Crystallogr. Sect. A **1990**, *46*, 467), refinement with full-matrix least-squares methods against F^2 (SHELXL-93: G. M. Sheldrick, unpublished results), graphical representation of the structure: XP (Siemens), yellow prisms $0.4 \times 0.1 \times 0.1$ mm, space group $P2_1/c$, monoclinic, $a = 8.938(2)$, $b = 14.528(3)$, $c = 20.225(4)$ Å, $\beta = 99.28(3)^\circ$, $V = 2591.9(9)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.102$ g cm^{-3}, 6363 measured, 3899 symmetry-independent reflections, of which 2531 observed ($I \leq 2\sigma(I)$), $R = 0.039$, wR^2 (all data) = 0.088, 244 parameters. 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-137407. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Linking Icosahedral, Strong Molecular Magnets $\{Mo^{VI}_{72}Fe^{III}_{30}\}$ to Layers—A Solid-State Reaction at Room Temperature**

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Dedicated to Professor Heinrich Vahrenkamp
on the occasion of his 60th birthday

The controlled generation of nanostructured materials and building units defines one of the contemporary challenges in chemistry. In this context, designed properties such as mesoporosity (in the form of well defined cavities or channels), electron and ion transport capabilities, and (high spin) nanomagnetism (including switching) are of particular interest[1]. Following the successful synthesis of nanostructured icosahedrally or spherically shaped clusters of the Keplerate type with, for example, the metal frame $\{(Mo)Mo_5\}_{12}Fe^{III}_{30}$ **1a**[2] of 30 high-spin, and in principle, switchable Fe^{III} centers, it is now possible to interconnect the strong molecular magnets of that type. The linking of the icosahedral entities, which is in itself an interesting crystallographic problem (see below), takes place in a solid-state reaction at room temperature.

The aforementioned clusters **1a** in the compound **1a**$\cdot \approx 150\,H_2O$ comprise Fe centers, with H_2O ligands which become linked according to the inorganic-condensation reactions known for the formation of polycations with a low activation energies[3] (Scheme 1). The corresponding reaction product **2** results from several subsequent reaction steps. Product **2**,

$$\cdots Fe(OH_2) + (H_2O)Fe\cdots \xrightarrow{-H^+}$$
$$\cdots Fe(OH_2) + (HO)Fe\cdots \xrightarrow{-H_2O/-H^+} \cdots Fe\text{-}O\text{-}Fe\cdots$$

Scheme 1.

with a layer structure, was characterized by elemental analysis, thermogravimetry (to determine the number of crystallized water molecules), bond valence sum (BVS) calculations,[4] spectroscopy (IR, Raman, UV/Vis, and ^{57}Fe Mössbauer), magnetochemical measurements, and single-crystal X-ray structure analysis.[5]

$$[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot \approx 150\,H_2O \qquad \mathbf{1}^{[2]}$$

$$[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}]\cdot \approx 80\,H_2O \qquad \mathbf{2}^{[5]}$$

Compound **2** crystallizes in the space group *Cm*ca. In this structure, every cluster unit of the **1a** type is covalently linked to four other units through Fe-O-Fe bridges (Fe-Fe = 3.79(4) Å) and thereby forms a two-dimensional layer structure (Figure 1). The geometrical parameters of each single cluster building unit in **2** are, as expected, equal to the corresponding values found in the discrete cluster **1a**.[2,5]. A

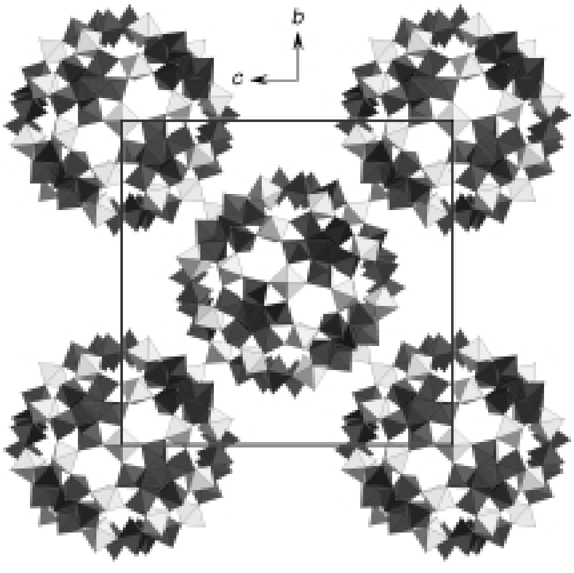

Figure 1. Structure of one layer of **2** as a polyhedral representation.

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remarkable result of this work is, besides the simplicity of the synthesis of **2**, the cross-linking of giant spheres in a solid-state reaction at room temperature as well as the packing of icosahedral units into a two-dimensional layer structure. The absence of C_5 crystallographic axes has led to a number of interesting investigations on the problem of packing icosahedra.[6] In the present case, the tiling that leads finally to the crystallographic grid is achieved by the covalent binding of the icosahedral units through oxygen atoms; these covalent bonds induce symmetry breaking. The observed electronic structure and the magnetism may be of interest in materials science, since the nanoscale building unit of the layer structure **1a**, which contains 30 high-spin Fe^{III} centers, represents the cluster with the highest number of paramagnetic centers known. The presence of 26 Fe^{III} centers, which are not involved in linking the spherical units, was confirmed not only from the structure analysis but also from the observed magnetism. The measured $\chi_{mol}T$ value of 112.9 $emu\,K\,mol^{-1}$ at room temperature fits well with the theoretical value of 113.7 $emu\,K\,mol^{-1}$ for 26 uncorrelated $S = 5/2$ centers.[7] The remaining four Fe^{III} centers (per cluster unit) of the Fe-O-Fe bridges are apparently so strongly coupled that they do not significantly contribute to the paramagnetism, a situation typical for μ-oxo-bridged, linear, dinuclear Fe^{III} complexes.[8] A suitable model system for the $(H_2O)(O)_4Fe(\mu\text{-}O)\text{-}Fe(O)_4(OH_2)$ groups in **2** is the recently described complex $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$, for which (due to the strong coupling) a $\chi_{mol}T$ value of only about 0.35 $emu\,K\,mol^{-1}$ per Fe^{III} center at room temperature was reported.[9] Plotting $1/\chi_{mol}$ versus T yields, on extrapolation due to the antiferromagnetic coupling, a Weiss temperature of $\Theta = -21.1$ K. The ^{57}Fe Mössbauer spectrum of **2** shows the anticipated similarity to **1** but a slight asymmetry of the two main peaks and of the quadrupole doublet ($\delta_1 = 0.51$ and $\Delta E_Q = 0.65\ mm\,s^{-1}$).

In the context of the cluster units, the following is noteworthy: When the freshly filtered, and thus not yet dry, crystals (type I; space group $P2_1/n$) which will form **2** after dehydration are immediately investigated by X-ray structure analysis at low temperature, their structure shows the discrete, not yet covalently linked clusters of $\{(Mo)Mo_5\}_{12}Fe^{III}_{30}$ (Figure 2).

Interesting aspects of the conversion process of the discrete spherical clusters in the solid state at room temperature, according to Scheme 2 (see also Figure 1 and 2), are 1) the discrete clusters approaching one another then finally covalently bonding during the drying process was observed by single crystal X-ray structure analysis[10] by means of the decrease in spacing between the spheres, and 2) the change to a space group of higher symmetry in an ordering process due to the covalent bonding of the spheres.

The reaction steps, according to Schemes 1 and 2, show a corresponding volume decrease of the unit cells and the decrease of the number of crystallized water molecules and represent a highly interesting process in solid-state physics and chemistry. For the proton transfers during the condensation process II → **2**, either the clusters or crystallized water molecules act as acceptors. This remarkable process is driven by the thermodynamically favorable formation and release of water molecules.[11]

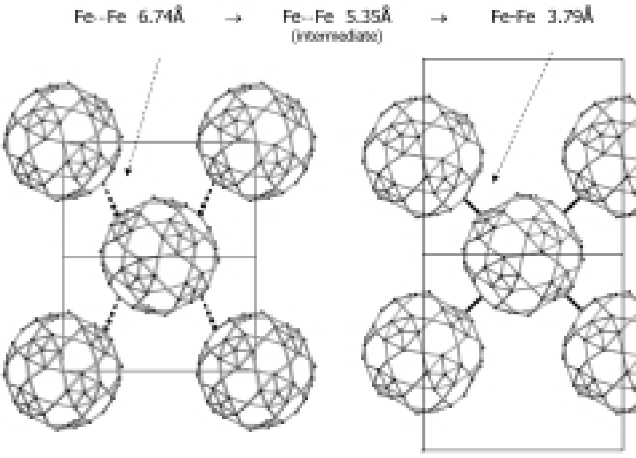

Figure 2. Wireframe representation of the metal frame of the cluster building units in **2** with an indication of covalent linking (right). The solid-state conversion process (see text) leading to **2** takes place according to Schemes 1 and 2.[10] The reaction proceeds from discrete cluster units present in the wet crystals freshly filtered from the mother liquor (type I; left) via an intermediate (type II; middle) with discrete units positioned at the minimum distance possible without bond formation.

discrete cluster $\xrightarrow{-\text{crystallized water}}$ discrete cluster $\longrightarrow$ layer structure **2**

freshly filtered crystals (I)	intermediate (II)	“dried” crystals

Scheme 2.

Experimental Section

To a solution of **1**[2] (1.0 g, 0.05 mmol) in H_2O (100 mL; **1** dissolves slowly), NaCl (0.5 g, 8.6 mmol) was added with stirring. The pH value of the solution was adjusted to approximately 2.0 with 1M HCl, then the reaction solution kept free of vibration in an open beaker (250 mL, wide necked) for crystallization. Yellow crystals of **2** (thin plates) were collected after 6 days by filtration through a glass frit, then washed with iced water and dried under air. Yield: 0.4 g (43 % based on **1**).

2: Characteristic IR bands (KBr; 1800–500 cm^{-1}): $\tilde{\nu} = 1620$ (m, $\delta(H_2O)$), 1535 (m, $\nu_{as}(COO)$), 1425 (w-m, $\nu_s(COO)$), 971 (m), 948 (m, $\nu(Mo{=}O)$), 855 (sh), 781 (s), 623 (w-m), 567 cm^{-1} (s); characteristic Raman bands (solid state; $\lambda_e = 1064$ nm, 1000–200 cm^{-1}): $\tilde{\nu} = 950$ (s), 908 (w), ($\nu(Mo{=}O)$), 835 (s), 510 (m), 370 (m), 238 cm^{-1} (w-m); UV/Vis (solid-state reflection spectrum, cellulose used as a white standard): $\lambda \approx 285$ (sh), 370 nm.

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[10] The space group of the intermediate II ($P2_1/n$; $a = 27.510(2)$, $b = 35.093(2)$, $c = 24.381(1)$ Å, $\beta = 89.51(1)°$, $V = 23537$ Å^3) is identical to the one found for "wet" crystals of type I that have been measured (at 183(2) K) immediately after filtration from the reaction solution ($a = 26.235(1)$, $b = 34.735(2)$, $c = 28.788(1)$ Å, $\beta = 96.35(1)°$, $V = 26073$ Å^3). During the "cluster approach" process according to Scheme 2, the Fe $\cdots$ Fe distance decreases as shown in Figure 2. The situation for the type II intermediate resembles the shortest distances possible between the cluster units without incurring covalent bonding. The formula for the discrete clusters in crystals from I and II is identical. The building unit of compound **2** is slightly different (loss of H_2O) due to the condensation described in Scheme 1. Whether the contents (acetate and molybdate fragments) of the cluster shell units in **1** and **2** are different—perhaps due to an opening of the spheres in solution—cannot be clearly determined because of the disorder problem (see the argument in ref. [5]). The negatively charged dinuclear molybdate fragments $\{Mo_2O_{8/9}\}$ are responsible for the charge balance during the formation of neutral **1a** clusters;[2a] a spherical cluster of the same type without these fragments but correspondingly more acetate ligands should also exist.

[11] Note added in proof (March 31, 2000): In the meantime we were also able to obtain the neutral spherical cluster of the type $\{Mo_{72}Fe_{30}\}$ with only CH_3COO^- ligands. This reduces the problem of determining the exact formula.[5]

Thirty Electrons "Trapped" in a Spherical Matrix: A Molybdenum Oxide-Based Nanostructured Keplerate Reduced by 36 Electrons

Achim Müller,* Syed Qaiser Nazir Shah,
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Björn Hauptfleisch, Stefan Leiding, and Kai Wittler

Dedicated to Professor Reinhardt Ahlrichs
on the occasion of his 60th birthday

Giant molecular spheres of variable size can be generated by linking pentagons with various spacers.[1, 2] Herein, we describe a route which facilitates the generation of unusual electronic structures based on polyoxomolybdate spheres: Each sphere, comprised of 12 pentagonal units, can act as a matrix for trapping 30 electrons on the spacers that correspond to the centers with a predominantly Mo^V character.

When the molecular giant sphere **1a**, consisting of 12 pentagonal units of the type $\{(Mo^{VI})Mo^{VI}_5\}$ and 30 $\{Mo^V_2\}$ spacers assembled with the structural characteristics of a Keplerate,[2] is oxidized, the deep blue, crystalline, molybdenum oxide acetate-type molecules containing **2** is formed. Product **2** was characterized by elemental analysis (including cerimetric titration to determine the (formal) number of Mo^V centers), thermogravimetry (to determine the number of crystal water molecules), spectroscopy (IR, UV/Vis, resonance Raman, ESR), magnetochemical measurements, extended Hückel (EH) MO calculations, and single crystal X-ray diffraction[3] including bond valence sum (BVS) calculations (to determine the positions of the H_2O ligands and to differentiate between Mo^{VI} and Mo^V centers).

$$(NH_4)_{42}[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4CH_3COO\}_{30}]\cdot{\approx}300\,H_2O\cdot 10\,CH_3COONH_4 \qquad \mathbf{1}^{[2]}$$

$$[\{(Mo)Mo_5O_{21}(H_2O)_4CH_3COO\}_{12}\{MoO(H_2O)\}_{30}]\cdot{\approx}150\,H_2O \qquad \mathbf{2}$$

Compound **2** crystallizes in the space group *C*2/*c*. In contrast to anionic **1a** (space group of **1**: $Fm\bar{3}$), the neutral cluster **2a** (Figure 1) does not form an (exact) closest cubic

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