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A bioinspired approach to control over size, shape and function of polynuclear iron compounds

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Contents

Abstract

Transition metal centres, clusters and aggregates are common in biological systems and fulfil a variety of functions. Nature has the ability to tailor the properties of such species by controlling the molecular and supramolecular environment of the metal centres through the influence of additional structure-directing chemical species. We have been inspired by this to develop synthetic methods which explore the effects of such templating species on the structure and properties of coordination compound aggregates. We have found that chelating ligands can be used to manipulate the hydrolysis of transition metal ions and direct

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structure and properties both at the molecular and supramolecular levels. Results for a series of iron(III) compounds formed with ligands based around the iminodiacetate moiety are presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Biomimetic chemistry; Polynuclear; Iron compounds; Magnetic materials

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1. Introduction

The synthesis of tailored compounds is an area of much interest to many chemists. For synthetic coordination chemists this involves adapting the local structure around metal ions to give fundamental building blocks which can be combined in a variety of ways to yield materials with specific properties. In practice, we are still at a stage where we have rather little control over these two variables, and a principle of post-rationalisation operates, whereby we determine the structure and properties of new compounds and then try to understand how these arise. Another approach to creating tailored materials is to seek inspiration from nature. In biological systems, chemistry is performed in a highly controlled fashion. Metal centres in different coordination environments are used to catalyse reactions, transport and store small gas molecules like oxygen, perform electron transfer reactions, and are also the building blocks for mineralised species [1]. These biominerals perform various functions such as providing structures like shells, teeth and bones, and acting as metal stores in metal ion homeostasis, and also providing means for sensing fields such as the gravitational and magnetic fields of the earth [2]. In Norwich we have taken inspiration from this astonishing versatility in controlling structure and function and have explored ways of tailoring materials using the natural hydrolysis of metal ions as a basic chemical driving force. Hydrolysis is the result of the activation by the metal ion of water ligands, which lose protons and tend to form hydroxide and oxide bridges between metal centres. Initially, this gives rise to oligomeric species, but these aggregate further until eventually an extended mineral structure results (Scheme 1). For many metal ions, hydrolysis leads to the formation of hydroxides which can then evolve into oxyhydroxides and oxides, displaying a variety of structural types and properties.

$$\{M(H_2O)_6\}^{\pm q} \rightleftharpoons \{M_x(O)_y(OH)_z(H_2O)_p\}^{\pm a} \rightleftharpoons M(OH)_q$$

Scheme 1.

Taking the specific case of iron, in the natural environment where oxidising conditions prevail, the hydrolysis reaction drives towards the production of iron(III) oxides, with α-Fe_2O_3 representing the ultimate stable form [3]. This poses a challenge for biological systems which have evolved using an extensive iron biochemistry developed originally when the environment was reducing and Fe(II) rather than Fe(III) the common oxidation level. In order to survive, biological systems, operating in a rich aqueous environment, have developed chemical means of controlling the hydrolysis of iron. In fact, biology has also developed intricate ways of influencing the precipitation of hydrolytic iron species, thereby directing the phase and form of a variety of biominerals. Our synthetic strategy has been to emulate these processes using chelating ligands to modify the natural hydrolysis reaction, which we can now write according to Scheme 2 [4].

$$\{FeL_m\}^{\pm q} + xsH_2O \rightleftharpoons \{Fe_xL_n(O)_y(OH)_z(H_2O)_p\}^{\pm a} \rightleftharpoons Fe(OH)_3$$

Scheme 2.

The chelating ligands enable us to introduce control over the metal environment through both direct interactions which can alter, for example, redox potential, Lewis acidity of the metal ion, accessibility of the metal site to other substrates, electronic structure and through supramolecular effects which can be mediated by hydrophilic, hydrophobic and π-stacking interactions. This mimics the strategy used by nature to effect similar controls over metal centres. As can be seen in Scheme 2, it should be possible to isolate compounds corresponding to the extreme left hand side of the equilibrium, where the coordination sphere of the metal is exclusively occupied by donor atoms from the ligands through to the final hydroxide hydrolysis product at the extreme right hand side of the equilibrium where it might be possible to detect the influence of the ligands by studying the phase and form of this product. The intermediate stages, where hydrolytic species which are still coordinated by the ligands are found, give us the most insight into how these ligands can be used to tailor properties.

In this article the structures and properties of a selection of hydrolytic intermediates formed starting with iron(III) salts in the presence of a variety of chelating ligands, L, in aqueous media corresponding to a general formula of $\{Fe_xL_n(O)_y(OH)_z(H_2O)_p\}^{\pm a}$ which have been synthesised in Norwich are reviewed. The purpose of using iron(III) is to create new molecular-based magnetic materials. In cases where the materials produced are aggregated cluster species there is the possibility of producing unusual properties, such as quantum tunnelling of spin states [5], as a result of boundary effects in 'zero-dimensional' systems [6], that is, materials which occupy an intermediate area between the molecular and the infinite. The iron storage protein, ferritin, provides a famous example of such a system from the natural world. When loaded with Fe(III), the protein can contain up to about 4000 iron centres adopting the form of a nanoparticle displaying superparamagnetic properties which have been extensively investigated by workers such as St. Pierre et al. [7,8], as well as the more recently described hysteresis and possible quantum tunnelling effects [9]. Here again, nature can provide an inspiration for producing novel materials, in this case possessing magnetic properties which could find applications in fields such as quantum computing.

1.1. *Choice of structure-directing ligands*

As stated above, the build up of cluster species will be controlled to some extent by the properties of the chelating ligand. The previous innovative research in the area by the groups of Lippard [10,11] and Wieghardt [12,13] resulted in the isolation and characterisation of a number of oxo and hydroxo linked Fe(III) aggregates. These are the products of hydrolytic reactions in the presence of chelating or bridging ligands such as triazacyclononane (tacn) and various simple carboxylates. While these aggregates are of inherent interest in terms of their structures and properties, it has proven difficult to adopt a rational approach to understanding the underlying hydrolysis reactions. This is partly a consequence of the difficulty of working in aqueous media, and in some cases a result of the limitations imposed by the inclusion of bridging carboxylato groups. In most cases, the reactions have been performed with only small amounts of water present and often using preformed aggregates such as $[Fe_3O(RCOO)_6(H_2O)_3]^+$ as building blocks [14]. In contrast, our approach is designed to allow the hydrolytic aggregate to build-up in aqueous solution and use additional ligand species to trap species corresponding to those indicated in Scheme 2. We have chosen chelating ligands based around the iminodiacetic acid molecule, $HN(CH_2COOH)_2 = H_2ida$. H_2ida can act as a tridentate ligand and the characterisation of the compounds formed with iron(III) illustrates some of the factors which direct structure and properties. The H_2ida molecule can also be modified and the compounds formed between iron(III) and these new ligands allow us to begin to understand the ways in which it should be possible to tailor molecular and supramolecular effects.

All the compounds described here have been synthesised and structurally characterised using single-crystal X-ray diffraction at Norwich.

2. Iron compounds formed with ligands based on iminodiacetic acid

2.1. Compounds formed with iron(III) and the ligand H_2ida

When excess ligand is supplied to the system (Fe:L = 1:3, for example) a mononuclear complex anion $[Fe(ida)_2]^-$ results (Fig. 1) [15] corresponding to the $[FeL_x]^-$, $x = 2$, species on the extreme left hand side of Scheme 2 for this system. The structure of this compound reveals that the tridentate ida^{2-} ligand coordinates in a *fac* configuration. As expected, the iron(III) is high spin and the compound acts as a simple paramagnet with a room temperature (r.t.) moment of 5.9 BM On raising the pH of solutions containing this complex there is a colour change from yellow/green to deep red, characteristic of the presence of an $[Fe{-}O{-}Fe]^{4+}$ centre. X-ray structure analyses reveal the presence of the complex anion $[\{Fe(ida)_2\}_2O]^{4-}$ (Fig. 2) isolable with a variety of suitable counterions such as K^+, Na^+, and $\{enH_2\}^{2+}$ [15]. This represents the hydrolytic intermediate species $\{Fe_2L_4(O)\}^{4-}$ in Scheme 2. In this species both iron centres are hexacoordinate which means that on each one ida^{2-} ligand is tridentate, while the other is only bidentate leaving a free carboxylate arm on each side of the unit. Since the oxide bridge between the two iron centres must originate from a coordinated water molecule we can propose either an S_N1 or S_N2 mechanism where the intermediate species, $\{FeL_2(H_2O)\}^-$, is either five- or seven-coordinate depending on whether the coordination of a water molecule occurs before or after the carboxylate arm detaches from the metal site. In any case, this oxo-bridged moiety proves highly resistant to further hydrolysis, presumably because of the inaccessibility of the metal site to water ligands. There are many examples of dinuclear compounds containing the $[Fe{-}O{-}Fe]^{4+}$ unit [16] and these always display strongly antiferromagnetically coupled high spin iron(III)

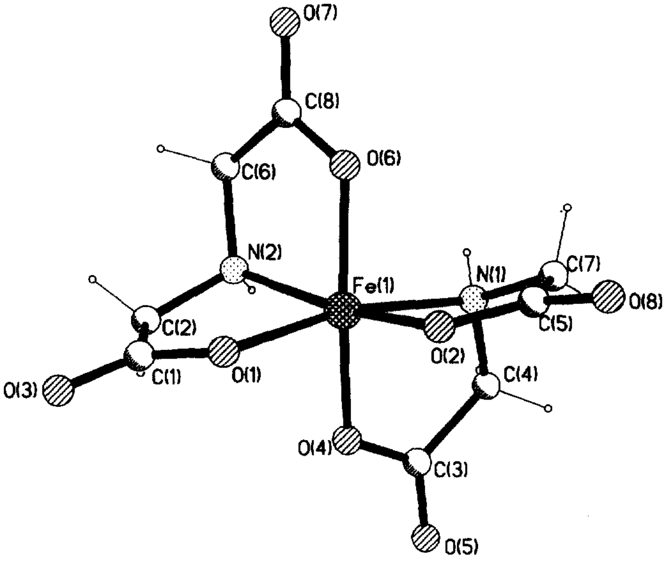

Fig. 1. The molecular structure of $[Fe(ida)_2]^-$.

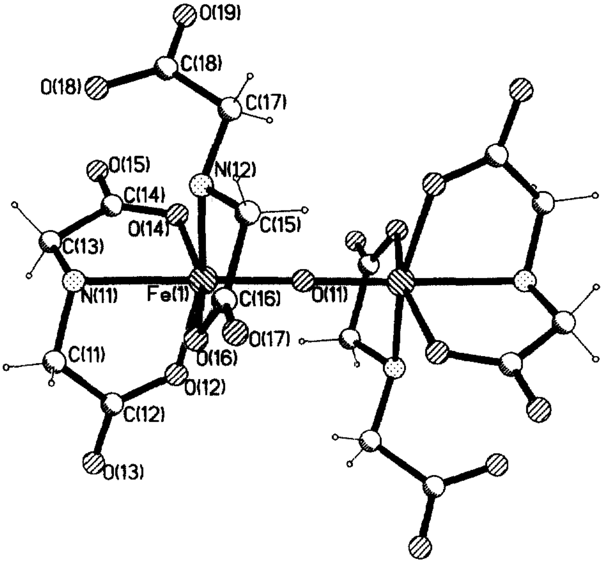

Fig. 2. The molecular structure of $[\{Fe(ida)_2\}_2O]^{4-}$.

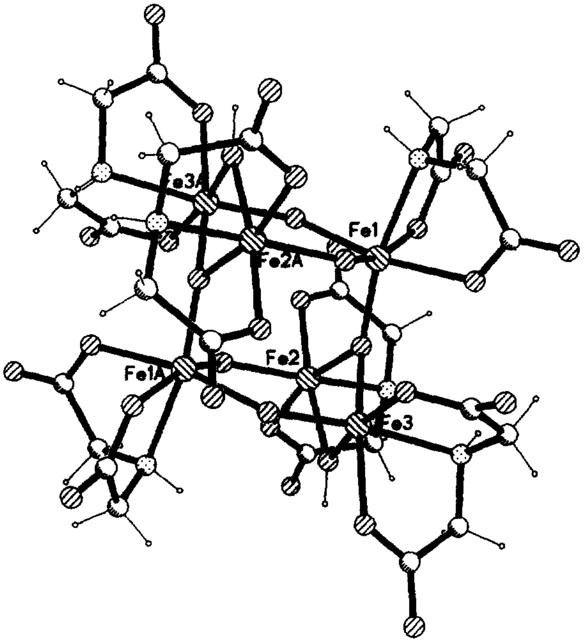

Fig. 3. The molecular structure of $[Fe_6(OH)_6(O)_2(ida)_6]^{4-}$.

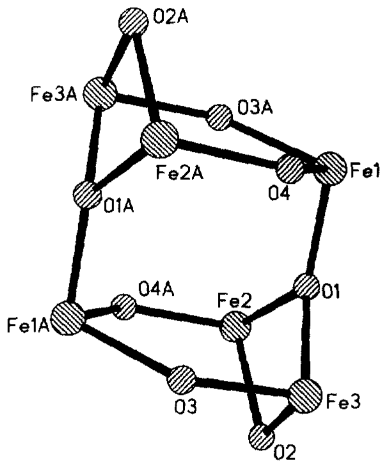

Fig. 4. The structure of the core of $[Fe_6(OH)_6(O)_2(ida)_6]^{4-}$.

centres as is found to be the case here, where r.t. moments of about 2 BM have been measured and 2 J values in the region of 140 cm^{-1} have been used to fit variable temperature susceptibility data [15].

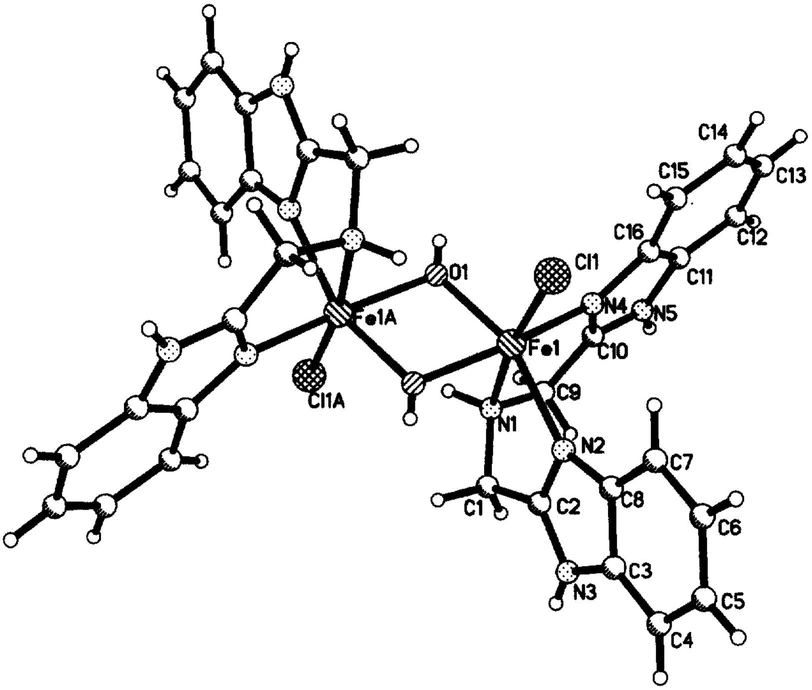

Fig. 5. The molecular structure of $[\{Fe(bba)(OH)(Cl)\}_2]^{2+}$.

In order to build larger aggregates it is necessary to provide more sites on the iron centres for water molecules to coordinate. This can be achieved quite simply by reducing the amount of ida^{2-} available in solution. Thus, with Fe:L = 1:1 the hexanuclear cluster anions, $[Fe_6(OH)_6(O)_2(ida)_6]^{4-}$ (Fig. 3) can be isolated and structurally characterised with K^+, Na^+, and $\{enH_2\}^{2+}$ counterions [15,17]. These aggregates correspond to the intermediate $\{Fe_6L_6(OH)_6(O)_2\}^{4-}$ and display an iron oxyhydroxide core structure (Fig. 4) in which the arrangement of the iron centres can be described as a distorted trigonal antiprism (i.e. pseudo-octahedral) with distances between the metals for the highly distorted octahedron in the range of 2.93–4.66 Å. The iron centres are connected by three types of bridge. The most obvious triangles in the trigonal antiprism are the pair containing the famous

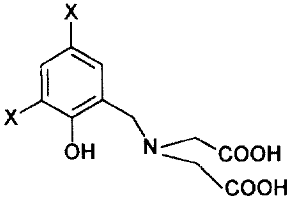

Fig. 6. $RN(CH_2COOH)_2$ ligands based on H_3hda, X = *t*-Bu, Me, Cl.

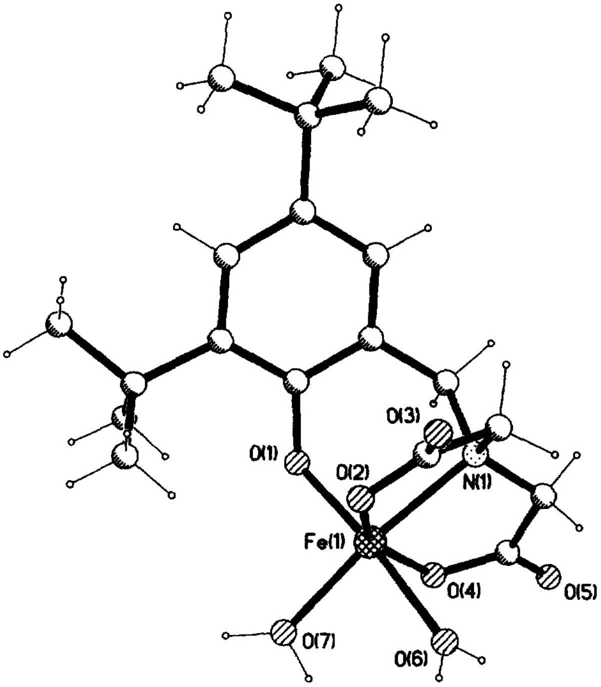

Fig. 7. The molecular structure of [Fe(buhda)(H_2O)$_2$].

$\{Fe_3O\}^{7+}$ motif [18], in which three iron centres are linked by an oxide ion (O1 and O1A). Here the triangles are isosceles rather than equilateral as a result of a short Fe–Fe distance along the base of the triangle where further bridging between the two irons is provided by a hydroxide ion (O2 and O2A). The apex of each triangle is linked by two hydroxide ions to the two irons of the base of the second triangle (O3, O3A and O4, O4A). This leaves three coordination sites on each iron centre which are occupied by facially coordinating ida^{2-} ligands. Indeed, it is this mode of coordination which makes this three-dimensional arrangement of the iron centres possible. The precursor to this aggregate could be a species such as $\{FeL(H_2O)_3\}^+$ where the three orthogonal water ligands are ideally disposed to produce this structure. The different pairwise connections amongst the iron centres leads to spin frustration effects which are manifest in the magnetic behaviour of the material. In high spin iron(III) systems displaying cooperative magnetic phenomena the predicted coupling of pairs of iron centres is always antiferromagnetic, and that is found to be the case here where the r.t. moment per Fe^{3+} is reduced from the expected 5.92 BM to about 4.0 BM [17]. However, on decreasing the temperature it is observed that the moment increases rather than decreases as would be expected for an antiferromagnet. This is the result of unequal magnitudes of coupling between pairs of iron centres which leads to uncompensated spin density and in this case a ground state spin of $S = 5$ rather than the predicted $S = 0$ for the antiferromagnetic limit [17,19]. In this way, it has been possible to produce a three-dimensional iron oxyhydroxide particle with a total spin of $S = 5$. Further analysis of the magnetic data reveals that the individual particles in the crystal structure are also magnetically coupled. There is a weak but detectable ferromagnetic coupling of the aggregates which opens up the possibility of engineering supramolecular effects in order to enhance such interactions and produce arrays of ferromagnetically coupled high spin-state clusters. This implies that there are two synthetic targets: to create aggregates with the highest ground state spins possible, which in the case of high spin Fe(III) equates to optimising spin frustration effects, and to engineer the supramolecular effects to optimise ferromagnetic coupling between these clusters.

2.2. New ligands based on H_2ida

The ligand set provided by H_2ida can be modified at the carboxylic acid groups or else a further arm can be attached to the imine N to create a tetradentate ligand.

2.2.1. Interaction of iron(III) with the ligand (bis)benzimidazolmethylamine, bba

The tridentate ligand (bis)benzimidazolmethylamine, bba, can be synthesised by reacting H_2ida with 1,2 phenylenediamine [20], thus, replacing the carboxylic acid donors with benzimidazole groups and creating a neutral ligand. When similar

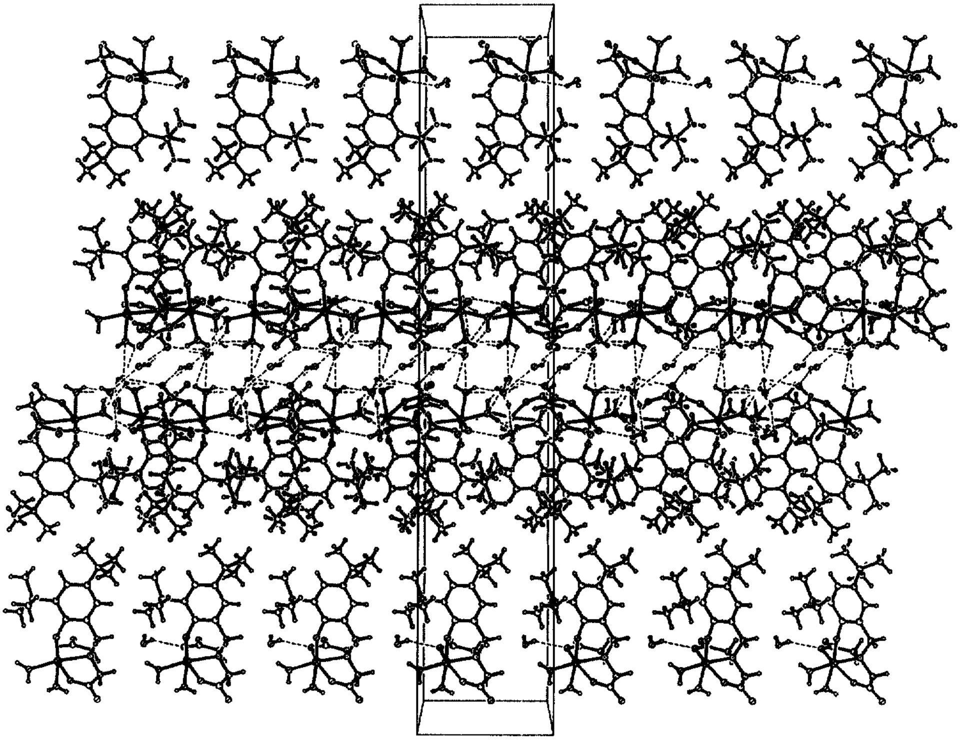

Fig. 8. The packing in $[Fe(buhda)(H_2O)_2]\cdot 3.5H_2O$ showing hydrophobic and hydrophilic regions.

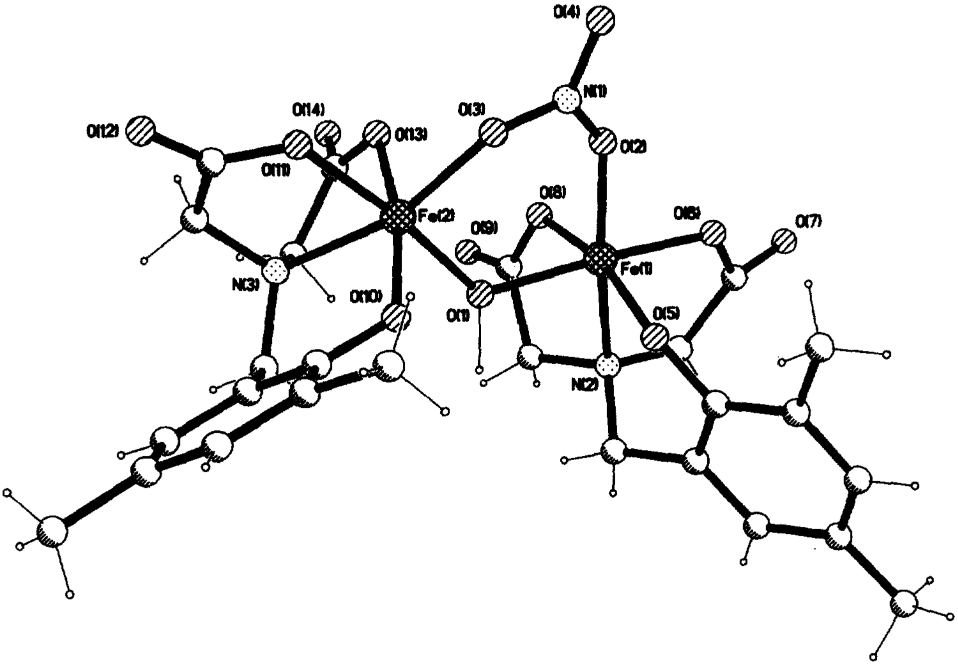

Fig. 9. The molecular structure of $[Fe_2(mehda)_2(OH)(NO_3)]^{2-}$.

reaction conditions to those used in the synthesis of the hexanuclear Fe/ida aggregates are employed dinuclear iron(III) species result which are dianions of formula $[\{Fe(bba)(OH)(X)\}_2]^{2+}$, where X^- derives from the iron(III) starting material. The structure of the dication where X = Cl is shown in Fig. 5 [21]. The effect of introducing much larger and softer donors in place of the carboxylates is to create a pocket around the di-iron unit. This appears to have two consequences.

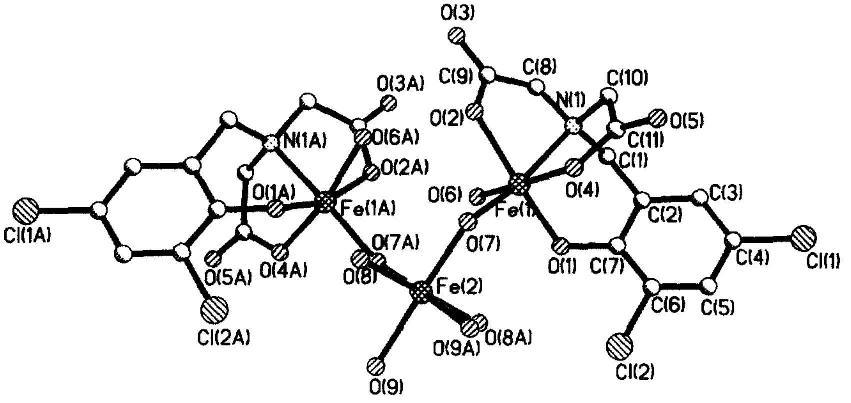

Fig. 10. $[\{Fe(chda)(H_2O)\}_2\{Fe(OH)_2(H_2O)_4\}]^+$.

Firstly, the ligands seem to stabilise the rather rare $[Fe_2(OH)_2]^{4+}$ unit. Although there are some examples of two iron centres being connected by diol bridges in the literature this is nowhere near as ubiquitous as the related $[Fe-O-Fe]^{4+}$ motif. Secondly, the steric bulk of the bba ligands makes it difficult for further iron(III) centres to interact with this unit. We can see that the triangular units in the hexanuclear Fe/ida compounds might derive from such diol bridged units by the interaction of a further iron centre with one of the hydroxides, which then is activated and loses a proton to give the μ_3-O bridge. A further point here is that by removing the charge on the ligand and increasing the positive charge on the aggregate it would seem that the competition at the sixth site in the coordination sphere of each iron(III) centre is won by available negatively charged ligands such as chloride rather than water molecules. Thus, the intermediate species synthesised here corresponds to $\{Fe_2L_2X_2(OH)_2\}^{2+}$.

2.2.2. *$RN(CH_2COOH)_2$ ligands*

Replacement of the imine proton by various donating arms leads to tetradentate ligands derived from H_2ida, of the general formula $RN(CH_2COOH)_2$. These ligands now leave only two vacant coordination sites on a hexacoordinate iron(III) centre, which in the first instance implies that aggregates will be constrained to growth in just two dimensions unless the oxide bridges become μ_4 or μ_6 [4].

It is also possible to use R groups on the $RN(CH_2COOH)_2$ ligands which can direct supramolecular effects as, for example, in the cases where the donor on R is a substituted phenol (Fig. 6). These ligands are all derived from (hydroxybenzyl)iminodiacetic acid, H_3hda, with substituents placed at the 4 and 6 positions on

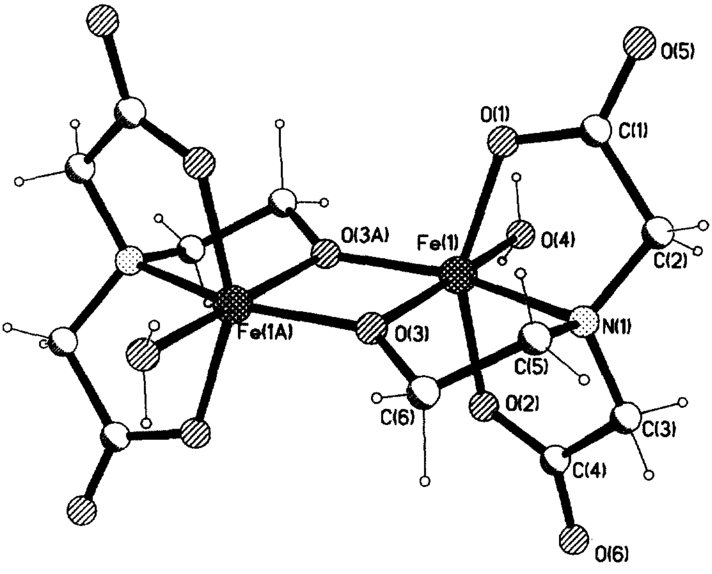

Fig. 11. The molecular structure of $[\{Fe(heidi)(H_2O)\}_2]$.

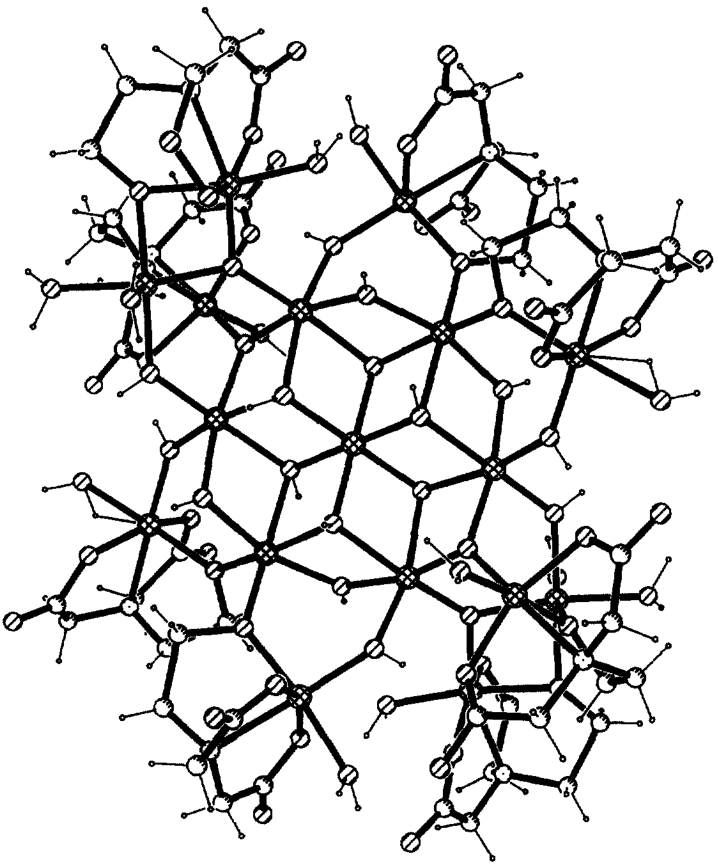

Fig. 12. $[\{Fe(heidi)(H_2O)\}_6\{Fe(heidi)(O)(H_2O)\}_2\{Fe(O)(OH)(H_2O)_2\}_2\{Fe_7(OH)_{14}\}]^{3+}$.

the phenyl ring. By varying the nature of the substituent we can change the long range interactions in the lattice as well as the acidity of the phenol –OH group. The compounds formed with three examples of these ligands illustrate the way in which aggregated species might build up and the way in which supramolecular interactions can be varied. The nature of the ligands is such that it becomes possible to make divisions between 'organic' and 'inorganic' regions of the structure, again paralleling the compartmentalisation possible in biological systems.

2.2.3. Compounds formed with iron(III) and $RN(CH_2COOH)_2$ ligands

With the ligand 4,6-$(t\text{-Bu})_2$-hda, H_3buhda, neutral mononuclear iron complexes of the formula $[Fe(buhda)(H_2O)_2]$ can be isolated [22]. From the molecular structure (Fig. 7) it can be seen that the complex divides into two regions: a rather hydrophobic portion corresponding to the phenyl group and its substituents, and a hydrophilic area around the iron centre with the carboxylate, phenolate and water ligands. A view of the packing in the crystal structure (Fig. 8) reveals that the individual molecules are aligned so that the hydrophobic portions interact with hydrophobic portions of other complexes and the hydrophilic areas are arranged to optimise hydrogen bonding among neighbouring molecules which is mediated by lattice water. Thus, there is a clear division of the structure into organic strips and inorganic aqueous 'streams'.

If the substituents on the phenyl ring are altered so that there are two methyl groups at the 4 and 6 positions to give the ligand 4,6-Me$_2$-hda, H$_3$mehda, then it becomes possible to isolate a dinuclear species, $[Fe_2(mehda)_2(OH)(NO_3)]^{2-}$ from solutions containing the ligand and iron(III) nitrate [22]. The molecular structure of this (Fig. 9) reveals that the two iron centres are linked by one hydroxide and one nitrate anion, although presumably a diol bridge would also be possible in the absence of nitrate. This observation of a bridging nitrate is rather unusual but might give insights into the way in which various anions can direct the phase of hydrolytic minerals. Such intermediates might also be important in aggregation processes where bridging anions can perhaps serve to stabilise Fe–OH–Fe linkages.

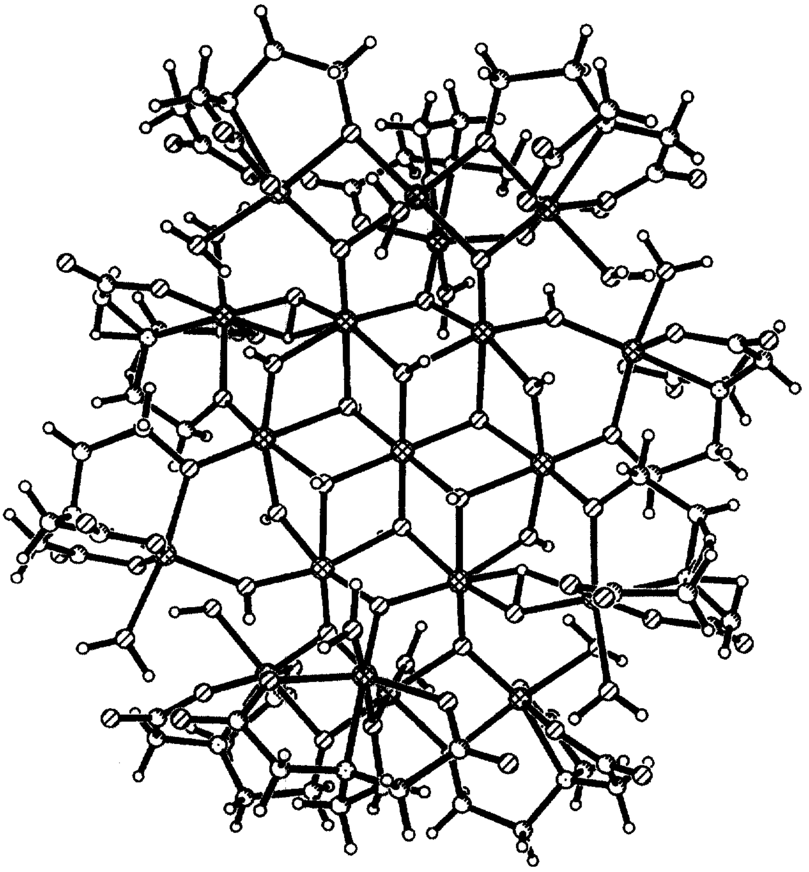

Fig. 13. $[\{Fe(heidi)(H_2O)\}_8\{Fe(heidi)(O)(H_2O)\}_2\{Fe(O)_2(H_2O)\}_2\{Fe_7(OH)_{14}\}]^+$.

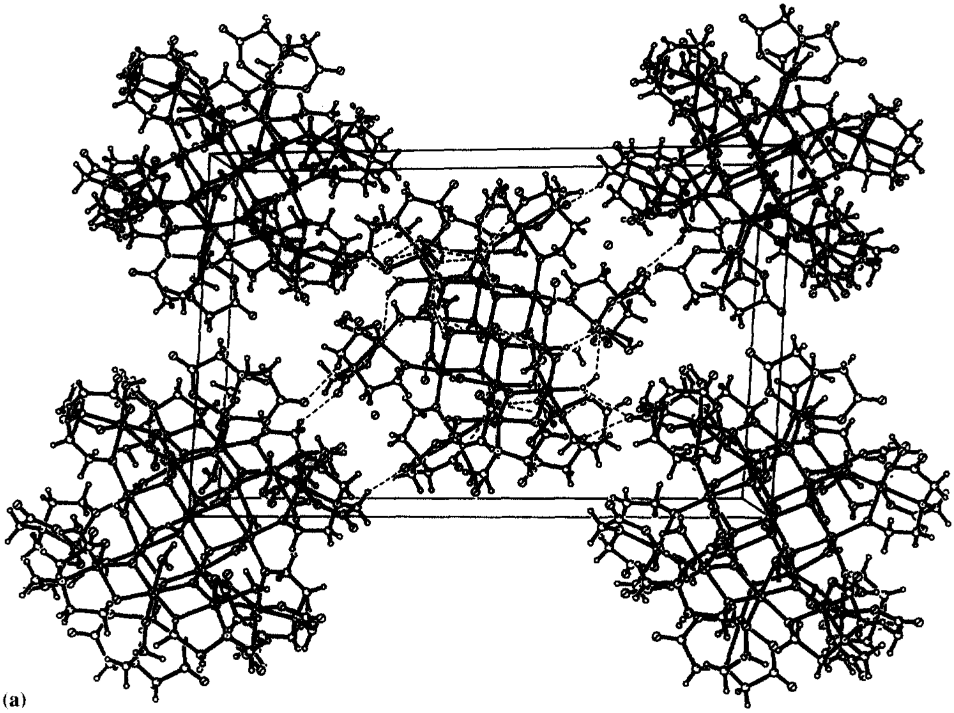

Fig. 14. The packing of the Fe_{17} and Fe_{19} clusters showing (a) the two interpenetrating lattices of clusters and (b) some of the hydrogen bonding pathways connecting the clusters.

A celebrated example of the effect of anions on structure is the formation of akaganéite, β-Fe.O.OH, which only occurs in the presence of chloride ions. This oxyhydroxide phase is something of a nuisance to car owners who live at the seaside and anyone involved in maritime activities since it is an even more problematic form of rust than the more normal lepidocrocite, γ-Fe.O.OH, having a structure which gives rise to a rather brittle solid, thereby exacerbating the effects of corrosion in such environments [3].

In the case where the susbstituents on the phenyl ring are two chlorines as in 4,6-Cl_2-hda, H_3chda, a trinuclear compound forms of the formula $[\{Fe(chda)(H_2O)\}_2\{Fe(OH)_2(H_2O)_4\}]^+$ (Fig. 10) [22]. This corresponds to an example of a hydrolytic intermediate where iron centres are either associated with the structure-directing ligand or else form part of the 'inorganic' hydrolytic aggregate. That is, the two $\{Fe(chda)(H_2O)\}$ units belong to the structure-directing portion associated with the ligand, while $\{Fe(OH)_2(H_2O)_4\}^+$ is wholly inorganic. A further activation of the coordinated water ligands on this unit to yield hydroxides or oxides can be envisaged which would lead to the formation of larger aggregates.

In these examples it has been possible to observe three species which are likely to be important precursors to larger aggregates and ultimately the hydrolytic mineral phase of the extreme right hand side of Scheme 2. These correspond to $\{FeL(H_2O)_2\}$, $\{Fe_2L_2X(OH)\}^{2-}$ (for $X = NO_3$) and $\{Fe_3L_2(H_2O)_6(OH)_2\}^+$.

2.2.4. Larger aggregates

The ligands $RN(CH_2COOH)_2$, where $R = CH_2CH_2OH$, CH_2COOH and $CH_2C(O)NH_2$, can be used to trap larger iron oxyhydroxide aggregates [23,24]. The ligand where $R = CH_2CH_2OH$, hydroxyethyl(iminodiacetic) acid, H_3heidi, has produced materials which we have been able to characterise and study in the greatest depth as described below.

2.2.5. Compounds with iron(III) and H_3heidi

The interaction of iron(III) with H_3heidi in Fe:L ratios of 1:1 results in the formation of the neutral dinuclear species $[\{Fe(heidi)(H_2O)\}_2]$ (Fig. 11) [23–25]. As in the case of the phenol donors described above, the OH group of the alcohol arm becomes deprotonated in this compound, but the resulting alkoxide bridges the two iron centres rather than acting as a simple monodentate arm. The coordination

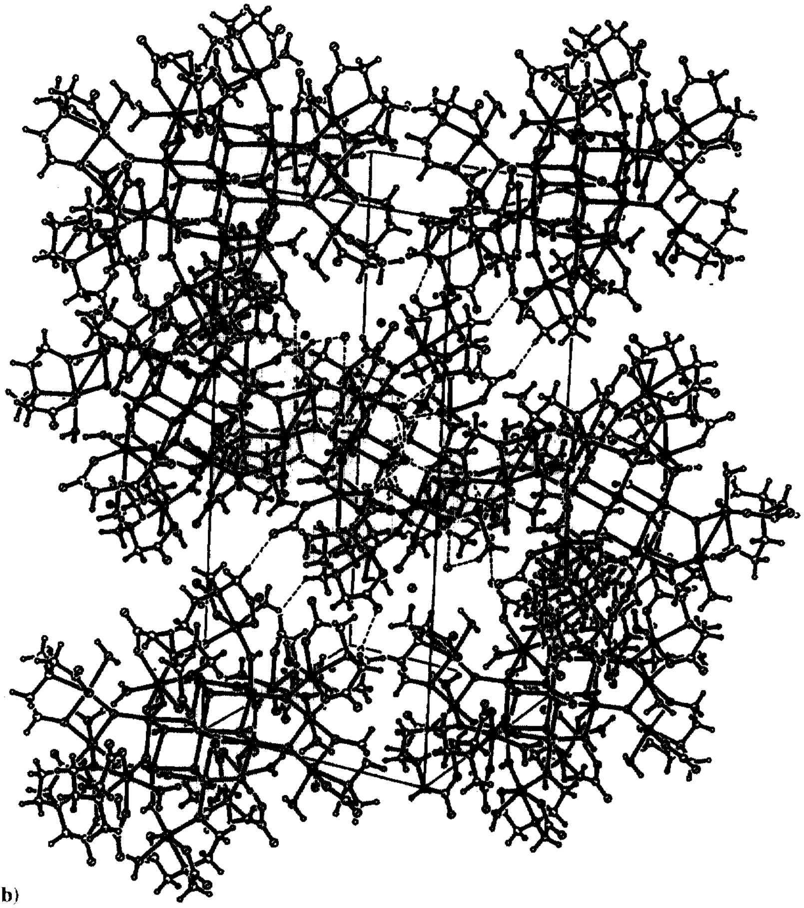

Fig. 14. (*Continued*)

spheres of the two iron centres thus contain the four donors from the heidi^{3-} ligands, with the fifth site taken by the bridging alkoxide oxygen of the heidi^{3-} ligand on the other iron centre and the sixth site occupied by a water ligand. This linking of two iron centres by the ligand appears to be a key to stabilising larger aggregates. If in aqueous solutions of iron(III) nitrate and the ligand the Fe:L ratio is changed to 2:1 two closely related cluster aggregates result [23–25], $[\{Fe(heidi)(H_2O)\}_6\{Fe(heidi)(O)(H_2O)\}_2\{Fe(O)(OH)(H_2O)_2\}_2\{Fe_7(OH)_{14}\}]^{3+}$ (Fig. 12) i.e. the hydrolytic intermediate corresponding to $\{Fe_{17}L_8(O)_4(OH)_{16}(H_2O)_{12}\}^{3+}$ and $[\{Fe(heidi)(H_2O)\}_8\{Fe(heidi)(O)(H_2O)\}_2\{Fe(O)_2(H_2O)\}_2\{Fe_7(OH)_{14}\}]^{+}$ (Fig. 13) i.e. the hydrolytic intermediate corresponding to $\{Fe_{19}L_{10}(O)_6(OH)_{14}(H_2O)_{12}\}^{+}$.

As has been described by us before, the two aggregates cocrystallise effectively giving interpenetrating lattices of $\{Fe_{17}\}$ and $\{Fe_{19}\}$ clusters (Fig. 14(a)) [24]. These aggregates contain iron(III) centres linked in a variety of ways. The division between organic and inorganic regions within the clusters themselves echoes the arrangement found in the iron storage protein ferritin [26,27]. We have shown that the inorganic core structure corresponds to a close packed $\{Fe^{III}(OH)_2\}^{+}$ arrangement as typified by brucite, $Mg(OH)_2$ [25]. This provides a clear example of how a boundary can affect structural type, since the infinite mineral structure for $\{Fe^{III}(OH)_2\}^{+}$ could not exist due to the positive charge. With the coat of ligand and iron(III) units bounding a portion of this mineral it is possible to compensate for nearly all of the excess charge to give compounds carrying small positive charge. The many different pairwise interaction pathways available within the particles lead to unusual magnetic behaviour. The magnetic susceptibility and magnetisation data for this system reveal that these clusters stabilise very high ground state spins in the region of $S = 33/2$ or greater [24]. Recent very low temperature work has revealed that the system displays hysteresis effects with some evidence for quantum tunnelling between spin states which is yet to be verified through further measurements [28]. It also seems likely that there are weak ferromagnetic interactions between the individual clusters which are probably mediated by the extensive hydrogen bonding network (Fig. 14(b)) created by the peripheral water ligands, carboxylate oxygens, lattice waters (60 for every pair of $\{Fe_{17}\}$ and $\{Fe_{19}\}$ clusters) and nitrate counterions (four for every pair of $\{Fe_{17}\}$ and $\{Fe_{19}\}$ clusters). This further example of hydrogen-bonding networks mediating magnetic interactions between clusters opens exciting prospects for engineering new molecular cluster based magnetic materials.

3. Outlook

The strategy of manipulating hydrolysis reactions in order to create aggregated magnetic particles has yielded insights into the ways in which templating ligands can be used to direct both the structure of the particles and the way in which these pack together in lattices and arrays. We are now in a position to build on these results to produce oriented arrays of interacting magnetic cluster species. We expect that it will be possible to utilise both hydrogen-bonding effects, for example to mediate magnetic interactions amongst individual clusters, and hydrophobic interactions, for example to produce oriented clusters, in order to create arrays with tailored properties.

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