Self-assembly of Fe^{III} complexes *via* hydrogen bonded water molecules into supramolecular coordination networks†

Ian McKeogh,[a] Jonathan P. Hill,[b] Emily S. Collins,[a] Thomas McCabe,[a] Annie K. Powell[c] and Wolfgang Schmitt*[a]

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We report a synthetic approach for the assembly of Fe^{III} complexes *via* hydrogen bonded water aggregates to give coordination networks that contain separated hydrophobic organic and hydrophilic inorganic areas; the amphiphilicity of the reaction system allows assembly into nanosized vesicular spheres that obey the building principles of the related crystalline solids.

The ability to create materials that display hierarchical organisation of structure *via* molecular self-assembly is a key issue in modern supramolecular chemistry and nanochemistry.[1] The assembly of polynuclear complexes into crystalline materials has yielded a variety of metal–organic frameworks and other hybrid organic–inorganic coordination networks. The development of rational synthetic approaches[2] allowed the preparation of compounds with potential applications in gas storage, separation and catalysis.[3] In the field of nanoscience, molecular self-assembly offers an alternative to the 'top-down' approach. The specificity and nanometre accuracy of such assembly processes enables supramolecular chemistry concepts to contribute to the fabrication of complex non-crystalline materials or to the realisation of molecular electronics devices at the solid-state/air interface.[4] A controlled assembly requires a detailed understanding of structure influencing forces and relies on the ability to influence intermolecular forces by considering chemical affinities and steric restrictions. Structural studies of crystalline coordination networks that incorporate amphiphilic molecular subunits can help to utilise relevant forces to produce related hierarchical non-crystalline assemblies.

We have previously investigated the structure-directing effects of iminodiacetic acid substituted phenols and naphthols (L) and characterised the supramolecular structures and properties of the resulting dinuclear complexes $[Fe_2(\mu\text{-OH})(\mu\text{-CO}_3)L_2]^{3-}$ or $[Fe_2(\mu\text{-O})(\mu\text{-CO}_3)L_2]^{4-/6-}$. In these compounds alkali metal counterions are linked to the negatively charged Fe^{III} complexes through the O-donors and are further networked to each other forming coordination assemblies where self-assembling processes organise vast areas of different polarities.[5,6] In these cases the packing motifs are the direct result of competing dipole–cation and induced dipole–dipole interactions. Hydrogen-bonds play a negligible role in these networks.

In contrast, the neutral monomeric Fe^{III} complexes, $[Fe(t\text{Bu}_2\text{hda})(H_2O)_2]\cdot 3H_2O$ (**1**) (hda = (hydroxybenzyl)iminodiacetic acid),[6] the novel complexes $[Fe(\text{Bc}_2\text{hda})(H_2O)(\text{MeOH})]\cdot 4H_2O$ (**2**) and $[Fe(C_{12},\text{Mehda})(H_2O)_2]\cdot nH_2O$ (**3**), which are subject of this account form under neutral reaction conditions. As for the dinuclear complexes, the amphiphilic character of the reaction systems, containing hydrophobic organic ligands and hydrophilic metal ions, favours the formation of layered lamellar structures where the areas of different polarities are separated. Whilst the van der Waals forces and related influences of the ligands are still preserved, the absence of alkali metal ions in the crystal structures minimises the dipole–cation interactions. Within the hydrophilic part H-bonded networks of coordination and constitution water molecules become dominant; their arrangement is strongly influenced by the substituents and space requirements of the organic ligand. Fig. 1 summarises this approach for trapping H-bonded water low-dimensional networks in supramolecular Fe^{III} coordination compounds.

Using $t\text{Bu}_2\text{hda}$ and Bc_2hda as ligands we crystallised two closely related monomeric Fe^{III} complexes, $[Fe(t\text{Bu}_2\text{hda})(H_2O)_2]\cdot 3H_2O$ (**1**)[6] and $[Fe(\text{Bc}_2\text{hda})(H_2O)(\text{MeOH})]\cdot 4H_2O$ (**2**). In both complexes, the O-donors of the organic ligands occupy *meridional* positions of the distorted octahedral coordination spheres whilst N- and carboxylate O-donors bind in *facial* positions (Fig. 2). The remaining two coordination sites, situated *cis* to each other, are vacant for coordinating

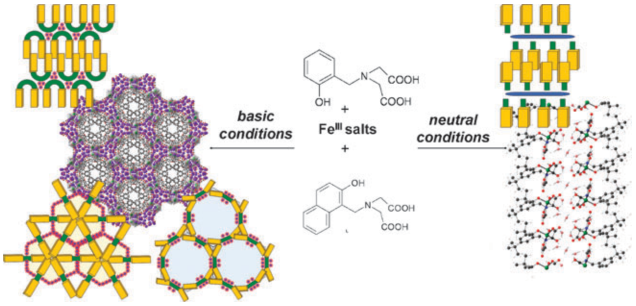

Fig. 1 Assembly of hda–Fe^{III} complexes. Pictograms illustrate some of the observed supramolecular structures (green: Fe, yellow: ligand, red: K, blue: H_2O).

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[a] University of Dublin, Trinity College, School of Chemistry, Dublin 2, Ireland. E-mail: schmittw@tcd.ie; Tel: +353 01 896 3495
[b] National Institute for Materials Science, 1-1 Namiki, Tsukuba, Japan
[c] Universität Karlsruhe (TH), Institut für Anorganische Chemie, Engesser Str. 15, 76128 Karlsruhe, Germany

† Electronic supplementary information (ESI) available: Enlarged images of the crystal structures, Comparison of IR and UV-Vis spectra of **1** and **3**, enlarged and additional TEM pictures of **3**; distances and angles of hydrogen bonds in **2**. See 10.1039/b711185a.

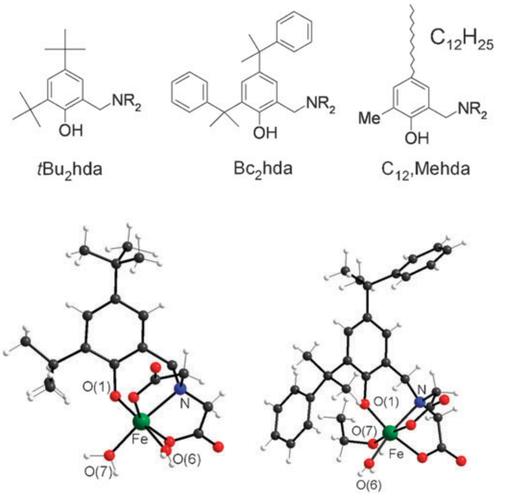

Fig. 2 Hda-ligands (top, R = CH_2COOH) and structures of the mononuclear Fe^{III} complexes in **1** (bottom left) and **2** (bottom right).

solvent molecules. As a consequence of the preparation method, in **1** two water molecules and in **2** one ethanol and one water molecule bind to the central transition metal ion. These two neutral coordination compounds crystallise in monoclinic crystal systems in the centrosymmetric space group *C*2/*c*. The two Fe^{III} compounds form a characteristic lamellar arrangement with the hydrophilic parts of the monomeric complexes situated in the crystallographic *bc*-plane and the organic hydrophobic moieties pointing parallel to the *a*-axis (Fig. 3). In both compounds H-bonded constitution water molecules link the separated complexes into networks. The difficulty in investigating associations of single water molecules lies with the fact that the hydrogen bonding between individual molecules is highly flexible with numerous aggregation possibilities often yielding disordered systems whose complicated potential energy surface with several low energy states permits a large number of possible configurations.[2] In **1** and **2** we observe ordered H-bonded networks.

In [Fe(tBu$_2$hda)(H_2O)$_2$]$\cdot$3H_2O (**1**) the water molecules are organised into 1D chains with a repeating structural motif displaying a mutuality to the crystal structure of ice I_h in the respect that both boat and chair conformations are represented in a defined H-bonded system. Fig. 3b illustrates this chain structure in **1**. The O–O distances of the hydrogen bonded water network in **1** vary between 2.76 and 2.87 Å and compare well with the distances observed in the modifications of ice; however the observed angles (74.5–137.2°) in **1** deviate significantly from the ideal tetrahedron angle of 109.5°. In [Fe(Bc$_2$hda)(H_2O)(MeOH)]$\cdot$4H_2O (**2**) one ethanol and one water molecule bind to the central transition metal ion thus preventing the formation of a similar H_2O network within the provided intermolecular void. The structural motif in the hydrophilic region of **2** can be described as a tape of fused $(H_2O)_{10}$ rings that run parallel to the crystallographic *c*-axis. Similarly to **1**, half of the $(H_2O)_{10}$ ring atoms are generated by a symmetry operation of an inversion with the inversion centre

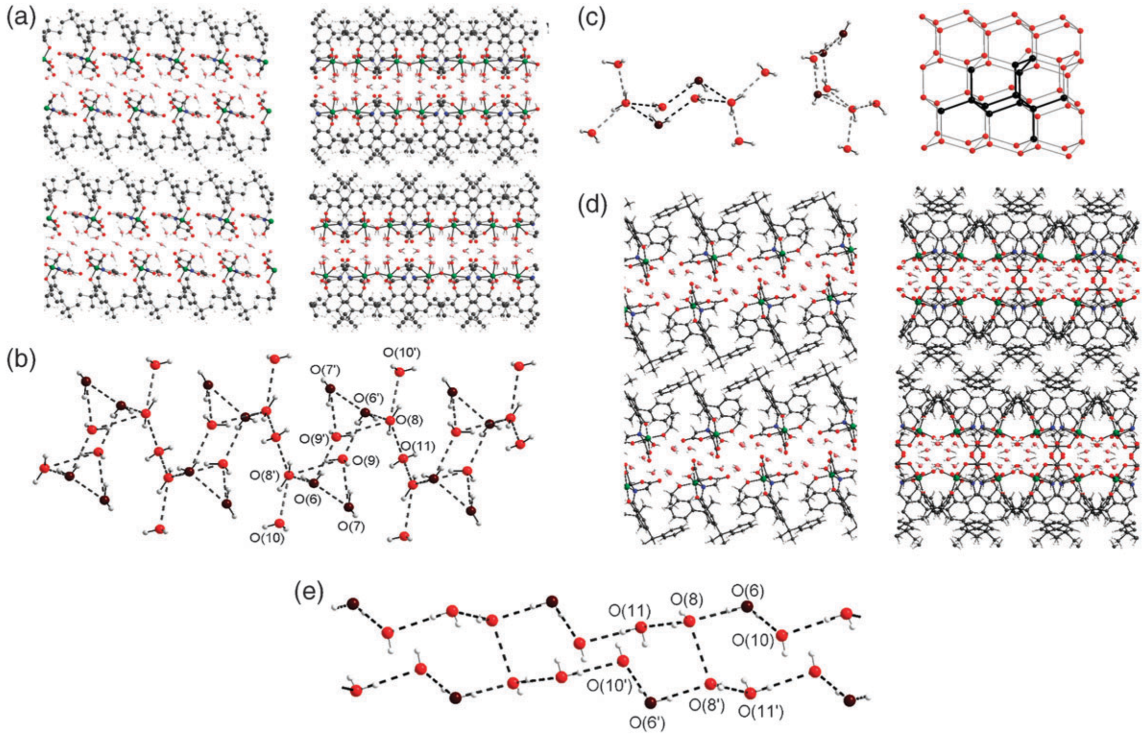

Fig. 3 (a) Layered lamellar structure of **1**, viewed in the direction of the crystallographic *b* axis (left) and *c* axis (right); (b) hydrogen bonded network of constitution and coordination (brown) water molecules in the hydrophilic region of **1** (′ corresponds to $1 - x$, $1 - y$, $1 - z$ positions); (c) similarities of the hydrogen bonded network in **1** with ice I_h; (d) layered lamellar structure of **2**, viewing in the direction of the crystallographic *b* axis (left) and *c* axis (right); (e) hydrogen bonded network of constitution and coordination (brown) water molecules in the hydrophilic region of **2** (′ corresponds to $-x$, y, $0.5 - z$ positions).

situated in the centre of the ring. The O–O distances in the hydrogen bonded water network of **2** vary between 2.64 and 2.89 Å; the angles between the O-atoms within the network range from 88.1 to 117.9°.

Given the influence of water on the structure and function of biological systems and its fundamental role in almost all branches of natural sciences it is not surprising that hydrogen bonded water aggregates have received much attention.[7] Accurate structural data of low dimensional water structures might facilitate elucidation of the complex interplay of physical, chemical and structural properties of water which is surprisingly still not fully understood. Coordination compounds, metal–organic framework (MOF) structures, and suitable organic compounds can provide ideal void spaces to trap fractions of ice or other hydrogen bonded water aggregates. Over the years many such structures have been characterised and categorised;[8] examples include defined oligomeric water aggregates $(H_2O)_n$ (n = 2–100),[9] 1D chains or tapes[10] and 2D layered structures.[11] Amongst these and other substances, compounds with hexameric $(H_2O)_6$ structural motifs have raised special attention since they reveal their relationship to naturally occurring ice polymorphs. Theoretical calculations identify several iso-energetic cyclic structural isomers of the (H_2O) hexamers; for instance "chair",[11*b*,*c*,12] "boat"[13] and "planar"[14] conformations have been characterised in crystalline hosts. The latter form also occurs in a high pressure polymorph and has recently been detected as a "quasiplanar" hexamer in a helium droplet.[15]

A characteristic feature of **1** and **2** is that they form lamellar structures where neutral layers are linked to each other through weak van der Waals forces,[5,6] similar to the packing motifs of surfactants and ideal for an assembly that exploits their amphiphilic character. The structure-directing influence of the organic ligands is not restricted to crystalline solids and the outlined hydrogen bonded networks can also be assembled into non-crystalline hierarchically ordered aggregates. We are interested in the self-assembly processes of single molecules into nanostructures[16] and we prepared an extended version of the hda ligand that contains a C_{12} alkyl chain *para* to the phenolic oxygen donor. Reaction with Fe^{III} salts in water results, under the expected experimental conditions, in the precipitation of the mononuclear Fe^{III} complex $[Fe(C_{12},Mehda)(H_2O)_2]\cdot nH_2O$ (**3**). The formation of this complex was confirmed by comparison of its IR and UV-Vis spectra with those of compound **1**. All spectra are nearly identical.

In order to confirm the expected layered, lamellar supramolecular arrangement of the mononuclear complexes we carried out transmission electron microscopy studies on the solid that precipitated from aqueous solution. Although the powdered samples of **3** are very sensitive to electron-beam induced damage it was not difficult to observe the expected ordered pattern resulting from a layered, lamellar packing motif. The observed inter-layer distance of *ca.* 3.5 nm is well in agreement with the expected dimension of the alkylated Fe^{III} complex and corresponds to the *d*-spacing determined by X-ray powder diffraction (Fig. 4). Molecular assembly of the mononuclear compound **3** was achieved by dispersing and heating the solid in ethanol–water mixtures or by drop-casting a solution of **3** onto a silicon surface. Under these conditions we observe the formation of spherical assemblies. The diameters of these spheres range from *ca.* 10 nm to *ca.* 500 nm. From our previous single crystal, powder diffraction studies and transmission microscopy studies it is most likely that the complexes in these aggregates adopt an arrangement similar to that observed in the corresponding crystalline compounds **1** and **2** where H-bonded water molecules mediate between the mononuclear complexes. The SEM observations suggest that the spheres form around aqueous droplets; in this respect they resemble liposomes of biological systems.

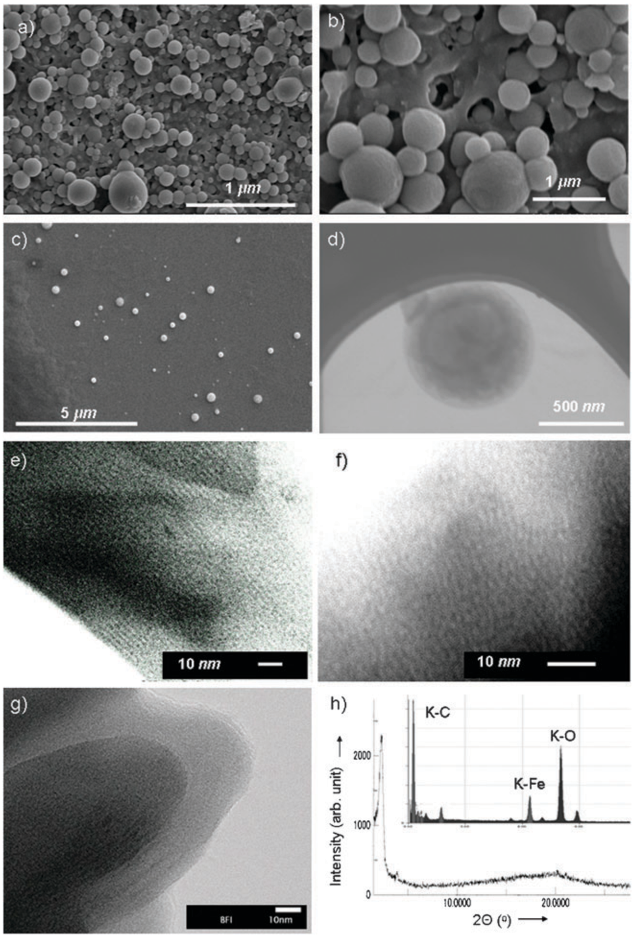

Fig. 4 SEM and TEM studies of **3**. (a)–(d) SEM observation of self-assembled spheres of **3**. (d) Spheres formed by drop casting of an ethanolic solution of **3** onto a flat Si surface. (e) and (f) TEM images identify a layered, lamellar arrangement of the Fe^{III} complexes in **3**. (g)–(h) (inset) Energy dispersive X-ray analysis of a spherical aggregate of **3**. (h) X-Ray powder diffraction of **3** reveals a signal at 2θ of 2.3° which corresponds to a *d*-spacing observed by TEM investigation.

In summary we report a synthetic approach to synthesise hydrogen bonded coordination networks with alternating hydrophobic organic and hydrophilic inorganic areas. The latter parts of the structures incorporate well defined assemblies of water molecules that mediate between the transition metal complexes and display similarities with solid ice polymorphs. Modification of the ligand structure allows self-assembly of these supramolecular arrangements into vesicular spheres whose structures have been investigated by XRD, transmission and scanning electron microscopy. Current research activities involve the investigation of how guests can be incorporated into the spherical aggregates and evaluation of their suitability for drug delivery applications.

Experimental

The ligands were prepared by Mannich reaction using the appropriate phenol, iminodiacetic acid and aqueous formaldehyde (40%).[17] **1**: Complex **1** was prepared and reported previously by us.[6] **2**: Compound **2** was prepared by reacting 0.07 g $FeCl_3 \cdot 6H_2O$ with 0.04 g Bc_2hda in 20 ml of ethanol. Addition of 10 ml of deionised water effected crystallisation of blue crystals within four days. **3**: Compound **3** was prepared by reacting the disodium salt of C_{12},Mehda (0.21 g, 0.45 mmol) and $FeCl_3 \cdot 6H_2O$ (0.135 g, 0.5 mmol) in water (50 ml). The blue solid precipitated out and was filtered off (yield 51%). Elemental analysis for dried sample of **3**; expected for $C_{24}H_{40}FeNO_7$: C 56.47%, H 7.90%, N 2.72%; found: C 55.98%, H 7.79%, N 2.73%.

Preparation of vesicular spheres: *Method 1:* 20 mg of **3** was dissolved in 15 ml absolute ethanol and to this solution deionised water (10 ml) was added. The resulting blue solution was drop-cast on a flat Si surface and imaged by SEM (Fig. 4c). *Method 2:* Alternatively, high yields of vesicular spheres were obtained by dissolving 5 mg of **3** in 10 ml of absolute ethanol. The addition of 10 ml of deionised water and heating the mixture to 80 °C resulted in a slightly cloudy dispersion. The spherical aggregates were separated from the solution by suction filtration using a 0.2 μm polycarbonate filter (Fig. 4a and 4b). Scanning electron micrographs were obtained using a Hitachi S-3500N and a Hitachi S-4800 microscopes. Coating with a *ca.* 4 nm thick Au layer was found to be advantageous for the SEM observation. Transmission electron microscopy was carried out on a JEOL FX 2000. The powder of **3** was placed on copper mesh for TEM analysis.

Single crystal X-ray data were measured on a Bruker Apex diffractometer at 200 K using graphite-monochromated Mo-Kα radiation. Structure solution was carried out by direct methods and full-matrix refinement against F^2 (all data) using SHELXTL.[18] All solvent H atoms, with the exception of one atom binding to O(10), in **2** were located in the Fourier Difference map and refined.

Crystal data for **2**: $C_{31}H_{45}FeNO_{11}$, 663.53 g mol^{-1}, blue plate, 0.25 mm × 0.25 mm × 0.1 mm, T = 200 K, monoclinic, $C2/c$, a = 44.988(18), b = 9.206(4), c = 16.552(6) Å, β = 108.938(7)°, V = 6484(5) Å^3, Z = 8, $F(000)$ = 2816, ρ_{calc} = 1.359 Mg m^{-3}, μ(MoKα) = 0.525 mm^{-1}, 32 168 reflections measured ($2\theta_{max}$ = 56.6°), of which 8039 unique (R_{int} = 0.0272), 429 parameters, wR_2 = 0.1143, S = 1.097 (all data), R_1 (6611 data with $I > 2\sigma(I)$) = 0.0393. CCDC reference number 660958. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711185a

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