Structure and Magnetic Properties of a Dodecanuclear Twisted-Ring Iron(III) Cluster**

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Supramolecular approaches have provided a new tool for the design of large magnetic clusters.[1, 2] Anion[2b, 3] and cation[4–6] recognition in particular provide the possibility of controlling the shape and the size of clusters. A clear example is the possibility to address the synthesis of molecular rings by exploitating host–guest interactions with alkali metal cations, because alkali metal cations of different ionic radius are hosted by rings of different size. Hexairon(III)[4a,b, 5] and hexamanganese(III)[4c] clusters with cyclic M_6O_{12} cores can easily accommodate Li^I and Na^I cations, both in the solid state and in solution, whereas Cs^I ions require larger rings, such as M_8O_{16}.[5] Small complex cations (NH_4^+),[7a] anions (ClO_4^-),[7b] or neutral molecules such as $(CH_3)_2CO$[8a] and Et_2NH[8b] have been found in the cavity of eight-membered iron(III), cobalt(III), or chromium(III) cycles in the solid state and may play a role in the formation of the host frameworks. However, several molecular rings exhibit hollow cores and apparently "unsupported" structures. In these cases, the cyclic structure is a result of the subtle balance between the binding constraints of the ligands and the coordination requirements of the metal.[2, 9, 10]

In an attempt to increase the size of the hexairon(III) coronates $[M'Fe_6(OCH_3)_{12}(dbm)_6]^+$ where M′ = Li or Na and Hdbm = dibenzoylmethane,[4a,b] we used larger alkali metal ions, such as K^I or Cs^I, and we found that a ring made up of twelve iron(III) ions, in $[Fe(OCH_3)_2(dbm)]_{12}$ (**1**), was obtained which did not host an alkali metal ion.

Compound **1** was obtained by reaction of equimolar amounts of $FeCl_3$ and Hdbm in the presence of either potassium or cesium methylate (4 equiv) in anhydrous methanol. The composition of the crystalline compound, $\mathbf{1}\cdot 6\,CHCl_3$, was established by elemental analysis and single-crystal X-ray diffraction analysis at 173 K. The molecular structure of **1** viewed perpendicular to the average plane through the metal centers is displayed in Figure 1. Each iron(III) ion in **1** has a distorted octahedral environment with six oxygen donors from methoxide and dbm ligands. Fe–O bond lengths are in the range 1.94–2.07 Å, while bond angles at the bridging oxygen atoms vary from 102.5 to 106.8° (average: 104.7°). The ring is not planar and has crystallographic C_1 point group symmetry. However, two idealized C_2 axes bisect four edges of the metal dodecagon (Fe1–Fe2 and Fe7–Fe8; Fe4–Fe5 and Fe10–Fe11, respectively), and a third lies perpendicular to the plane of Figure 1 which leads to idealized D_2 symmetry. The Fe–Fe distances are in a narrow range (3.113–3.156 Å), whereas the Fe-Fe-Fe angles (α) vary considerably from about 117.3 to 136.2° following a well-defined, smooth pattern around the ring. Ring closure considerations for a planar twelve-membered ring require $\alpha = 150°$, while in edge-sharing octahedra the optimal angle is 120°, as observed in the Fe_6 species (av 119.8°).[4a,b] The α angles around Fe1, Fe2, Fe7, and Fe8 are very close to this limit (av 118.4°), while the remaining α angles do not exceed 137°, with maxima at Fe4, Fe5, Fe10, and Fe11. Bis(μ-OR) units can thus easily support large cycles if the geometrical restraints of a planar ring are relaxed. The resulting molecular geometry is unprecedented and closely resembles a non-planar, twisted "ribbon".

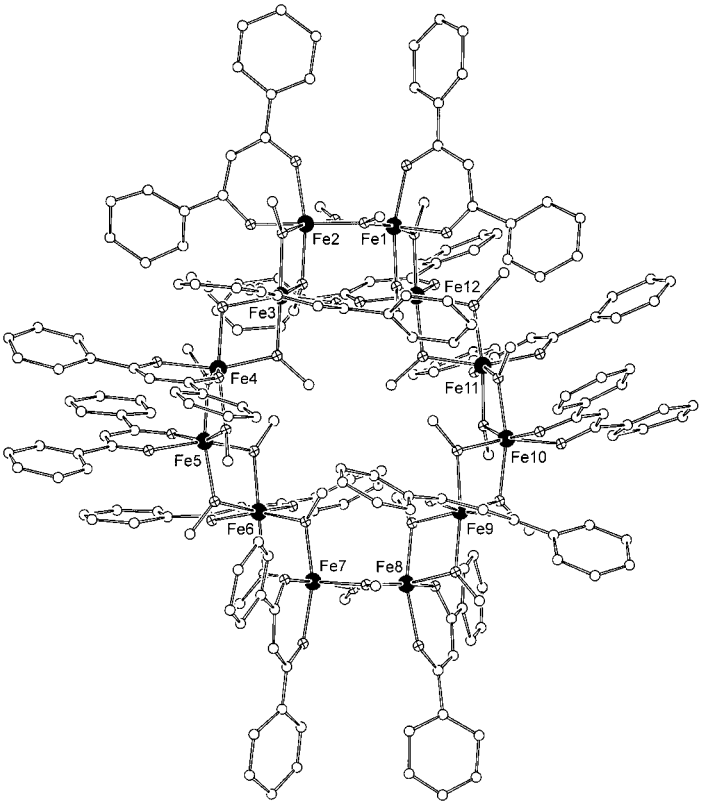

Figure 1. Ball-and-stick representation of **1**, viewed perpendicular to the average plane through the metals. Iron atoms are drawn as large black spheres, oxygen and carbon atoms are depicted as small cross-hatched and open circles, respectively. For clarity, only iron atoms are labeled and hydrogen atoms are omitted. Selected nonbonded distances [Å] and angles [°]: Fe1–Fe2 3.115(4), Fe2–Fe3 3.133(5), Fe3–Fe4 3.138(5), Fe4–Fe5 3.156(5), Fe5–Fe6 3.130(5), Fe6–Fe7 3.155(5), Fe7–Fe8 3.113(5), Fe8–Fe9 3.137(5), Fe9–Fe10 3.123(5), Fe10–Fe11 3.156(5), Fe11–Fe12 3.130(5), Fe12–Fe1 3.144(5); Fe2-Fe1-Fe12 118.1(1), Fe1-Fe2-Fe3 117.3(1), Fe2-Fe3-Fe4 132.4(2), Fe3-Fe4-Fe5 135.9(1), Fe4-Fe5-Fe6 135.5(1), Fe5-Fe6-Fe7 131.9(2), Fe6-Fe7-Fe8 119.3(1), Fe7-Fe8-Fe9 119.0(1), Fe8-Fe9-Fe10 134.2(1), Fe9-Fe10-Fe11 136.2(1), Fe10-Fe11-Fe12 135.7(1), Fe11-Fe12-Fe1 131.4(2).

The dbm moieties follow the smooth oscillations of the dodecairon backbone and are positioned on all sides of the cluster to provide a hydrophobic shell which conveys a fairly large solubility in organic solvents to **1**. The ^1H NMR spectrum recorded at 200 MHz in CD_2Cl_2/CD_3OD (3/1) shows the paramagnetically shifted peaks of *m*-Ph and *p*-Ph protons of dbm at $\delta = 10.0$ and 6.9, respectively, in the

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appropriate ratio of 2:1 (Figure 2a). Addition of three equivalents of either $NaBPh_4$ or $LiBPh_4$ to the bright orange solution leads to major changes in the NMR spectrum. Although the signal from *p*-Ph protons is masked by the strong resonance of tetraphenylborate anion, the peak from the *m*-Ph protons is progressively replaced by resonances at

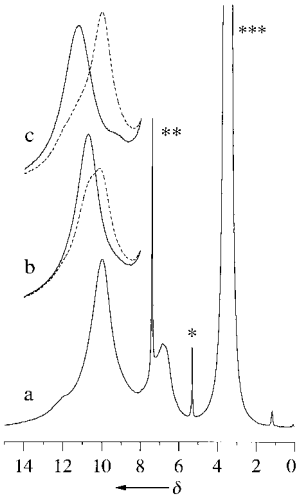

Figure 2. a) ^{1}H NMR spectrum of **1** recorded at 300 K in CD_2Cl_2/CD_3OD (3/1). Spectra recorded 10 min (– – –) and 360 min (——) after the addition of $NaBPh_4$ (b) or $LiBPh_4$ (c). Solvent peaks: * = $CHDCl_2$, ** = $CHCl_3$, *** = CH_3OD.

$\delta = 10.7$ and 11.3 upon the addition of the sodium and lithium salt, respectively. The spectra are time-dependent, which indicates that a slow equilibrium occurs (Figure 2b and c). The final spectra, which are observed after about six hours, are identical to those recorded for the $Na \subset Fe_6$ and $Li \subset Fe_6$ coronates.[4a] Crystals of the two compounds were recovered by slow concentration of the solutions in the NMR tubes. We conclude that **1** can be quantitatively converted to hexa-iron(III) coronates by reaction with sodium or lithium salts in solution [Eq. (1)].

$$[Fe_{12}(OCH_3)_{24}(dbm)_{12}] + 2M'^{+} \longrightarrow 2[M'Fe_6(OCH_3)_{12}(dbm)_6]^{+} \quad (1)$$

The origin of the slow equilibrium must be associated with the need to break the large rings into at least two fragments.

Although the largest known ring-shaped iron(III) compound is a octadecanuclear wheel described by Lippard et al.,[9] compound **1** is the largest cyclic ferric cluster yet reported with chemically equivalent bridging units.[10a,b] Therefore, it was of particular interest to investigate its magnetic properties in the solid state. The magnetic susceptibility measured in the range 2.3–254 K with an applied field of 1 T is indicative of antiferromagnetic interactions between the high-spin iron(III) ions ($S = 5/2$). The broad maximum at 155 K in the curve of χ_M as a function of T (Figure 3) can be nicely fit by a Heisenberg $S = 5/2$ quantum chain model with $J = 22.2\ cm^{-1}$ and $g = 2.00$ ($\mathbf{H} = J\Sigma_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$).[11a] The departures from the calculated behavior at low temperature must arise from finite-size effects and the discreteness of the energy levels in **1**. For a ring of N ions, an energy gap $\Delta E \approx 4J/N = 7.4\ cm^{-1}$ is

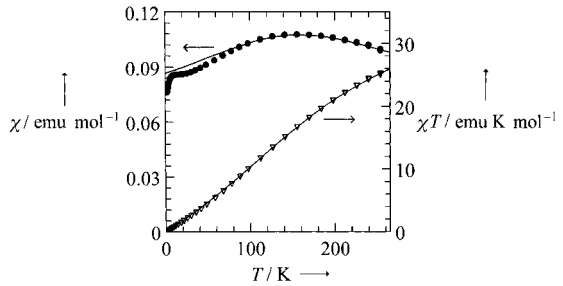

Figure 3. Molar magnetic susceptibility of a microcrystalline sample of **1** measured at 1 T as a function of temperature. The solid line represents the best-fit curve, as described in the text.

predicted between the ground $S = 0$ and the first excited $S = 1$ state.[4b, 10a, 11b] χ_M should then drop to zero for $T \ll \Delta E$, while it extrapolates to a nonzero value in an infinite Heisenberg chain of half-integer spins.[11a] The calculated J value is close to that found in dialkoxo-bridged iron(III) complexes with similar Fe-O-Fe angles, such as $Na \subset Fe_6$ coronates ($\approx 20\ cm^{-1}$).[4a,b, 12]

The present study shows that host–guest interactions and template effects may indeed be useful to address the synthesis of specific clusters and to determine the shape of the aggregate. However, in some cases, they may not be able to favor the largest possible clusters.

Experimental Section

The synthesis was performed under an argon atmosphere. Methanol was distilled over $Mg(OCH_3)_2$ shortly before use. Hdbm (Aldrich) and $FeCl_3$ (Carlo Erba) were used without further purification. Potassium methylate was used as a 25 % solution in methanol (Fluka), whereas cesium methylate was prepared by careful addition of Cs metal to anhydrous methanol. A solution of Hdbm (5 mmol) and potassium methylate (or cesium methylate) (20 mmol) in anhydrous methanol (60 mL) was added dropwise to iron(III) chloride (5 mmol) dissolved in anhydrous methanol (20 mL). After the addition was completed, the mixture was stirred for a further 30 min and the resulting yellow-orange precipitate was filtered off and dried with an argon flux. The dry precipitate was dissolved in $CHCl_3/CH_3OH$ (1/1) and a small amount of insoluble material was filtered off. Slow diffusion of methanol vapors into the clear solution afforded yellow rodlike crystals in a few days. The crystalline material was separated by filtration, dried under vacuum and analyzed. Elemental analysis: calcd for $[Fe(OCH_3)_2(dbm)]_{12} \cdot 0.67\,CHCl_3$, $Fe_{12}C_{204.66}Cl_2H_{156.66}O_{48}$ (%): C 58.88, H 4.95, Fe 16.09; found: C 58.88, H 4.83, Fe 16.01. Crystal structure data for **1**: $C_{210}H_{210}Fe_{12}Cl_{18}O_{48}$, $M_r = 4810.08$, crystal dimensions $0.2 \times 0.1 \times 0.1\ mm^3$, monoclinic, space group $P2_1/c$, $a = 30.530(5)$, $b = 22.780(5)$, $c = 32.050(5)$ Å, $\beta = 93.400(5)^\circ$, $V = 22251(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.436\ g\ cm^{-3}$, $2\theta_{max} = 36^\circ$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega - 2\theta$ scans, $T = 173(2)$ K. Of the 13875 reflections collected, 13343 were independent and were used in the structure refinement (Lorentz and polarization but no absorption correction applied). The structure was solved by direct methods (SIR-97)[13a] and refined on F_o^2 by use of the SHELX-97 program package.[13b] Disordered chloroform molecules were located in the lattice and refined with fractional occupancies to give a total of six $CHCl_3$ molecules per cluster. All Fe and most Cl atoms were refined anisotropically, while hydrogen atoms were added in idealized positions and treated isotropically. Restraints were applied to the anisotropic thermal parameters of Cl atoms and to the geometry of a few phenyl rings. The current values of $R1$ and w$R2$ are 0.0967 [$I > 2\sigma(I)$] and 0.3174 (all data) for 1370 parameters, which mainly reflect the bad X-ray quality of all the crystals examined. The maximum and minimum residual electron density is 1.135 and $-0.636\ e\ Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-110011. Copies of the data can be obtained

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free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Covalent Surface Functionalization and Self-Organization of Silica Nanoparticles**

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The large-scale manufacture of nanometer-scale particles with definite size and shape is a great challenge in materials chemistry.[1] Perhaps even more exciting is the development of versatile methodologies that focus on the covalent functionalization of these particles,[2] and which have an outstanding impact on fundamental research and on chemical and biochemical engineering: functionalized particles play an important role, for example, in pharmaceutical drug delivery systems,[3] in the production of dispersion paints,[4] in the optimization of catalysts,[5, 6] and in processes involving adhesives, varnishes, and lubricants.[7] Silica particles might be particularly useful for applications where toxicity must be excluded. They can conveniently be prepared by the classical method of Stöber et al.[8] Without surface modification these particles tend to coagulate and eventually transform, by polycondensation of their surface OH groups, into (nano)-porous glass or ceramics.[9] Many applications, however, require strictly nonaggregated nanoparticles.

Most of the recent literature concerning surface functionalization is based on the weak adsorption of surfactants or polyelectrolytes.[10] Up to now covalent coating of the hydrophilic SiO_2 surface has mostly been accomplished with silanes that contain lipophilic ligands. This leads to stable dispersions in several organic solvents;[11, 12] for instance, the surface modification of colloidal CdSe clusters by means of organoselenides has been reported.[13] The covalent coating of nanostructured metals with thiol molecules is also well known.[14] All these techniques prevent aggregation by appropriate surface modification. Philipse and Vrij have coated silica spheres with a dense layer of (3-methacryl)oxypropyltrimethoxysilane and these particles can be dispersed in several organic solvents.[15] Hard sphere behavior was obtained by coating the surface with a monolayer of octadecyl alcohol.[16] These coatings make the particles chemically inert, which prohibits agglomeration. Concomitantly, however, further functionalization is hardly possible.[17]

Herein we present a covalent surface functionalization of silica nanoparticles that simultaneously excludes aggregation. Nearly monodisperse silica particles prepared by a modified Stöber synthesis are coated with a silane that contains two carboxylic acid groups. Particles with more than 10000 negative surface charges are generated upon dissociation in polar solvents. On the one hand these strictly nonagglomerated particles, as we demonstrate, exhibit novel colloidal

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