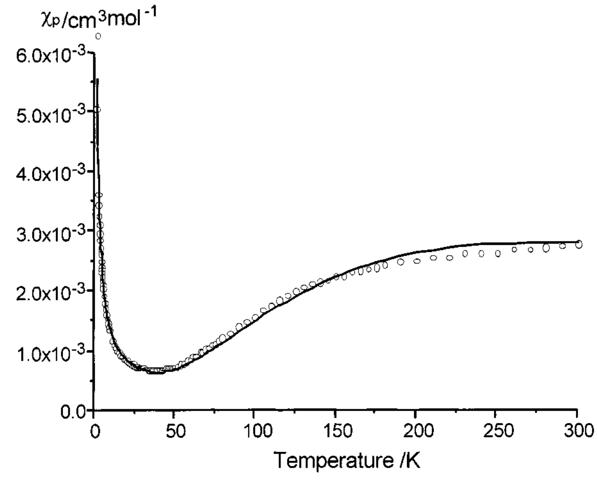

Figure 3. The molar susceptibility of **1** per unit dimer as a function of temperature (circles = experimental values, solid line = calculated for $J = -92 cm^{-1}$)

Although structurally **1** forms an Fe_6 cluster with two coupling pathways: *J* mediated by the μ_2-oxide bridge and *J'* through the carboxylate links, we expect $|J| >> |J'|$. Thus neglecting *J'* allows us to use a simple Heisenberg dimer model:[13]

$$\hat{H} = -2J\mathbf{S}_A \bullet \mathbf{S}_B$$

$$\chi_{dimer} = \frac{2Ng^2\mu_B^2}{k_BT}\frac{\left(e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x}\right)}{\left(1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}\right)}$$

where $x = J / k_BT$

The equation is often convoluted with a paramagnetic contribution from monomeric impurities (P) and a temperature independent component (C):[14]

$$\chi = (1 - P)\chi_{\mathrm{dimer}} + 2P\chi_{\mathrm{monomer}} + C$$

The iron(III) ion has a $^6A_{1g}$ ground term and should show Heisenberg behaviour with the temperature-independent contribution zero and the g value exactly 2.0. Fixing these and allowing the two other parameters to vary freely we obtain a good fit with $J = -82(1)\ \mathrm{cm^{-1}}$ and $P = 0.4\%$.

A better fit could be obtained by allowing a nonzero temperature-independent component. This gave $J = -92(1)\ \mathrm{cm^{-1}}$, $P = 0.3\%$ and $C = 0.00032\ \mathrm{cm^3{\cdot}mol^{-1}}$. In part, the problem to determine J precisely stems from the fact the J is so large, and even at room temperature the spins remain quite strongly coupled. It is interesting to note that the value of J is very sensitive to the value of C even though it is only a fraction of the estimated diamagnetic correction. Although temperature-independent behaviour may be caused by Van Vleck paramagnetism, in this case we believe that the constant (C) corresponds to a further diamagnetic correction since Pascal's constants are only approximate and no allowance had been made for the contribution of the sample capsule. We therefore conclude that the value of J for **1** is $-92(1)\ \mathrm{cm^{-1}}$. This large value of J is similar to those found in other materials where a near linear Fe−O−Fe exchange pathway is present.[15]

Conclusion

The small cavity size generated by the oxygen prism in **1** (14.11 Å^3) means that the cluster should only form in the presence of metal cations with an ionic radius similar to that of Na^+. Preliminary studies show that this may well be the case, with infrared evidence indicating that it is possible to synthesise the cluster with Ca^{2+} and Eu^{3+} templating the assembly but not with K^+, Mg^{2+} and Li^+. Hexamer formation was confirmed by the occurrence of the Fe−O−Fe asymmetric stretch at 845 cm^{-1} and the general similarity of the fingerprint region of the spectrum (1600−400 cm^{-1}). Presumably, the extra positive charge introduced by these cations will be compensated for by the presence of an additional one or two nitrate anions. The encapsulation of an ion such as Eu^{3+} or Tb^{3+} offers the possibility of creating luminescent species with long lifetimes. We are currently undertaking further characterisation of these reactions and their products.

Experimental Section

General Remarks: The magnetic behaviour of a powdered sample of **1** was measured on a Quantum Design MPMS SQUID magnetometer between 2 and 300 K in an applied field of 50 G. The molar susceptibility was corrected for diamagnetism using a value of $\chi_{\mathrm{dia}} = -890 \times 10^{-6}\ \mathrm{cm^3{\cdot}mol^{-1}}$ determined from Pascal's constants. Single crystal X-ray data were collected on a Bruker SMART-CCD equipped with an Oxford Cryostream low temperature device.

***N*-(2-hydroxypropyl)iminodiacetetic Acid (pida):** DL-1-Amino-2-propanol (7.5 g, 0.1 mol), ethylbromoacetate (33.4 g, 0.2 mol) and potassium hydrogen carbonate (20.0 g, 0.2 mol) were refluxed in EtOH (50 cm^3) for 24 hours. The solid KBr formed was filtered off and the solvent removed in vacuo. The resultant pale yellow oil was refluxed in H_2O (80 cm^3) and 37% HCl (2 cm^3) for 24 hours. The solution was then reduced down to 30 cm^3 and placed in the fridge. In four days white crystals of $C_7H_{13}NO_5$ (6.12 g, 32%) formed. − $C_7H_{13}NO_5$ (191.18): calcd. C 43.98, H 6.85, N 7.33; found C 43.73, H 7.15, N 7.33. − ^1H NMR (250 MHz, D_2O): δ = 1.20 (d, 3 H, CH_3), 3.30 (m, 2 H, CH_2), 4.05 (s, 4 H, CH_2), 4.15 (m, 1 H, CH).

Pida Hexamer, $[Fe_6(C_7H_{11}NO_5)_6(\mu_2\text{-}O)_3Na][NO_3]\cdot 18H_2O$ (1): A solution of *N*-(2-hydroxypropyl)iminodiacetic acid (2.5 mmol) and sodium hydroxide (7.5 mmol) in water (10 cm^3) was added slowly with stirring to a solution of hydrated iron(III) nitrate (2.5 mmol) in water (10 cm^3). The pH of the resultant red solution was 2.47. Red hexagonal crystals of **(1)** formed in 59% yield after three weeks. − $C_{42}H_{104}Fe_6N_7NaO_{54}$ (1927.40): calcd. C 26.15, H 5.43, Fe 17.37, N 5.08; found C 25.94, H 4.97, Fe 17.45, N 5.24.

Pida Dimer, $[(FeC_7H_{10}NO_5)_2]\cdot 6H_2O$ (2): A solution of the barium salt of *N*-(2-hydroxypropyl)iminodiacetic acid (2.5 mmol) and sodium hydroxide (5 mmol) in water (10 cm^3) was added slowly with stirring to a solution of hydrated iron(III) nitrate (2.5 mmol) in water (10 cm^3). The pH of the resultant green solution was 2.54. Green crystals of **2** formed in 32% yield after three months. − $C_{14}H_{32}Fe_2N_2O_{16}$ (596.12): calcd. C 28.21, H 5.41, Fe 18.74, N 4.70; found C 28.14, H 5.21, Fe 18.61, N 4.94.

X-ray Crystallographic Study

Crystal Data for 1: $[Fe_6(C_7H_{11}NO_5)_6(\mu_2\text{-}O)_3Na][NO_3]\cdot 18H_2O$, red hexagonal block of dimension 0.45 × 0.33 × 0.31, M = 1927.4, trigonal, space group $P6(3)$, $Z = 2$, $a = b = 14.1386(7)$ Å, $c = 22.3076(16)$ Å, $U = 3861.9(4)$ Å^3, $D_c = 1.658\ \mathrm{g\ cm^{-3}}$, $T = 150(2)$ K, $F(000) = 2004$, Mo-K_α radiation (λ = 0.71073), $\mu = 1.217\ \mathrm{mm^{-1}}$, 28695 reflections measured in the range $2.47° \le \theta \le 28.29°$, unique 6173 ($R_{\mathrm{int}} = 0.0514$) which were used in all calculations. The structure was solved by direct methods and refined using full-matrix least-squares on F^2 to $R1 = 0.0543$, $S = 0.991$, for 5145 reflections with $F > 4\sigma(F)$ and 368 refined parameters, $wR2$ (all data) = 0.1411.

Crystal Data for 2: $Fe_2C_{14}H_{32}N_2O_{16}$, green needles of dimension 0.35 × 0.06 × 0.05, M = 596.12, monoclinic, space group $C2/c$, $Z = 4$, $a = 14.0792(15)$ Å, $b = 11.6006(12)$ Å, $c = 14.5675(12)$ Å, $\beta = 97.415(2)$, $U = 2359.4(4)$ Å^3, $D_c = 1.678\ \mathrm{g\ cm^{-3}}$, $T = 150(2)$ K, $F(000) = 1240$, Mo-K_α radiation (λ = 0.71073 Å), $\mu = 1.309\ \mathrm{mm^{-1}}$, 6203 reflections measured in the range $2.28° \le \theta \le 25.00°$, 2079 unique ($R_{\mathrm{int}} = 0.091$) which were used in all calculations. The structure was solved by direct methods and refined using full-matrix least-squares on F^2 to $R1 = 0.0541$, $wR2 = 0.1396$, $S = 1.070$, for 1698 reflections with $F > 4\sigma(F)$ and 188 refined parameters, $wR2$ (all data) = 0.1562.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137361 (**2**), CCDC-137362 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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