Solvothermal Syntheses

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[Fe_{19}] "Super-Lindqvist" Aggregate and Large 3D Interpenetrating Coordination Polymer from Solvothermal Reactions of [$Fe_2(OtBu)_6$] with Ethanol**

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Abstract: *The syntheses, crystal structures, and physical properties of* $[HFe_{19}O_{14}(OEt)_{30}]$ *and* $\{Fe_{11}(OEt)_{24}\}_\infty$ *are reported.* $[HFe_{19}O_{14}(OEt)_{30}]$ *has an octahedral shape. Its core with a central Fe metal ion surrounded by six* μ_6*-oxo ligands is arranged in the rock salt structure.* $\{Fe_{11}(OEt)_{24}\}_\infty$ *is a mixed-valence coordination polymer in which* Fe^{III} *metal ions form three 3D interpenetrating (10,3)-b nets. The arrangement of the* Fe^{III} *ions can also be compared to that of Si ions in* α*-*$ThSi_2$*. Thus, the described structures are at the interface between molecular and solid-state chemistry.*

Unlike some early transition metals that form polyoxometalates, molecular iron–oxygen compounds containing exclusively oxo or hydroxo groups are unknown. To synthesize discrete polynuclear iron oxo complexes, the inorganic core has to be protected by an organic shell.

A large number of iron-based compounds containing multiple metal centers has been published. Amongst the largest known iron–oxygen aggregates are nuclearities of 22,[1] 19,[2–4] 18,[5,6] 17,[7–9] 16,[10,11] 14,[12–14] and 13.[15,16] These polynuclear iron–oxygen aggregates evidence a great diversity in composition, which is strongly influenced by the ligands used. However, the most common structural motif in these systems are edge-sharing FeO_6 octahedrons. An emerging field of interest concerns biologically relevant frameworks similar to the iron-oxygen core of the ferritin protein.[15]

Molecular metal–oxygen compounds can be considered as 3D extracts of metal oxides. One indication for the achieved three-dimensionality of large aggregates is the number of incorporated μ_6-oxo groups. There are several examples of polyoxoferrates with one μ_6-oxo group.[17–22] They possess a highly symmetrical hexanuclear Lindqvist [Fe_6O_{19}] core.[23] The fusion of two such [Fe_6O_{19}] octahedra by one common edge results in the well-known decametalate structure comprising a [$Fe_{10}O_{28}$] framework.[24–26] Interestingly, only few molecular metal–oxygen compounds with more than three μ_6-oxo groups have been reported.[27–30]

In the present work, we aimed for the synthesis of polynuclear iron–oxygen species comprising more than two μ_6-oxo groups. For the formation of highly aggregated and spherical metal–oxygen complexes, small organic moieties of simple alkoxo groups (methoxo or ethoxo) appeared to be the most suitable. Each just allows the saturation of a small area, minimizing the ratio between surface and volume of the aggregate. Thus, we postulated that this should lead to complexes with spherical-like shapes.

The solvothermal reaction of [$Fe_2(OtBu)_6$][21,31] with ethanol and tetrabutylammonium ethoxide at 115 °C resulted in the formation of **1** (see the Supporting Information). Single-crystal X-ray diffraction analysis revealed its structure to be [$HFe_{19}(\mu_3\text{-}O)_8(\mu_6\text{-}O)_6(OEt)_6(\mu\text{-}OEt)_{24}$] (Figure 1 and Figure 2; Supporting Information, Table S1).[46]

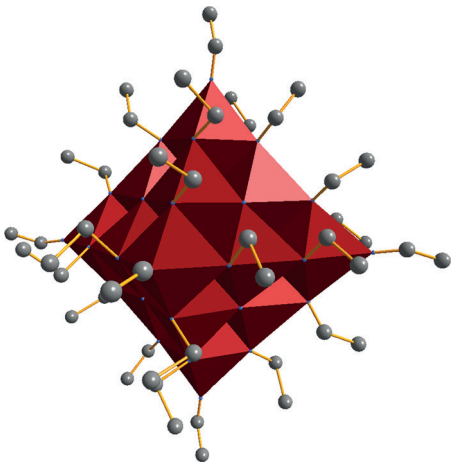

Figure 1. Polyhedral Diamond[32] plot of **1**.

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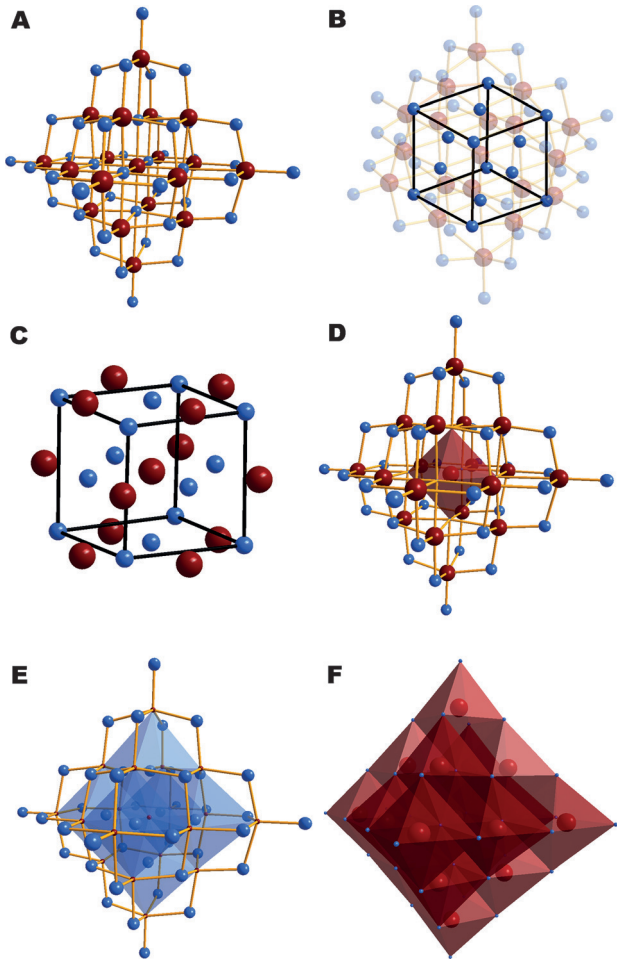

Figure 2. A) Iron–oxygen framework of **1** (Fe dark red, O blue). B) fcc array of oxygen atoms with μ_3-O atoms on the corners and μ_6-O atoms on the faces. C) 3D extract from the slightly distorted ccp structure of the fragment core. D) Illustration emphasizing the central [Fe(μ_6-O)$_6$] site. E) Edge-connected octahedral coordination spheres of the six μ_6-O atoms. F) 19 edge-connected [FeO$_6$] octahedra.

Complex **1** contains exclusively Fe^{III} metal ions. Valence sum calculations (Supporting Information, Tables S2 and S3),[33] ATR-FT-IR (Figures S2–S6), and Mössbauer studies (Figures S7–S9) did not provide any indication for the presence of Fe^{II}. Thus, one oxo or one ethoxo group has to be protonated for charge balance.[34] Moreover, IR spectroscopic studies point to a significant intramolecular proton transfer between μ_3-oxo groups and ethoxo ligands (Supporting Information, Figures S2–S6). Therefore, the formula of this new aggregate should be $[Fe_{19}O_{13}(OH)_{1-x}(HOEt)_x(OEt)_{30-x}]$ (with $x \in [0,1]$).

The iron–oxygen framework ($[Fe_{19}O_{44}]$) of **1** (Figure 2A) exhibits an approximate O_h symmetry. The aggregate comprises six μ_6-oxo groups that surround the central iron site in a nearly perfect octahedral manner (Figure 2D). Its structure can be considered as a 3D extract from the rock salt or Wüstite lattice (Figure 2B,C). However, **1** is the first molecular compound featuring a [M(μ_6-O)$_6$] site. Apart from that [M(μ_6-O)$_6$] entities can only be found in close packed structures. This [Fe_{19}] aggregate is the smallest possible unit which covers all structural elements of a cubic close packed (ccp) structure. Figure 2E shows that a "reversed" Lindqvist fragment "[O_6Fe_{19}]" is obtained, wherein the metal positions are occupied by oxygen atoms. The oxygen atoms are octahedrally "coordinated" by iron with a "μ_6-iron" atom in the center. While the normal Lindqvist structure contains six [MO_6] octahedra connected via common edges, this "super-Lindqvist" aggregate consists of 19 [MO_6] octahedra connected via common edges (Figure 2F). The known $[Ti_{12}Nb_6O_{44}]^{10-}$ ion possesses a similar overall shape (octahedral [$M_{18}O_{44}$] instead of [$M_{19}O_{44}$] framework), but contains no central metal ion and, as a consequence, no [M(μ_6-O)$_6$] site.[35] In fact, this interesting ionic compound is not a proper expansion of the Lindqvist architecture and has to be considered as a matchless independent type of polyoxometalate structure.

The static and dynamic magnetic properties of **1** were studied as a function of the temperature and applied magnetic field (Supporting Information, Figures S10–S13). From the extrapolated saturation of the 1.85 K magnetization of ca. 20 μ_B (with 7 T applied magnetic field; Supporting Information, Figure S10) and the odd number of $S = 5/2$ Fe^{III} metal ions in **1**, an $S_T = 19/2$ spin ground state can be deduced for the [$Fe_{19}O_{13}(OH)(OEt)_{30}$] complex. This estimation is also in good agreement with the maximum of the χT product measured to be 46.8 $cm^3 K mol^{-1}$ at 11 K (Figure S10) and that agrees relatively well with the expected spin-only value of 49.875 $cm^3 K mol^{-1}$. The steep decrease of the χT product below 11 K is likely the result of a certain amount of magnetic anisotropy and/or weak antiferromagnetic interactions between the aggregates. Indeed, the Mössbauer and micro-SQUID[36] measurements confirm the presence of a magnetic anisotropy and tiny antiferromagnetic intermolecular interactions (−7 mK), respectively, for **1** (Supporting Information). Using ac susceptibility (Figure S12) and micro-SQUID[36] (Figure S13) techniques, slow dynamics of the magnetization of **1** could be detected at low temperatures, and below 0.8 K, M vs. H hysteresis loops were observed. The single-molecule magnet (SMM) properties of **1** were confirmed by observing the increase of the coercitivity with a growing dc field sweep-rate and decreasing temperature (Figure S13).

By increasing the reaction temperature from 115 to 160 °C, the mixed-valence species $[Fe_{11}(OEt)_{24}]_\infty$ (**2**) was produced (Supporting Information). Its high sensitivity to oxidation and hydrolysis made the preparation and handling of samples very challenging. Since **2** oxidizes so quickly, it was not possible to measure useful Mössbauer or magnetic data so far. Nevertheless, after solving the problem of twinning, the crystal structure could be determined very precisely by single crystal X-ray crystallography (Table S1).[46]

Surprisingly, this homoleptic compound **2** exhibits a polymeric structure. As depicted in Figure 3A, the asymmetric unit consists of nine iron atoms. Valence-sum calculation determined the oxidation state of Fe1 and Fe7 to be +III, while the other iron atoms are in the state of +II (Supporting Information, Table S4). The iron metal ions differ also in their coordination spheres. Even though, they are all exclusively coordinated by ethoxo ligands, the Fe^{II} ions have a coordina-

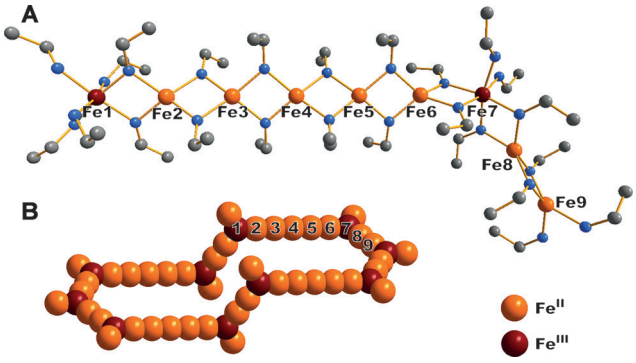

Figure 3. A) Iron ions with filled coordination spheres in the asymmetric unit of **2**. B) Smallest loop of iron ions in the polymeric (10,3)-b net of **2**.

tion number of 4 while the Fe^{III} ions have a coordination number of 6. Fe1 and Fe7 are octahedrally coordinated. Fe2–Fe6 show a strongly distorted tetrahedral sphere, being almost square planar. Fe8 and Fe9 have a less distorted tetrahedral coordination sphere. As the iron metal ions are bridged by two μ-ethoxo groups, Fe1 and Fe7 are linked to three other iron atoms in a trigonal planar geometry. The Fe^{II} ions are only connected to two other iron metal ions linearly.

Homoleptic transition-metal complexes with small alkoxides are unusual. Even more unusual are square planar $Fe(OR)_4$ groups.[37] There are only very few examples found.[38,39] In one case, two $Fe(OR)_4$ groups are connected by a common edge to a $Fe_2(OR)_6$ fragment.[40] The fact that five more or less square planar $Fe(OR)_4$ groups are aligned in the asymmetric unit of **2** makes this compound unique.

Figure 3B shows that curved hexagonal rings are formed in **2**. The smallest ring with a zigzag-shape contains 42 iron ions. Larger rings with a C-shape consist of 46 iron ions. The rings are expanded by the Fe^{III} sites to a 3D net. Considering only the Fe^{III} knots, the net has a (10,3)-b topology. The Fe^{III} arrangement is almost identical to that of Si in α-$ThSi_2$. The hexagonal combs of **2** have an approximate length of 50 Å and width of 16 Å (Figure 4).

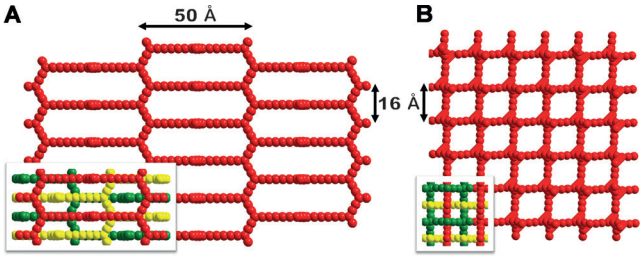

Figure 4. Section of the polymeric coordination network of **2**. A) View along the crystallographic *a*- or *b*-axis. B) View along the *c*-axis.

In many (10,3)-b nets, different net layers are 3D interpenetrating each other.[41,42] In case of the coordination polymer **2**, three independent equivalent nets are interwoven (Figure 4). Examples for similar arrays are $[Ag_2(pz)_3](BF_4)$,[43] $[CrP_3S_{9+x}]$ ($x \approx 0.25$),[44] and $[Ag(bipy)]NO_3$.[45]

In summary, we show that the variation of reaction conditions has a major impact on our system. The facile solvothermal reaction of $[Fe_2(OtBu)_6]$ with tetrabutylammonium ethoxide in ethanol yields large aggregates. By temperature control, the aesthetically very pleasing molecule **1**, the so-called $[Fe_{19}]$ "super-Lindqvist" aggregate, or the convoluted coordination polymer **2** are obtained. Even though, elaborate ligand design seems to be more promising, our serendipitous discoveries show that highly interesting and complex polyoxometalates can be constructed by using simple ligands like ethanol under the right conditions.

Keywords: coordination polymers · iron · polyoxometalates · single-molecule magnets · solvothermal syntheses

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