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VIP **Polyoxometalates**

Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$**

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Dedicated to Professor Peter Day on the occasion of his 70th birthday

In the field of polyoxometalate chemistry, porous spherical molybdenum oxide-based clusters of the type $\{(Mo^{VI})Mo^{VI}_5\}_{12}(\text{linker})_{30}$,[1] called Keplerates,[2a,b] are notable not only from an aesthetic point of view[2c] but also because they show properties of interest for different areas of science. Some of these clusters can act as artificial cells exhibiting gated pores while interacting specifically with their environments; others are of interest for several aspects of materials science.[3–5] In detail, of interest are a) solution properties in connection with a new type of assembly process leading to vesicles, including magnetic ones,[6a,b] b) the option to employ the characteristic interactions with amphiphiles for the generation of monolayers and Langmuir–Blodgett films[6c] as well as highly ordered honeycomb nanostructures at air–water interfaces,[6d] c) the integration into sol–gel-derived silica to obtain unprecedented hybrids,[6e] and d) the discovery of novel magnetic properties,[6f] which are of interest for the understanding of Kagomé lattices' spin states.[6g,h]

While Keplerates of the mentioned type with binuclear linkers $\{Mo^{V}_2O_4\}^{2+}$ have been synthesized by partly reducing an aqueous molybdate solution in the presence of appropriate bidentate bridging ligands[1b,7] (leading in the case of acetate to $\{Mo^{V}_2O_4(OOCCH_3)\}^+$ linkers), Keplerates of the type $\{(Mo)Mo_5\}_{12}M_{30}$ ($\equiv\{Mo_{72}M_{30}\}$) can be obtained directly by the addition of mononuclear linkers M such as Fe^{3+}, Cr^{3+}, and VO^{2+} to a dynamic library of the pentagonal units $\{(Mo)Mo_5O_{21}(H_2O)_6\}^{6-}$,[8] or by reaction of, for example, Fe^{3+} with $\{(Mo)Mo_5\}_{12}\{Mo_2\}_{30}$ ($\equiv\{Mo_{132}\}$), thereby exchanging binuclear for mononuclear linkers.[9] As the pentagonal $\{(Mo)Mo_5\}$-type units appear in this context as transferable ligands (parallels have been made between infinite coordination polymers and discrete metallosupramolecular arrays), the mentioned clusters can be called coordination polymers with spherical periodicity.[8c,10] This analogy points to a route for the planned syntheses of other corresponding molecular spheres based on a careful selection of appropriate ligands and metal ions with specific coordination behavior. Herein we report the synthesis of a $\{(W)W_5\}_{12}\{Mo_2\}_{30}$ ($\equiv\{W_{72}Mo_{60}\}$)-type species with 30 $\{Mo^{V}_2O_4(\text{acetate})\}^+$ linkers with metal–metal bonds and 12 unprecedented pentagonal $\{(W)W_5O_{21}(H_2O)_6\}^{6-}$ ($\equiv\{(W)W_5\}$) ligands, which are necessary for the formation of the spherical cluster and are generated in a dynamic library of tungstates (see below). Whereas the $\{(Mo)Mo_5\}$-type building blocks were known to occur in $[Mo_{36}O_{112}(H_2O)_8]^{8-}$ present at low pH values in H_2O,[11] no corresponding pentagonal unit has been observed to date among the thousands of polyoxotungstates. On the basis of the present work, there is the option for the extension of the molybdate-based Keplerate chemistry to the tungstates, which is possible owing to the use of the transferable pentagonal $\{(W)W_5\}$-type units now available; this allows, for example, the synthesis of $\{(W)W_5\}_{12}M_{30}$ clusters, which are of importance for materials science aspects, with the above-mentioned magnetic M^{3+} linkers.[12a] Transferable, pentagonal building blocks are extremely rare in chemistry but are, generally speaking, relevant for the construction of curved giant species, such as the often highlighted hedgehog $\{Mo_{368}\}$ cluster.[4,5] On the other hand, pentagons in a general sense play a unique role starting from modern solid-state chemistry and dating backwards via many topics to the ideas of the ancient Greek mathematicians.[13] In any case, the present discovery allows us to follow new interesting routes in chemistry and materials science, especially because the surface properties of tungsten oxide based systems are different from those of the molybdates. Whereas the high formation tendency of the spherical shell of the type $(\text{pentagon})_{12}(\text{linker})_{30}$ based on pentagonal units has been discussed earlier in terms of a general chemical principle,[12b] it is also evident that the formation of the present pentagonal units can be considered in the framework of a "constitutional dynamic chemistry" formulated by Lehn, that is, with respect to systems responding to external stimuli (see below).

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Compound **1** was obtained by "recrystallization" of the red-brown microcrystalline ammonium salt of **1a** (obtained by treating an acidified aqueous solution of sodium tungstate containing a rather high concentration of acetate with $(NH_4)_2[Mo^V{}_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ in aqueous solution after adding dimethylammonium chloride. **1**, which crystallizes in the space group $R\bar{3}$, was characterized by elemental analysis, thermogravimetry (to determine the crystal water content), redox titrations (to determine the number of Mo^V centers), spectroscopic methods (IR, Raman, UV/Vis, and ^1H and ^{13}C NMR) and single-crystal X-ray structure analysis[14] including bond valence sum (BVS) calculations.

$$[(CH_3)_2NH_2]_{48}[\{(W^{VI})W^{VI}{}_5O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo^V{}_2O_4(CH_3COO)\}_{30}]\cdot \text{ca. } \{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \equiv [(CH_3)_2NH_2]_{48}\cdot \mathbf{1a}\cdot \text{ca. } \{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \quad \mathbf{1}$$

The anionic capsule **1a** is built up of 12 pentagonal units of the type $\{(W^{VI})W^{VI}{}_5\}$ that are positioned at the vertices of an icosahedron and connected by 30 $\{Mo^V{}_2O_4(CH_3COO)\}^+$ linking groups (Figure 1). Correspondingly, the seven-coordinated W centers of the 12 pentagonal units span an icosahedron and the 30 linkers a distorted truncated icosahedron. The single-crystal X-ray structure analysis additionally shows the presence of six disordered acetate ligands positioned under the pentagonal units; each of them connects a central W atom to a peripheral W atom.

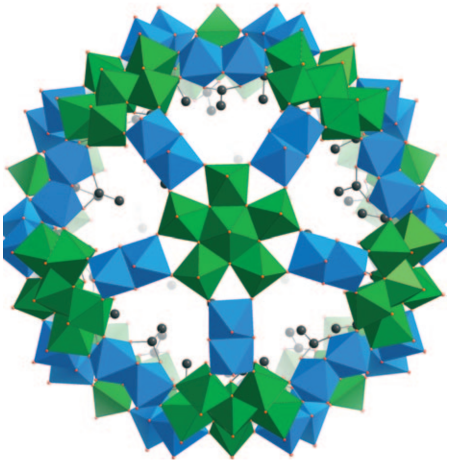

Figure 1. Structure of **1a** with perspective view along a fivefold symmetry axis highlighting a pentagonal $\{(W^{VI})W^{VI}{}_5\}$-type unit (in the center) and the five related $\{Mo^V{}_2O_4\}^{2+}$ ($=\{Mo^V{}_2\}$) linkers stabilized by the acetate ligands (not visible) attached to it. ($\{(W^{VI})W^{VI}{}_5\}$ groups green, $\{Mo^V{}_2\}$ bridges blue and both in polyhedral representation, C atoms black spheres).

The construction of $\{Mo_{132}\}$- and $\{W_{72}Mo_{60}\}$-type Keplerates requires the presence of pentagonal units $\{(M)M_5\}$ (M = Mo or W) along with suitable linkers. While it was known that $\{(Mo^{VI})Mo^{VI}{}_5\}$-type fragments (or building blocks) are abundant in acidified molybdate solutions, that is, occur in the $[Mo_{36}O_{112}(H_2O)_8]^{8-}$ anion,[11] a related situation does not apply for tungstate chemistry. None of the polyoxotungstates reported to date,[15] including the largest ones,[16] contains the corresponding important pentagonal $\{(W)W_5\}$ units.[17] Aqueous tungstate solutions at pH values of about 4 contain ψ-, β-, and α-metatungstates, which are built up of WO_6 octahedra (metastable β- and thermodynamically stable α-$[H_2W_{12}O_{40}]^{6-}$ species have Keggin-type structures).[15] The linkers, which are important for the syntheses of the two Keplerates mentioned above, can either be produced in situ from molybdate solutions under reducing conditions (which led to the deliberate synthesis of $\{Mo_{132}\}$-type clusters)[1] or added in the form of $[Mo^V{}_2O_4(C_2O_4)_2]^{2-}$, as in the case of the synthesis of **1** and of the corresponding $\{Mo_{132}\}$ compound.[18] The formation of **1a** under the present conditions demonstrates that the reaction is symmetry-driven and free-energy-favored.

The Raman spectra of **1** in H_2O have been recorded for various concentrations, starting from a nearly saturated solution (i.e. ca. 1 g mL^{-1}); no significant change was observed upon dilution. This finding indicates that self-assembly into supramolecular structures does not occur in aqueous solutions under these conditions (see below). The solution spectrum of **1** is practically identical to that of solid **1** (Figure 2), which supports the stability of **1a** in solution. (The same holds for the $\{Mo_{132}\}$-type species with different ligands.[1,19]) Though the spectrum is, as expected, similar to that of its $\{Mo_{132}\}$ counterpart, [1,7c] significant (but expected) differences arising from a change in the M=O bond polarizability are observed: the line at 976 cm^{-1}, which is assigned to the $\nu(W{=}O_{term})$ A_g-type vibration (assuming I_h symmetry), is much more intense than the corresponding line of the $\nu(Mo{=}O_{term})$ vibration of $\{Mo_{132}\}$, in agreement with the higher bond polarizability of the terminal W=O bond (effect not caused by the different excitation lines). $\nu(W{=}O_{term})$ at 976 cm^{-1} also occurs at higher wavenumbers than the corresponding vibrations of $\{Mo_{132}\}$ (the weak band at ca. 957 cm^{-1} of **1a** could be assigned to the $\nu_s(Mo{=}O_{term})$ vibration of the linkers) in accordance with the higher W=O bond strength in **1a**. This leads to a lower electron density on the corresponding O atoms, which changes the nanosurface properties (see below).

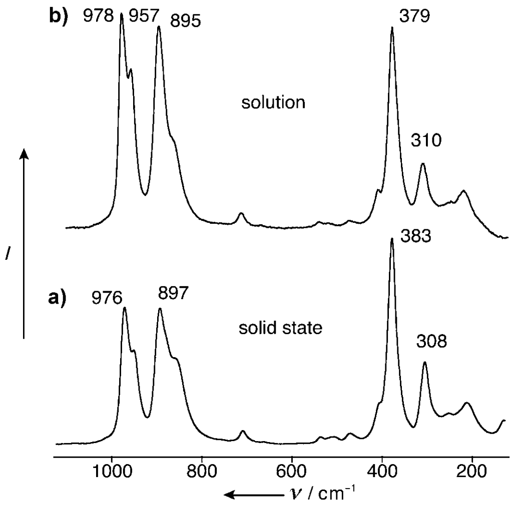

Figure 2. Raman spectra ($\lambda_{exc} = 765$ nm) of **1** a) in the solid state and b) in aqueous solution as evidence of the stability of **1a** in solution; see text for a discussion of the related metal oxide surface characteristics.

Further evidence for the stability of $\{W_{72}Mo_{60}\}$ clusters in solution is provided by NMR spectroscopy studies. The ^{1}H NMR spectrum of **1** in D_2O (Figure 3 a) shows two sharp singlets at $\delta = 2.84$ and 1.97 ppm, which are assigned to the methyl groups of the dimethylammonium cation and to free acetate, respectively. The broad feature centered near 1 ppm is attributed to coordinated acetate. The latter signal clearly exhibits several components spanning approximately 1 ppm, which indicates non-equivalent ligands; this finding is consistent with the results of the single-crystal structure analysis for **1**. The ^{13}C NMR spectrum of **1** in D_2O (Figure 3 b) shows partially overlapping broad resonances for the methyl (maxima at ca. $\delta = 23.6$ and 24.8 ppm) and carboxylate groups (maxima at ca. $\delta = 178.9$, 179.8, and 180.6 ppm) of coordinated acetate ligands, while the resonances of free acetate are hardly detectable at $\delta = 22.1$ and 177.4 ppm. No significant change, in particular no increase in the intensity of free acetate signals, is observed upon raising the temperature to 353 K. (Our attempts to obtain a clean ^{183}W NMR spectrum of **1** in solution were unsuccessful. Broad features were observed, likely arising from the expected fast relaxation of the ^{183}W nuclei in such large species.) Most spectroscopic measurements were performed on deaerated solutions, which, however, did not appear to be especially sensitive to oxidation. Raman and ^{1}H and ^{13}C NMR spectroscopy therefore demonstrate the stability of **1a** in aqueous solutions, a feature shared with its $\{Mo_{132}\}$ counterpart.[19]

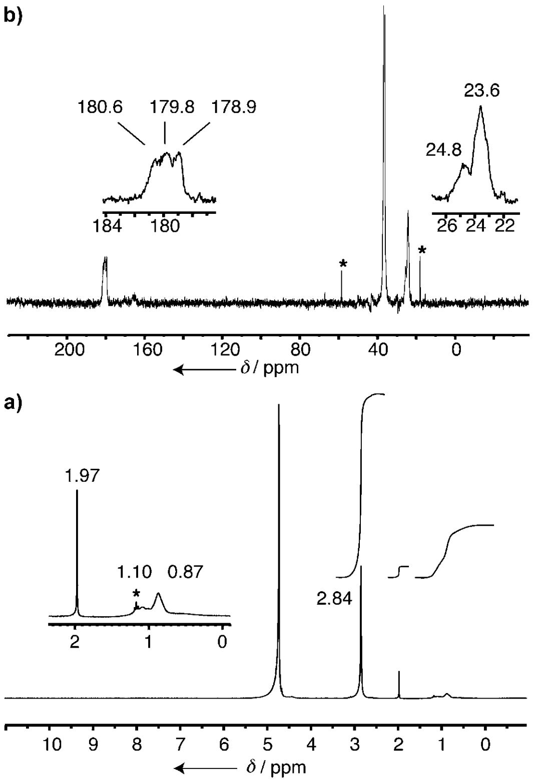

Figure 3. NMR spectra of **1** in D_2O solutions: a) 300.13 MHz ^{1}H spectrum ($c = 0.5$ mmol L^{-1}) with relative integration of $(CH_3)_2NH_2^+$ and of free and coordinated acetate resonances, in agreement with the stoichiometry of **1**; b) 125.7 MHz ^{13}C spectrum ($c = 20$ mmol L^{-1}). The signals of residual ethanol are marked by *.

Detailed knowledge of the properties of the structurally well-defined nanosurfaces of the present type of metal oxide based system is of interest for several aspects of materials science. In this context, we have studied solution properties of the new cluster **1a** and compared them to those of the molybdenum analogue $\{Mo_{132}\}$.[6a] Both cluster anions are soluble in polar solvents owing to their high negative charges and the hydrophilic nature of their surfaces. The $\{W_{72}Mo_{60}\}$ clusters, which exist in aqueous solution as discrete, hydrophilic macroanions carrying a few more charges than the $\{Mo_{132}\}$ ones (these contain fewer integrated acetate ligands[1]), show self-assembly when acetone is introduced into the solution to decrease the solvent polarity. In solvents containing 30–75 vol % acetone, the macroions **1a** form spherical, single-layer, hollow, vesicle-like blackberry-type structures, as confirmed by static and dynamic laser light scattering studies. The size of the assemblies increases with increasing acetone content, while a linear relationship between the hydrodynamic radius R_h of the assemblies and ε^{-1} is observed (Figure 4; ε is the solvent dielectric constant). This relationship is consistent with our previous results obtained for $\{Mo_{132}\}$ macroions in water/acetone mixed solvents.[6a,20] The supramolecular structure formation occurs when the macroions carry some (but not too many) negative charges, which leads to attraction influenced by the cations positioned between the anions.[6a,20] But when the macroions are too highly charged, the strong electrostatic repulsion prevents them from moving close to each other. Nor does assembly occur if the clusters are (almost) uncharged, owing to the lack of the above-mentioned charge-based effect, for example, in pure acetone solution. Importantly, the $\{W_{72}Mo_{60}\}$ blackberry-type structures have a smaller average size than the $\{Mo_{132}\}$ ions under the same conditions, owing to the higher charge density on $\{W_{72}Mo_{60}\}$ clusters (for an explanation, see reference [6b]). The influence on the surface charge caused by the larger number of integrated acetate ligands of **1a** overcompensates the influence of the smaller bond

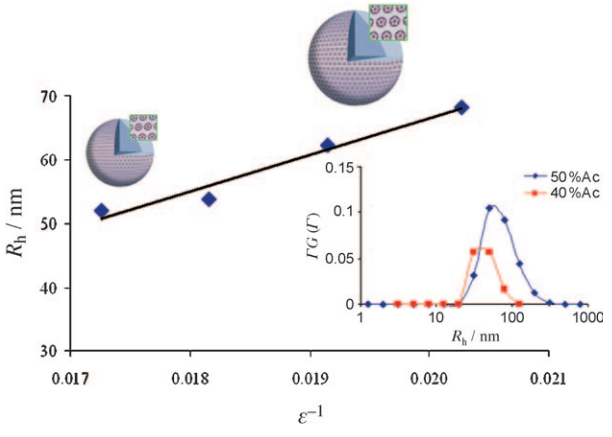

Figure 4. The $\{W_{72}Mo_{60}\}$ macroions self-assemble in water/acetone solutions into blackberry-type structures, the size of which increases with increasing acetone content, that is, decreasing dielectric constant. Inset: CONTIN analysis[23] of the dynamic light scattering results for $\{W_{72}Mo_{60}\}$/water/acetone solutions containing 40 and 50 vol % acetone.

polarity of the W=O bonds corresponding to a smaller electron density on the O atoms (see above).

It is an important result that the high formation tendency of the spherical cluster **1a** influences the composition of the units present in the dynamic library. Pentagonal units of the type $\{(W)W_5\}$ were not observed in any known polyoxotungstate but are necessary for the formation of **1a** and corresponding spherical and, generally speaking, giant curved species. In the present scenario, we can refer to constitutional dynamic chemistry, as described by Lehn, "whereby a chemical entity, be it as well molecular as supramolecular, undergoes continuous change in its constitution through dissociation into various components and reconstitution into the same entity or into different ones".[21] Another impressive directly related example is provided by the formation of the $\{Mo_{72}Fe_{30}\}$-type Keplerate containing an encapsulated Keggin ion (a new type of supramolecular species with a cluster noncovalently bound inside a cluster). The necessary pentagonal units are formed by an unprecedented reaction of $[PMo_{12}O_{40}]^{3-}$ with Fe^{3+} ions and finally generate the spherical shell through linking with the Fe^{3+} ions. This result was originally discussed with reference to "supramolecular Darwinism,"[13] as the terms "adaptation" and "protection" as well as "symbiosis" hold, and was later referred to and highlighted by Lehn in the statement, "The supramolecular organization drives the selection of the components giving the 'fittest constituent'".[21]

Experimental Section

1: $Na_2WO_4\cdot 2H_2O$ (8.0 g, 24.25 mmol) and $NaCH_3COO\cdot 3H_2O$ (36.0 g, 264.6 mmol) were dissolved in degassed water (100 mL) while the pH value of the reaction mixture was adjusted to approximately 4 with degassed 100 % acetic acid (60 mL). After the finely powdered oxalato complex $(NH_4)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$[22] (9.0 g, 16.13 mmol) was added quickly, the solution was heated under an argon atmosphere for 90 min at 120 °C (oil bath temperature) under vigorous stirring (color change to dark brown). The solution was cooled to room temperature, and the red-brown microcrystalline powder was filtered off, washed thoroughly with ethanol, and dried with diethyl ether (yield: 1.8 g, 15 % based on W). Then $(CH_3)_2NH_2Cl$ (200 mg, 2.45 mmol) was added to a solution of the obtained microcrystalline product (200 mg, 0.0056 mmol) in water (10 mL). After two to three days, the red-brown crystals were filtered off, washed with ethanol, and dried with diethyl ether. In ongoing studies, attempts are being made to improve the yield (Thesis, C. Schäffer). Elemental analysis (%) calcd: C 6.61, N 2.16, W 37.18, Mo 16.17 (values refer only to $250H_2O$ corresponding to the relevant (i.e. for the analysis) loss of crystal water); found: C 6.6, N 2.4, W 37.9, Mo 17.1 (W and Mo analyses were performed by Mikroanalytisches Labor Egmont Pascher, An der Pulvermühle 3, 53424 Remagen, Germany). Cerimetric titrations: $60\pm 2\,Mo^V$. IR (KBr pellet; characteristic bands): $\tilde{\nu} = 1625$ (m, $\delta(H_2O)$), 1539 (m, $\nu_{as}(COO)$), 1440 (m), 1420 (m, $\delta(CH_3)$, $\delta_{as}(NH_4^+)$, $\nu_s(COO)$), 972 (m) and 960 (w-m, ν(W=O)), 879 (m), 812 (vs), 733 (s), 658 (w), 577 (s), 519 (w), 470 cm^{-1} (w). Characteristic Raman bands: see Figure 2. ^1H NMR (D_2O): $\delta = 2.84$ (s, $(CH_3)_2NH_2^+$), 1.97 (s, free $CH_3CO_2^-$), 1.10, 0.87 ppm (coordinated $CH_3CO_2^-$). ^{13}C NMR (D_2O): $\delta = 180.6$, 179.8, 178.9 (coordinated $CH_3CO_2^-$), 35.77 ($(CH_3)_2NH_2^+$), 24.8, 23.6 ppm (coordinated $CH_3CO_2^-$). Characteristic UV/Vis bands (H_2O, absorption): $\lambda = 240$, 375 nm (vs, br).

Raman spectra were collected with a Kaiser Optical Systems HL5R Raman spectrometer equipped with a near-IR laser diode working at 785 nm. The laser power was adjusted to 15–20 mW at the sample position for all spectra. The average resolution is 3 cm^{-1}.

^1H and ^{13}C NMR spectra of **1a** were obtained from D_2O solutions at 300.13 and 125.7 MHz on Bruker AvanceII 300 and DRX 500 spectrometers, respectively. Chemical shifts were referenced to external tetramethylsilane by setting the methyl resonance of residual ethanol to 1.17 (^1H) and 17.33 ppm (^{13}C). A commercial Brookhaven Instrument laser light scattering spectrometer equipped with a solid-state laser operating at 532 nm was used for static and dynamic light scattering experiments. The data, analyzed by the CONTIN method,[23] can be used to determine the average hydrodynamic radius R_h of the particles. Detailed descriptions of the SLS and DLS technique can be found in an earlier publication.[6a]

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[13] The "magic" pentagons play an extraordinary role in culture and the history of science as well as in modern solid-state chemistry and physics, beginning with the Pythagoreans (the pentagram was the emblem of their school), via Archimedean and Keplerian type tilings, Fibonacci chains, Goethe's Faust (the pentagram) to Weyl and Penrose. They are of interest in many scientific disciplines: in discrete mathematics (one of the five regular bodies is built up of pentagons), in architecture and art history (in the sense of Fuller's domes and in the context of the golden section), in solid-state chemistry and physics (in the context of the fascinating quasicrystals and hybrids of real and quasicrystals), in virology (owing to the structure of spherical viruses), and last but not least in modern synthetic chemistry, allowing novel design strategies of curved species, that is, of molecular spheres (fullerenes and Keplerates) and wheels (molybdenum-blue-based) as well as of others, such as the {Mo_{368}} cluster (A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, A. Dress, *Angew. Chem.* **2002**, *114*, 1210 – 1215; *Angew. Chem. Int. Ed.* **2002**, *41*, 1162 – 1167); remarkably, the {$(M)M_5$}-type units also play a role in catalysis, while it was proposed that they are even precursors in case of the syntheses of the corresponding vanadium molybdenum oxide based catalysts. The pentagonal units can be considered as magic, as Casper and Klug were inspired by Fuller's domes to understand the structure of spherical viruses; see section title "Viral Capsids Resemble Geodesic Domes" and a picture of the latter (Figure 32.12) in: D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., Wiley, New York, **1995**, pp. 1082 – 1083; see also Ref. [1b]. Related information: a) *Quasicrystals, Networks, and Molecules of Fivefold Symmetry* (Ed.: I. Hargittai), VCH, New York, **1990**; b) A. Müller in *Facetten einer Wissenschaft: Chemie aus ungewöhnlichen Perspektiven* (Eds.: A. Müller, H.-J. Quadbeck-Seeger, E. Diemann), Wiley-VCH, Weinheim, **2004**, pp. 65 – 90; c) S. C. Glotzer, A. S. Keys, *Nature* **2008**, *454*, 420 – 421; d) A. Müller, P. Kögerler, H. Bögge, *Struct. Bonding (Berlin)* **2000**, *96*, 203 – 236; e) M. Sadakane, N. Watanabe, T. Katou, Y. Nodasaka, W. Ueda, *Angew. Chem.* **2007**, *119*, 1515 – 1518; *Angew. Chem. Int. Ed.* **2007**, *46*, 1493 – 1496; f) W. Ueda, M. Sadakane, H. Ogihara, *Catal. Today* **2008**, *132*, 2 – 8.

[14] Crystal data for **1**: $W_{72}Mo_{60}C_{196}N_{55}O_{788}H_{1229}$, $M = 35964.94\ \mathrm{g\,mol^{-1}}$, space group $R\bar{3}$, $a = 32.816(1)$, $c = 74.547(3)$ Å, $V = 69525(5)$ Å^3, $Z = 3$, $\rho = 2.577\ \mathrm{g\,cm^{-3}}$, $\mu = 9.790\ \mathrm{mm^{-1}}$, $F(000) = 50826$, crystal size $= 0.18 \times 0.18 \times 0.18\ \mathrm{mm^3}$. A total of 142514 reflections ($1.49 < \theta < 28.50°$) were collected, of which 36198 reflections were unique (R(int) $= 0.0767$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0595$ for 20316 reflections with $I > 2\sigma(I)$, $R = 0.1368$ for all reflections; max/min residual electron density 2.502/−2.019 e Å^{-3}. Crystals of **1** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three-circle goniometer with 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\phi = 0$, 88, and 180°) at a detector distance of 5 cm). (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen **1997/2001**; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001). CCDC-701392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Interestingly, pentagonal {$(M)M_5$}-type units occur without M=O (double) bonds in solid-state structures of some lower-valence molybdenum and tungsten oxides, e.g., Mo_5O_{14} (L. Kihlborg, *Ark. Kemi* **1963**, *21*, 427 – 437) and $W_{18}O_{49}$ (A. Magnéli, *Ark. Kemi* **1949**, *1*, 223 – 230; M. Lundberg, M. Sundberg, A. Magnéli, *J. Solid State Chem.* **1982**, *44*, 32 – 40); see also: D. L. Kepert, *The Early Transition Metals*, Academic Press, London, **1972**, pp. 260 – 263 and F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, **1980**, p. 847 and Figure 22-C-2. In this case, the formation of the pentagonal units seems to be favored by the high temperatures of the solid-state reactions.

[18] The molybdenum analogue of **1a** {Mo_{132}} can correspondingly easily and deliberately be prepared from its two components, pentagonal units and binuclear linkers: A. Müller, C. Kuhlmann, H. Bögge, unpublished results.

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