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A New Cylindrical, Six-Membered Iron(III) Inclusion Cluster Consisting of Three Oxo-Bridged Diiron Subunits Linked by Carboxylate Bridges[§]

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Introduction

We are interested in the systematic tuning of the chemical properties of coordination complexes to act as efficient catalysts for the activation and subsequent conversion of small molecules. During the course of such studies, the spontaneous self-assembling of molecular units can lead to the formation of unexpected supramolecular aggregates.[1−5] We have recently come across a six-membered Fe(III) cluster that consists of a rather unique combination of oxo and carboxylato bridging groups, by which a cylindrical inclusion cluster with sodium is formed. Although several carboxylate ligated iron clusters have been reported in the literature,[1−5] the cluster reported in this contribution exhibits significantly different bridging ligands and overall geometry.

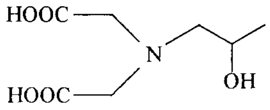
The synthesis of polynuclear oxo- and hydroxo-bridged iron complexes has received much attention in chemistry[6−8] and biology[6,9] owing to the widespread occurrence of such units in organisms. These types of complexes give insight into aspects of hydrolysis and polymerization of Fe(III) that occur during the mineralization processes in the iron storage protein ferritin.[6,10] For example μ-oxo-bridged diiron complexes are known for their biological importance in the storage and transport of dioxygen (hemerythrin),[6,9,11] and their activities in phosphatases (purple acid phosphatases)[6,9,12] and in methane monooxygenases.[6,9] Their structures and redox and magnetic properties have been intensively investigated and are summarized in several reviews.[8,9,13,14] In most of these complexes the μ-oxo-diiron units are stabilized by additional carboxylate bridges. However, this is not the case in the structure reported in this paper.

Fascinating model complexes for iron-oxygen aggregation with up to 19 iron centers have been characterized[15−22] and reviewed by different groups.[3−5] Over the past several decades chemists have made progress in preparing molecules that provide three-dimensional structures intended to complement the properties of cationic[19,23−27] and anionic[28,29] molecules or atoms in order to encapsulate such species selectively.

Results and Discussion

The isolated cluster (see Figure 1) belongs to the space group $R\bar{3}c$ and consists of six Fe(III) centers that exist as three μ-oxo diiron dimers. The iron centers are bridged by carboxylate groups from the hpida chelate attached to each iron center. The octahedral coordination sphere of the iron centers is formed by the following bonds: Fe−N(imido); Fe−O(acetate); Fe−O(propanol); Fe−O(bridging acetate from this metal chelate); Fe−O(bridging acetate from the neighboring metal chelate); and Fe−O(oxo bridge). The iron centers form a cylinder with a distorted prismatic framework that includes a sodium ion held in place by six oxygen atoms, one originating from each of the six bridging carboxylate groups leading to an essential stabilization of the overall geometry (see Figure 1). Various crystallization attempts, in which the positively charged counterion was varied

N-(2-hydroxypropyl)imino-diacetic acid (hpida)



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[§] Dedicated to Prof. Dr. Dieter Sellmann on the occasion of his 60th birthday.

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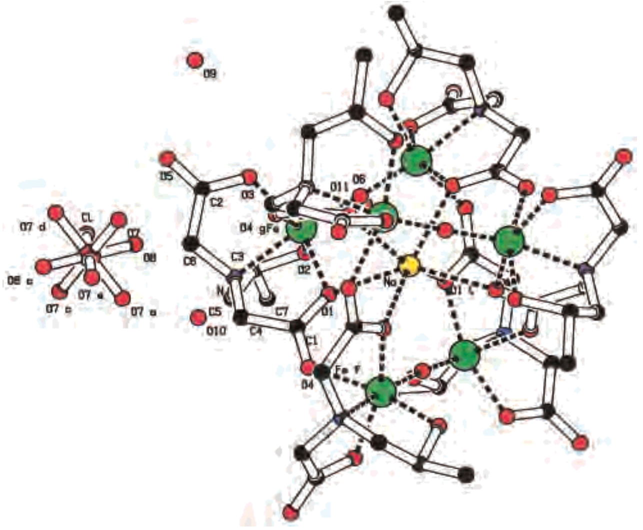

Figure 1. ORTEP plot of the six-membered iron(III) inclusion cluster.

in order to obtain empty or related inclusion clusters, failed. For the counterions Li^+ and Cs^+ dimeric complexes[30] similar to $[(Fe^{III})_2(edg)_2(H_2O)_2]$[15] (edg = $N(CH_2COOH)_2(CH_2CH_2OH)$) were isolated, whereas, for K^+, Rb^+, Ba^{2+}, and NH_4^+, no suitable crystals were found. Mainly ClO_4^- or NO_3^- was used as anionic counterion. This observation led us to conclude that only slight changes in these sensitive stabilizing effects lead to a disturbance of this unique coordination geometry. This means that the sterically well-defined host cavity formed during the self-assembly process is only suitable to accommodate sodium ions.

Due to the selected space group, the chemical formula, and the density of the compound, a difficulty arose in positioning the ClO_4^- ion. During the course of the structure determination it became necessary to locate the ClO_4^- ion on a centrosymmetric point position (Wyckoff notation 6b with $\bar{3}$ point symmetry in space group $R\bar{3}c$ (No. 167 of IT)) and to assume disorder in the crystal. Lower symmetry space groups were excluded during the refinement.

According to the structural data, two crystallographic equivalent sets of three iron centers form the carboxylate-bridged triangles, which are in turn coupled via the three μ-oxo groups. Therefore, in reference to the proposed nomenclature of Pecoraro et al. for inorganic-based molecular recognition agents, analogous to metallacrowns, -cryptates, or -calixarenes, the complex could be described as a sandwich, $\{Na[12\text{-}MC_{Fe(III)N(COO^-)}\text{-}3]_2(\mu_2\text{-}O)_3\}\cdot ClO_4$ (in comparison to organic crown ethers such as 12-crown-3 (12-C-3), analogous metallacrowns can be presented as $[12\text{-}MC_{M(OX)N(ligand)}\text{-}3]$), triple μ-oxo-bridged metallacrown inclusion cluster with a cavity size of approximately 0.50 Å.[24,31−33] Viewing the molecule in this way, the cluster is a Na(I) cryptate with the analogous architecture of a confacially fused pair of metallacrowns, yet unknown for iron-based clusters.

Each iron center is linked to three other iron centers via two bridging carboxylates and one bridging oxo group (Figure 2). The iron atoms show a distorted octahedral coordination sphere, with bond lengths of 1.77 Å for the O−Fe bond in the almost linear μ-oxo bridge with an Fe−μ-O−Fe angle of 175.22°, and 2.22 Å for the trans-positioned Fe−N bond. The Fe−O distances for the bound carboxylates and the alcohol group vary between 1.99 and 2.10 Å.

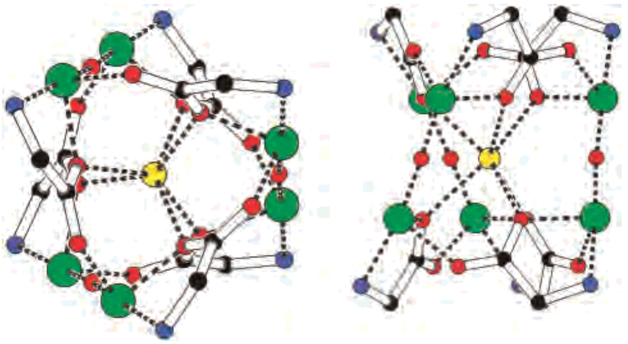

Figure 2. Reduced molecular structure of the core: (a, left) view along the *z*-axis; (b, right) view along the *x*-axis. Color code: Fe (green), N (blue), C (black), O (red), Na (yellow).

The iron cores of the hexanuclear aggregates generate a stretched prismatic geometry, where at a time three Fe centers are at the corners of two regular triangles. The triangles are twisted by 15°, which leads to the distorted prismatic framework. This in turn leads to a 3-fold symmetry along the *z*-axis through the middle of both triangles and the center of the prism, where the sodium ion is located (see Figure 1). The bond distance for Fe−Fe along the edge of one triangle is 5.34 Å, the shortest Fe−Fe distance along the μ-oxo bridge is 3.54 Å, and the Fe−Fe distances along the prismatic surface and diagonal are 5.50 and 6.74 Å, respectively. The cluster carries a positive charge, with ClO_4^- as counterion. The elementary cell consists of six molecules, which leads, in reference to comparable complexes, to an unexpected and incredibly large cell size of ∼11000 Å^3 (Figure 3). The well-defined positions of the oxygen atoms for the crystal waters O_9−O_{11} and the small distances between these atoms (∼2.8 Å) and from them to the O atoms of the cluster carboxylates (∼2.6−2.8 Å) led to the conclusion that bridging hydrogen bonds are presumably essential and enable crystallization.

Mössbauer Measurements. The Mössbauer spectrum recorded at 4.2 K of the cluster compound (Figure 4) shows a quadrupole doublet with an isomer shift typical for trivalent high-spin iron ($\delta = 0.49$ mm s^{-1}) and an unusually large splitting ($\Delta E_Q = 2.05$ mm s^{-1}) which is due to the distorted octahedral coordination sphere. It is possible to fit the spectrum equally well assuming a superposition of two quadrupole doublets with slightly different splittings. A small impurity of paramagnetic Fe^{3+} (≈2%) is detectable.

Magnetic Measurements. The temperature dependence of the magnetic susceptibility was measured in the range 4−295 K using a vibrating sample magnetometer (Foner type magnetometer). The product χT as a function of temperature for the Fe_6 cluster is shown in Figure 5. A strong temperature dependence is observed with χT decreasing continuously from 3.1 cm^3 mol^{-1} K at ambient temperature nearly linearly down to 0.2 cm^3 mol^{-1} K at 50 K. Below 50 K the data become more flat, tending to zero. The value of $\chi T = 3.1$ cm^3 mol^{-1} K is very small compared to the expected spin-only value of six uncoupled Fe^{3+} ions, namely, 26.3 cm^3 mol^{-1} K. The magnetism of the compound in the upper temperature range can therefore be interpreted by a very strong intramolecular antiferromagnetic spin exchange coupling in the μ-oxo−diiron units of the cluster. The data in the low-temperature range (≤50 K) are thought to

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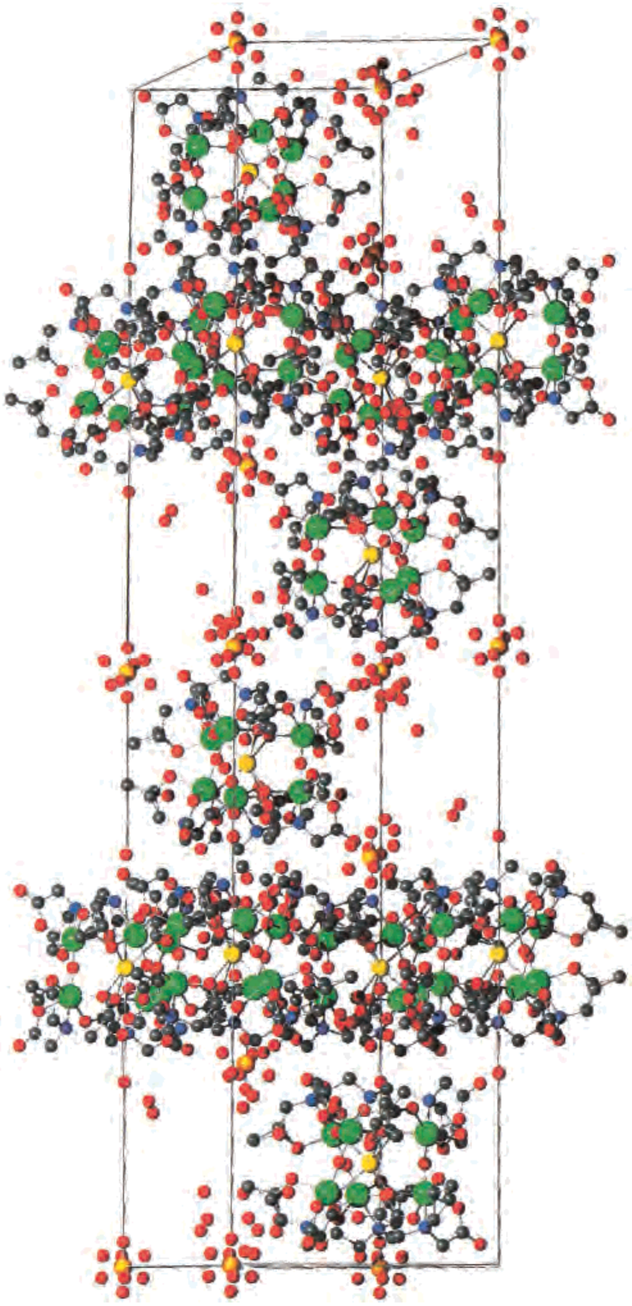

Figure 3. Unit cell of $6(C_{42}H_{60}Fe_6N_6O_{33})^{+}\cdot 6(ClO_4^{-})\cdot 84H_2O$.

arise largely from a small amount of paramagnetic species which could also be detected in the Mössbauer spectrum.

Attempts to fit the magnetic susceptibility data to the isotropic Heisenberg−Dirac−van Vleck model[34] for dimers ($H = -2JS_1S_2$, where $S_1 = S_2 = {}^5/_2$ and $g = 2.0$ (fixed)) including the molecular field approximation to account for the interdimer coupling between the μ-oxo−diiron units of the cluster through carboxylate bridges were successful (solid curve in Figure 5). This model seems to be appropriate and yields a coupling constant J of -91 cm^{-1} which is quite similar to values reported for several Fe−O−Fe dimer complex compounds in which the Fe−Fe distance is in the range 3.4−3.6 Å and the Fe−O−Fe angle between 140° and 180°.[7] Fitting of the data with the program package MINUIT (CERN)[35] led to a value for the interdimer coupling constant zj' of -3.0 cm^{-1}. This value and the quality of the fit did not depend on the selected fitting conditions, from which we conclude that a strong antiferromagnetic coupling exists within the Fe−O−Fe dimer and a weak ferromagnetic coupling between the dimer units is present. The monomeric paramagnetic impurity is estimated to be on the order of 2%, which is in good agreement with the Mössbauer result.

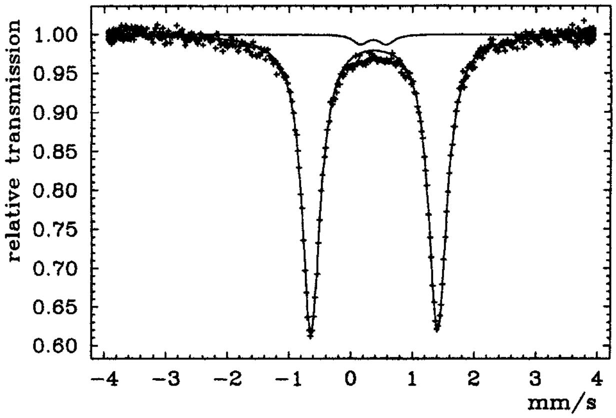

Figure 4. Mössbauer spectrum of the iron(III) inclusion cluster recorded at 4.2 K.

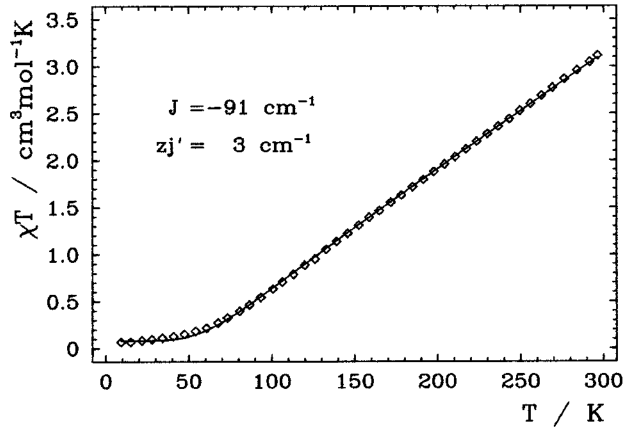

Figure 5. Temperature dependence of the magnetic susceptibility of the inclusion cluster in the range 2−300 K. The solid line corresponds to the best fit values (see text).

Experimental Section

The ligand N-(2-hydroxypropyl)iminodiacetic acid (hpida) was obtained from Akzo Nobel Chemicals GmbH and used without further purification. $[Na\subset\{(Fe_3(hpida)_3)_2(\mu\text{-}O)_3\}]ClO_4\cdot 14H_2O$ was prepared by adding an aqueous solution (40 mL) of hpida (0.955 g, 5 mmol), neutralized with solid NaOH, to 1.29 g (2.5 mmol) of $Fe(ClO_4)_3\cdot 9H_2O$ dissolved in 10 mL of $HClO_4$ (0.1 M). The brown solution was treated with solid Na_2CO_3 (final pH around 2). The mixture was stirred for 2 h at room temperature, 100 mL of acetone was added, and then the mixture was left at 4 °C for several months. The red-brownish crystals that deposited were suitable for X-ray diffraction analysis.

Elemental anal. Calcd for $[Na\subset\{(Fe_3(hpida)_3)_2(\mu\text{-}O)_3\}]ClO_4\cdot 14H_2O$: C, 26.7; H, 4.7; N, 4.5. Found: C, 27.1; H, 5.0; N, 4.3.

Crystal Structure Determination: ENRAF-Nonius CAD4 diffractometer; Mo$_{K\alpha}$, ($\lambda = 0.7107$ Å), data collection with $\omega/2\theta$ scans at 200 K, trigonal, $R\bar{3}c$ (No. 167), $a = b = 14.146(5)$ Å, $c = 65.690(7)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 11384(6)$ Å^3, $Z = 6$, $\mu(Mo_{K\alpha}) = 1.3$ mm^{-1}, $\rho_{calc} = 1.65$ g/cm^3, crystal size (mm) = 0.15 × 0.38 × 0.50, $2\theta_{max} = 47.8°$, ψ-scan absorption correction ($T_{max} = 0.64$, $T_{min} = 0.76$). Total data: 11414. Unique data: 3954. Data with $I > 4\sigma(I)$: 3197

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reflections, $N_{\text{parameter}} = 346$. Structure solution[36] and refinement[37] on $|F^2|$ led to a model with disordered ClO_4^- ions; final R value = 0.039, GOF = 1.24; minimum and maximum residual density (e/Å^3): −0.55 and 0.91. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, Deposition Number CCDC 136825. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, international code +(1223) 336-033; e-mail, teched@chemcrys.cam.ac.uk).

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Supporting Information Available: A figure depicting the structural unit of the cluster seen along [100] and [001]. An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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