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[5] Crystal structure analysis of **2**: space group *Cmca*; $H_{382}Fe_{30}C_{20}Mo_{80}O_{476}$; $M = 17591.96\ \mathrm{g\,mol^{-1}}$; $a = 36.815(2)$, $b = 34.403(2)$, $c = 35.056(2)$ Å, $V = 44399(4)$ Å^3, $Z = 4$, $\rho = 2.63\ \mathrm{g\,cm^{-3}}$, $\mu = 3.25\ \mathrm{mm^{-1}}$, $F(000) = 33800$, crystal size $0.28 \times 0.24 \times 0.02\ \mathrm{mm^3}$. Dried crystals of **2** were measured at 183(2) K on a Bruker axs SMART diffractometer (three-circle goniometer with a 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere data collection at 0.3° wide ω scans over three runs of 606, 435, and 230 frames ($\phi = 0°$, 88°, and 180°) from a 5.00 cm-distant detector). A total of 111705 reflections ($1.50° < \Theta < 24.97°$) were collected, of which 19819 unique reflections ($R(\mathrm{int}) = 0.1308$) were used. An empirical absorption correction using equivalent reflections was performed with the SADABS program. The structure was solved with the program SHELXS-97 program and refined using the SHELXL-93 and SHELXL-97 programs (G. M. Sheldrick, University of Göttingen, **1997** and **1993**) to $R = 0.045$ for 9308 reflections with $I > 2\sigma(I)$ and a max./min. residual electron density of $2.06/-1.17\ \mathrm{e\,Å^{-3}}$. The problem of locating the disordered molybdate fragments of the type $\{Mo_2O_{8/9}\}$ and the acetate ligands is equivalent to the situation in **1**,[2] although in the present case the lower symmetry leads to a significantly reduced disorder (the certainty of the number of both of these structural elements is ±1 in the formula). To confirm the above statements, multiple crystal-structure analyses were carried out for the intermediate structures. Not all positions of noncoordinated H_2O molecules inside the sphere and in the crystal lattice could be refined for the same reason as above. Structure graphics were produced with DIAMOND 2.1 program (K. Brandenburg, Crystal Impact GbR, **1999**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138290. 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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[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⋯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

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Hartmut Bögge, Marc Schmidtmann, Paul Kögerler,
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 *C2/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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packing. The neutral cluster **2a** is, like the cluster anion **1a**, composed of 12 pentagonal units but, in contrast to **1a**, these are partially reduced. The pentagons are interlinked through 30 O=Mo(H_2O) spacers (Mo=O about 1.67 Å; Mo–H_2O (*trans*) about 2.30 Å) which form themselves, like the midpoints of the $\{Mo_2^V\}$ units in **1a**, into an Archimedean solid, namely, an icosidodecahedron (12 pentagons and 20 triangular areas). The Mo=O groups point towards the center of the sphere.

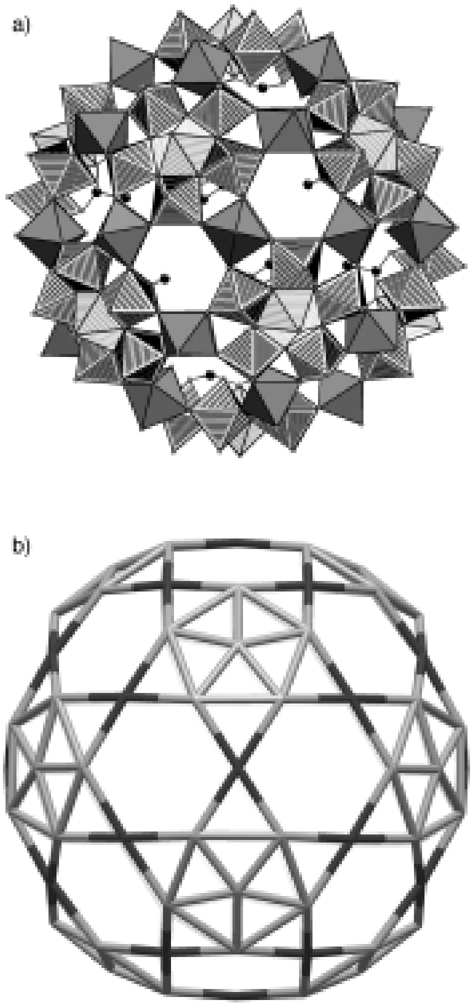

Figure 1. a) Polyhedral representation of the structure of **2a** in the direction of a C_2 axis in crystals of **2** (acetate ligands as a ball-and-stick representation), and b) wireframe representation of the $\{Mo_{102}\}$ metal skeleton. The building units, the {(Mo)Mo$_5$} pentagons with central pentagonal bipyramids linked by the O=Mo(H_2O) spacers (dark gray), can be readily identified in (a).

In agreement with the intense blue color, **2a** can be assigned as a mixed valence species of type II according to the Robin–Day scheme.[4] Of the (total) 36 Mo(4d) electrons (formal Mo^V centers, as determined by cerimetric titration of the neutral cluster), 30 electrons are mostly localized on the 30 Mo atoms which act as spacers (conforming to the significant BVS value of 5.3 of these sites), while the remaining 6 electrons are mostly delocalized over the Mo centers of the 12 pentagonal groups.[5a] The predominant localization of the 4d electron density on the aforementioned 30 Mo centers can also be shown qualitatively by EHMO calculations. At room temperature, **2** is ESR inactive due to the very strong exchange interactions.[5b]

In contrast to the classic, highly soluble molybdenum blue species, the isolation of which is based on the distruction of their strong hydration shell (due to the large number of terminal H_2O ligands) in aqueous solution[6], the generation and isolation of species such as **2** does not require such a process since the hydrophilicity of the surface, and hence the solubility of the cluster, is much lower.

Despite the relatively high number of (formal) Mo^V centers in **2a**, it is remarkable that a structure with Mo^V-Mo^V dumbbells (that is, with localized Mo-Mo bonds) does not result. The partial oxidative local degradation of the former $\{Mo_2^VO_4\}^{2+}$ spacers under mild reaction conditions corresponds formally to the scheme $\{Mo_2^V\} \rightarrow \{Mo^V\} + Mo^{VI}$ and subsequent formation of soluble polyoxomolybdates(VI). Here, no restructuring occurs since the 30 Mo^V centers, products of the former $\{Mo_2^V\}$ groups, are trapped in the spherical matrix of pentagons. It is interesting that this reaction takes place on functional linker groups positioned on the surface of the giant sphere, which inevitably leads to a change in the size of the molecule. Further oxidation does not occur because the neutral cluster **2a**, formed by this slow, partial oxidation, has a low solubility and precipitates after it forms. Precipitation prevents subsequent oxidation reactions of **2a** which would otherwise easily take place in solution.

Apart from being a novelty in the chemistry of clusters, the blue species **2a** ranks as an exceptional molybdenum oxide cluster for the following reasons: **2a** belongs neither to the group that forms Mo^V-Mo^V dumbbells because of a high Mo^V/Mo^{VI} ratio,[7, 8] nor to the group without trapped 4d electrons because of a low Mo^V/Mo^{VI} ratio. The latter group usually shows a delocalization of the 4d electrons, as in the example of the classic soluble molybdenum blue species.[9] Remarkably, no pronounced electron delocalization in the form of "electron hopping" can be observed.[8, 10] The unusual electronic structure of an icosidodecahedral $\{Mo^V\}_{30}$ fragment is the result of the described special reaction type.

Experimental Section

To a red-brown solution of **1** (1.4 g, 0.05 mmol, in 25 mL H_2O), HCl (25 %, 1.5 mL) and NaCl (2.2 g, 37.65 mmol) were added. The reaction solution was stirred for 1 h at room temperature in presence of air, filtered, and stored in a closed 50-mL Erlenmeyer flask at room temperature. Blue rhombohedral crystals of **2** were collected after 3 d by filtration, washed several times with water and dried under air. Yield: about 0.29 g (31 % based on **1**).

Characteristic IR bands for **2** (KBr): $\tilde{\nu} = 1620$ (m, $\delta(H_2O)$), 983 (m, ν(Mo=O)), 961 (m, ν(Mo=O)), 749 (w), 680 (w), 629 (w), 551 (m), 464 cm^{-1} (m); characteristic resonance Raman bands ($\lambda_e = 1064$ nm; diluted with KBr): $\tilde{\nu} = 765$ (s, breathing vibration of the bridging oxygen atoms between Mo^V and Mo^{VI} centers), 659 (m), 440 cm^{-1} (s); UV/Vis (solid-state reflection spectrum, cellulose used as a white standard): $\lambda \approx 300$ (br), 750-800 nm (br) (intervalence charge transfer (IVCT) with $Mo^V \rightarrow Mo^{VI}$ character); correct elemental analysis; cerimetric titration for 36 electrons.

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[3] Crystal structure analysis of **2**: $H_{492}C_{24}Mo_{102}O_{534}$; $M = 19114.06\ \mathrm{g\,mol^{-1}}$, space group $C2/c$, $a = 44.586(1)$, $b = 26.365(1)$, $c = 44.565(1)$ Å, $\beta = 104.21(1)^\circ$, $V = 50782\ \text{Å}^3$, $Z = 4$, $\rho = 2.500\ \mathrm{g\,cm^{-3}}$, $\mu = 2.550\ \mathrm{mm^{-1}}$, $F(000) = 36768$, crystal size $= 0.20 \times 0.08 \times 0.06\ \mathrm{mm^3}$. Crystals of **2** were removed from the mother liquor and immediately measured at 183(2) K on a Bruker axs SMART diffractometer (three-circle goniometer with a 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere of data collection at 0.3° wide ω scans over three runs of 606, 435, and 230 frames ($\phi = 0^\circ, 88^\circ, 180^\circ$) from a 5.00 cm-distant detector). A total of 148391 reflections ($1.54 < \Theta < 26.99^\circ$) were collected, of which 54698 unique reflections ($R(\mathrm{int}) = 0.0811$) were used. An empirical absorption correction on the basis of symmetry-equivalent reflections was performed with the SADABS program. The structure was solved and refined with the SHELXS-97 and SHELXL-97 programs (G. M. Sheldrick, University of Göttingen, **1997**) to $R = 0.0713$ for 23929 reflections with $I > 2\sigma(I)$ and a max./min. residual electron density of $2.816/-3.078\ \mathrm{e\,Å^{-3}}$. Structure graphics were produced with the DIAMOND 2.1 program (K. Brandenburg, Crystal Impact GbR, **1999**). Due to disorder, not all positions of the water molecules inside the sphere and in the crystal lattice were localized. The same note applies to the acetate ligands. 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-138289. Copies of the data can be obtained 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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A Molecular Knot with Twelve Amide Groups—One-Step Synthesis, Crystal Structure, Chirality[**]

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In memory of Eberhard Steckhan

Molecular knots are a little known class of substances.[1] Hitherto only some of the (historically first) phenanthroline type (Dietrich-Buchecker and Sauvage, 1989),[2] of the nucleic-acid type (Seeman, 1992),[3] and of the crown/quat type (Stoddart et al., 1997)[4] have been synthesized. We report here on probably the simplest synthesis of a new molecular trefoil knot in 20% yield, which proceeds under self-organization. Besides a 96-membered araliphatic skeleton this knot only includes twelve CONH groups.

In the course of the synthesis[5] of higher [*n*]catenanes[1]—with more than two interlacing wheels—we planned to prepare larger amounts of macrocycle **4**,[6] which should be favorable as a (ditopic) concave (host) template in the synthesis of [2]- and [3]catenanes.[7] For this purpose we treated the proven substrates 2,6-pyridinedicarboxylic acid dichloride **1** and diamine **2**[6] under dilution conditions (concentration 10^{-3} mM)[5] in dichloromethane together with the auxiliary base triethylamine. This reaction gave besides **3** (yield 15%) and **4** (yield 23%) a colorless product in 20% yield which had a molecular weight of m/z 2718.6 (MALDI-TOF-/FAB-MS), a melting point of >325 °C, and an R_f value

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