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Soluble Molybdenum Blues—"des Pudels Kern"[†]

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ABSTRACT

The earlier tremendous interest in molybdenum blue solutions—an enigma for generations of chemists—became even more pronounced when it turned out that the basic building units correspond to giant wheel-shaped clusters with nanostructured cavities, displaying exceptional aesthetic beauty. This discovery will stimulate new ideas in supramolecular chemistry, colloid chemistry, and materials science. The giant wheels represent nanosensors and nanoreactors, enabling the initiation of chemical processes at different positions, like a "structured landscape", and can even be used as robust synthons for the construction of compounds with typical solid-state structure, a situation comparable to crystal engineering.

Introduction

"This is a substance or group of substances about which there has been much discussion" is a statement found in an older standard textbook of inorganic chemistry.[1] The history of soluble molybdenum blue (solid-state and heteropoly blues will not be considered here) dates back to Carl Wilhelm Scheele's report from 1783,[2] although the "blue waters" from Idaho Springs or the Valley of the Ten Thousand Smokes might have been known to man much earlier. This natural molybdenum blue, the mineral ilsemannite, has almost the same composition as most of the products obtained by very different laboratory procedures, such as the action of a considerable number of various reducing agents on acid molybdate(VI) solutions, electrolytic reduction, the chemical or electrochemical oxidation of Mo, MoO_2, and other low-valent Mo-containing educts, or the reaction of molybdate with $MoCl_5$. J. J. Berzelius[3] obtained his molybdenum blue samples according to the latter type of reaction, and he was also the first to give a composition $(Mo_5O_{14} \cdot nH_2O)$. Later reports gave the formula MoO_x with $2.5 < x < 3$, actually suggesting that more than one type of Mo blue species exists (for early reports in the literature cf. refs 4 and 5). Almost all students and technicians dealing with chemistry over the last two centuries came into contact with molybdenum blue, but it took almost the same period of time to unveil the real

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Claire Serain, born 1970, graduated from the Université Claude Bernard, Lyon I (France), and is now working under the supervision of A. Müller for her Ph.D. degree at the University of Bielefeld.
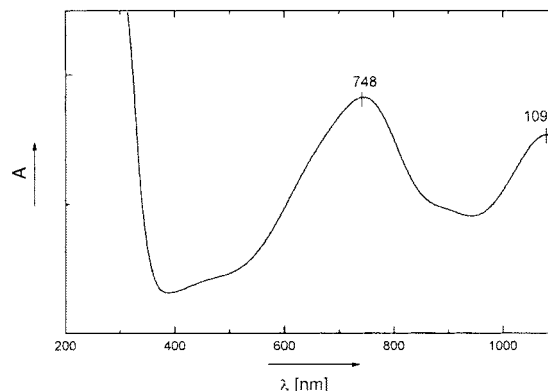
FIGURE 1. Typical electronic absorption spectrum of aqueous MB solutions, here obtained by the reduction of a molybdate solution with $SnCl_2 \cdot 2H_2O$.

nature of the species, including their structures, responsible for the deep blue color. In this Account, we hope to explain this phenomenon and why it is by no means trivial to define the specific qualities of this material: a novel, fascinating, and incomparable class of compounds. The title refers to the fact that generations of chemists tried to crystallize compounds from Mo blue solutions and to determine the formulas without success. But we are now in a position to do so since "des Pudels Kern" or the essence of the matter is now known and lies in destroying the hydration shell of the species, all of which contain giant wheel-shaped building blocks.

Properties of Molybdenum Blue (MB) Solutions

Solutions of molybdenum blue (MB) are almost instantaneously obtained by the reduction of Mo^{VI}-type species in acid solutions (pH $\leq$ 3). Reducing agents may be metals (Al, Pb, Mo, Cu, Zn, Cd, Hg), B_2H_6, $NaBH_4$, N_2H_4, NH_2OH, H_2S, SO_2, SO_3^{2-}, $S_2O_4^{2-}$, $S_2O_3^{2-}$, $SnCl_2$, $MoCl_5$, $MoOCl_5^{2-}$, Mohr's salt, formic acid, ethanol, ascorbic acid, tartaric acid, thiourea, hydroquinone, D-glucose, sucrose, gaseous H_2, or CO (under pressure). They may also be obtained by electrolytic reduction, photochemically, or with γ-irradiation.[4–6] All authors describe their products as "molybdenum blue", although from the relevant properties it is clear that not always completely identical solutions are formed (for a typical electronic absorption spectrum, see Figure 1, cf. refs 5 and 7). Under stronger reducing conditions, brown species are formed which show, in general, the presence of $Mo^V–Mo^V$ dumb-bells as building blocks.[8] Common to these solutions is that negative colloids are formed which can be bleached by charcoal, by adsorption to silk or cotton, and by oxidation. On adding electrolytes such as ammonium chloride or other salts, polymerization and/or precipitation takes

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[†] "des Pudels Kern" i.e., the poodle's core or the essence of the matter (Goethe, Faust I).
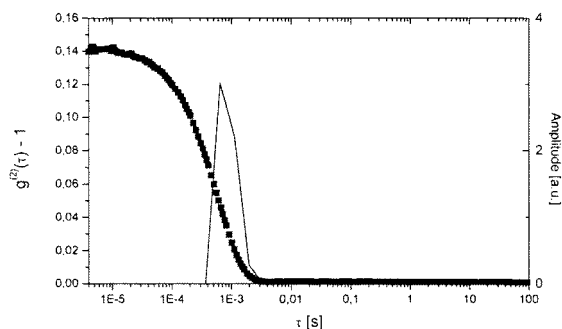
FIGURE 2. Typical light-scattering intensity autocorrelation function (■) and the calculated distribution of relaxation times (full line) of $Na_{24}[Mo_{144}O_{437}H_{14}(H_2O)_{56}] \cdot$ ca. $250H_2O$ in methanolic solution (concentration, 0.1 mg·ml^{-1}). Dynamic light-scattering results prove that aggregation takes place in the solution, and particles with a hydrodynamic radius of about 40 nm are found.

place. The solutions exhibit a Tyndall effect, and under the ultramicroscope a submicronic particle size has been observed.[4]

MB precipitates are highly soluble in ionizing solvents, such as ethanol, butanol, and ethyl acetate, but insoluble in solvents with low dielectric constants. At the beginning of the twentieth century, molar masses were determined cryoscopically from aqueous solutions obtained either by electrochemical reduction or by the reaction of molybdate with Mo powder. The earlier obtained values between 440 and 481 seemed to fit best for undissociated Mo_3O_8 (calcd 416), and for many authors later these values represented the stoichiometry attributed to "molybdenum blue",[4] an assumption which has proved to be rather misleading, as we know today.

Although we can now isolate various well-defined crystalline species from such solutions and characterize them in detail using also single-crystal X-ray structure analyses, the solutions are still not completely understood, but all species seem to contain giant wheel-shaped building blocks. For example, by dissolving MB crystals containing a chainlike arrangement of these building blocks (see below) in methanol, an almost monodisperse colloid with a hydrodynamic radius of 40 nm is formed (shown from dynamic light-scattering experiments; see Figure 2) which organizes into even higher aggregates upon evaporation of the solvent under the ESEM (Figure 3).[9]

A straightforward fast identification of a MB-type solution is possible by measuring the resonance Raman spectrum (with $\lambda_e = 1064$ nm; Figure 4). This spectrum is rather insensitive to the reaction conditions, a fact which can now be understood[5] since the structures of many isolated crystalline materials, all containing the same building block, have become known.

The first real breakthrough in solving some of the basic problems mentioned above was when we succeeded in isolating crystals—suitable for X-ray structure analysis—from MB solutions. Since then, by carefully controlling the reaction conditions, we have obtained a series of related novel compounds (Table 1; the results are based
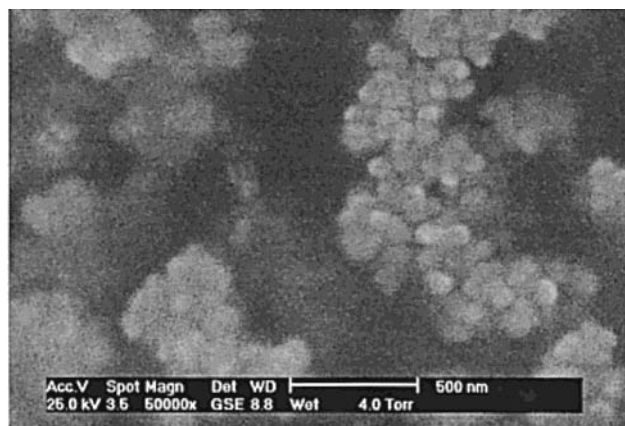
FIGURE 3. Scanning electron microscope (Philips ESEM XL30) image showing aggregates with a diameter of about 80 nm which are formed in a methanolic solution of $Na_{22}[Mo_{146}O_{442}H_{14}(H_2O)_{58}] \cdot$ ca. $250H_2O$ (concentration, 0.1 mg·ml^{-1}). It is evident that the aggregates also tend to form larger arrangements.
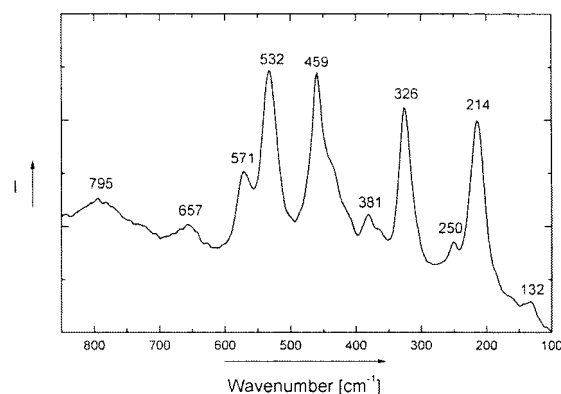
FIGURE 4. Characteristic resonance Raman spectrum ($\lambda_e = 1064$ nm) of a typical MB solution. The spectrum is rather insensitive to the reaction conditions (cf. text) and also nearly identical (except for the intensity of the band at ca. 800 cm^{-1}) with the spectra of different crystalline compounds as all contain the wheel-shaped cluster unit.

on several single-crystal X-ray structure analyses per compound) which offer many fascinating and exciting aspects for different areas of chemistry, supramolecular chemistry, and materials science.

MB Species Formation in Solution—Facile and High-Yield Syntheses of Crystalline Materials

The precipitation and isolation of the giant MB cluster anions caused difficulties for generations of chemists in the past but also during the initial phase of our related investigations. Unfortunately, it was not realized earlier that the crystallization problems were caused by the extremely high solubility of this type of species due to the very large number of H_2O ligands. But this problem could now be solved by using a high electrolyte concentration which destroys the hydration shell (see below). All crystalline precipitates obtained under slightly different reaction conditions show the presence of discrete giant ring-shaped units, e.g., of the $\{Mo_{154}\}$ (with and without defects) and $\{Mo_{176}\}$ types[10–19] (see Table 1). Each of these

Table 1. MB Compounds with Nanosized Rings: Building Units and Bond Valence Sum Values Relating to the Structures[a]

compound with approximate crystal water content	building units[b]	structure	BVS[c] (Mo)	BVS[d] (μ_3-O)	ref
$Na_{26}[Mo_{142}O_{432}(H_2O)_{58}H_{14}]\cdot$ca. 300$H_2O$	$\{Mo_2\}_8\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings	5.6	(1.4)	10
$(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot$ca. 350$H_2O^a$	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings	5.7	1.2	11
$Na_{14}[Mo_{154}O_{462}H_{14}(CH_3OH)_8(H_2O)_{62}]\cdot$ca. 400$H_2O\cdot$ ca. 10CH_3OH^e	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings	5.5	1.2	12
$Na_{15}\{0.5[Mo_{154}O_{462}H_{14}(H_2O)_{70}]\cdot0.5[Mo_{152}O_{457}H_{14}$ $(H_2O)_{68}]\}\cdot$ca. 400H_2O	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14} +$ $\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	two different discrete rings, one of which possesses a defect	5.6 5.6	1.2 1.2	13
$Li_{16}[Mo_{176}O_{528}H_{16}(H_2O)_{80}]\cdot$ca. 400$H_2O^a$	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	discrete rings	5.6	1.3	14
$Na_{16}[Mo_{176}O_{528}H_{16}(CH_3OH)_{17}(H_2O)_{63}]\cdot$ca. 600$H_2O\cdot$ ca. 30CH_3OH	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	discrete rings	5.7	1.3	15
$Na_{24}\{0.5[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot0.5[Mo_{144}O_{437}H_{14}$ $(H_2O)_{60}]\}\cdot$ca. 350H_2O	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14} +$ $\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings with defects and chains built up by rings with defects	f	f	16
$Na_{24}[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot$ca. 250$H_2O$ ^{a}	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	chains built up by rings with defects	5.8	1.2	17
$Na_{22}[Mo_{146}O_{442}H_{14}(H_2O)_{58}]\cdot$ca. 250$H_2O$	$\{Mo_2\}_{10}\{Mo_8\}_{14}\{Mo_1\}_{14}$	chains built up by rings with defects	5.6	1.2	13
$Na_{16}[Mo_{152}O_{457}H_{14}(H_2O)_{66.5}]\cdot$ca. 300$H_2O$	$\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	layers built up by rings with defects	5.6	1.2	16
$Na_{21}[Mo_{154}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot$ca. 300$H_2O$	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	layers with attached $H_2PO_2{}^-$ groups	5.6	1.2	18

^{a} Formulas of some earlier reported compounds corrected according to the now accepted type of protonation for compounds with $b = 14$ building units (tetradecameric case) or $b = 16$ (hexadecameric case). ^{b} The general formula for the discrete pure molybdenum oxide-based unit is $[\{Mo^{VI}_2O_5(H_2O)_2\}^{2+}_{b-x}\{(Mo^{VI/V}_8O_{26}(\mu_3\text{-}O)_2H_m(H_2O)_3Mo^{VI/V})^{(4-m)-}\}_b]^{(2b-bm+2x)-} \equiv [\{Mo_2\}_{b-x}\{Mo_8\}_b\{Mo_1\}_b]^{(2b-bm+2x)-}$ ($b =$ number of building units per set = number of compartments referring to Figure 7 = number of protonations at the equatorial μ_3-O atoms or in the $\{(\mu_3\text{-}O)_2O_2\}$ compartment (for $m =1$) = half of the (formal) number of Mo^V centers; $x =$ number of defects or missing $\{Mo_2\}^{2+}$ units). ^{c} Average BVS value for the Mo centers which span the b incomplete $\{Mo_5O_6\}$-type double cubanes, built up by (parts of) the $\{Mo_8\}$ and $\{Mo_1\}$ units (Figure 7). The (formal) number of Mo^V centers per ring is for all compounds $2b$ (or two per compartment) according to the related constant BVS (Mo) values and other experimental data (see text). ^{d} Average BVS value for the μ_3-O atoms of the $b =14$ or 16 $\{(\mu_3\text{-}O)_2O_2\}$-type compartments (Figure 7), which indicates protonation at the equatorial μ_3-O atoms or within the $\{(\mu_3\text{-}O)_2O_2\}$compartments. The finally accepted value for the number of protons m per compartment is 1, mainly according to the results of the numerous cation analyses. This value corresponds to a disorder of the kind that only one of the two μ_3-O atoms of a compartment is protonated. This situation ($m = 1$) is also more plausible, as the other possibility ($m = 2$) leads to a rather small H−H distance in the compartment (cf.: Baur, W. H. On H···H distances and the van der Waals radius of hydrogen in inorganic and organic compounds. *Acta. Crystallogr.* **1992**, *B48*, 745−746). ^{e} Because of the rather high resolution of the crystal structure, Na$^+$ positions could be determined for the first time, proving their importance for the structure formation. ^{f} The structure is not sufficiently resolved to calculate reasonable BVS values.

compounds can now be obtained in pure crystalline form in a high yield and within a rather short time.

Fortunately, there is also the possibility of a spectroscopic detection of the formation of MB species starting from special well-defined cluster educts containing similar building units of the $\{Mo_{17}\}$ and/or $\{Mo_8\}$ types (see below) in solution, e.g., by means of resonance Raman spectroscopy (this method constitutes a good basis when studying conditions for the generation of ever larger species of the present type, as stability regions of clusters can be determined and further possible aggregation processes under different conditions can be recognized upon changing the pH values and the redox potentials). Starting, for instance, with a solution of the $\{Mo_{36}\}$-type cluster ($[Mo_{36} (NO)_4O_{108} (H_2O)_{16}]^{12-}$) with two $\{Mo_{17}\}$ groups linked by two $\{MoO_2\}$units,[20] the related $\{Mo_{57}M_6\}$-type cluster with three $\{Mo_{17}\}$ groups[20] (see Figure 5) is formed after addition of, for instance, the strong electrophilic linker $\{V^{IV}O\}^{2+}$ under reducing conditions. In solutions containing this cluster, the (more reduced) wheel-shaped cluster $[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]^{28-}$ ($\{Mo_{154}\}$)[11]— the first fully characterized MB-type species—forms upon further acidification and reduction. Interestingly, the $\{Mo_{154}\}$-type clusters—such as the pure isopolyoxometalate analogue containing 14 $\{MoO\}^{4+}$ instead of 14 $\{MoNO\}^{3+}$ groups (Figure 6)—turned out to comprise the prototype of the MB species, or at least its prototype building block.

If we synthesize MB-type compounds starting from most simple educts, we should realize that the dominant species in a nonreduced molybdate solution at pH ≈ 1 is—based on Raman spectroscopic investigations—the isopolymolybdate $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ $\{Mo_{36}\}$ (an analogue of the $\{Mo_{36}\}$ cluster with four $\{MoNO\}^{3+}$ instead of four $\{MoO\}^{4+}$ groups[20]) which, under formal consideration, consists of two $\{Mo^{VI}_{17}O_{60}(H_2O)_2\}^{18-}$ ($\{Mo_{17}\}$) units (Figure 5) stabilized by protonation and two $\{MoO_2\}^{2+}$ groups acting as linkers. The $\{Mo_{17}\}$ units can be described as being built up from two $\{Mo_8\} \equiv \{Mo^{VI}_8O_{28}(H_2O)_3\}$ units fused via a $\{Mo_1\}$ unit at the center of inversion. The reduction results in a different kind of linking of the $\{Mo_8\}$ building blocks in the obtained MB species. (As these are more negatively charged, they lie correspondingly— described simply—more apart from each other, as presented below.) This $\{Mo_8\}$ building unit is the basic fragment of all known MB-type ring-shaped cluster species (see Table 1, Figure 6, and ref 21).

A facile synthetic approach toward a pure crystalline product containing a MB-type anion corresponds to the use of $Na_2S_2O_4$ as reducing agent in a strong acidic solution and, of utmost importance, in the presence of a high electrolyte concentration. The mixed-crystal compound $Na_{15}[Mo^{VI}_{126}Mo^V_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^V_{28}O_{457}$ $H_{14}(H_2O)_{68}]_{0.5}\cdot$ca. 400$H_2O$ **1** ($\equiv Na_{15}[\mathbf{1a}]_{0.5}[\mathbf{1b}]_{0.5}\cdot$ca. 400$H_2O$) containing archetypal wheel-shaped anions with and without defects can thus be obtained in pure and crystalline form.[13] Several MB compounds with other structures (see Table 1) can be precipitated in the same way under slightly different reaction conditions.
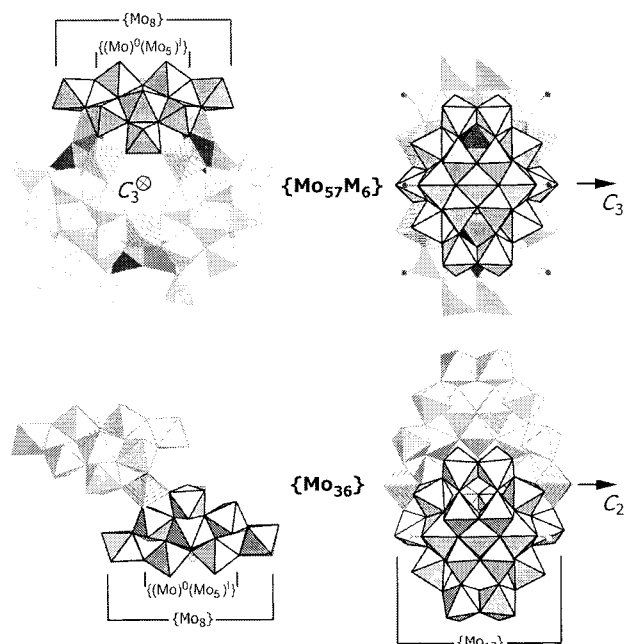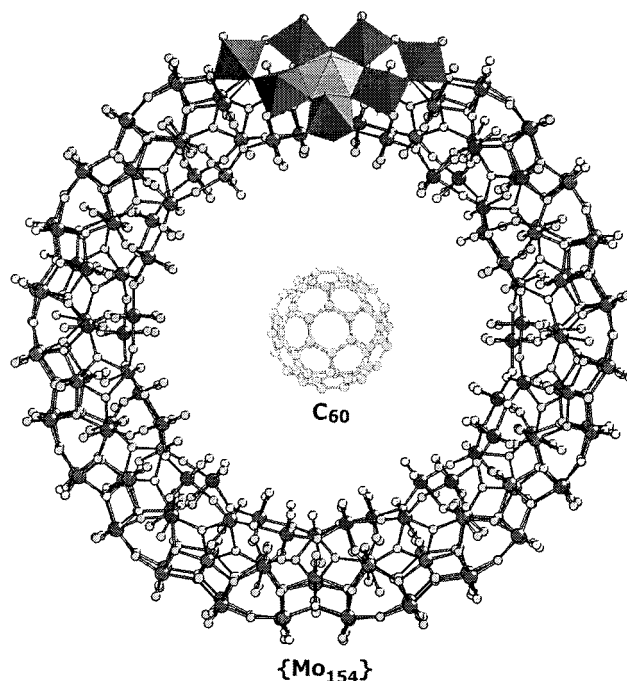
FIGURE 5. Polyhedral representation of the $\{Mo_{57}M_6\}$ cluster with its basic building blocks and their constituents along the C_3 (upper left) and along one of the three C_2 axes (upper right). On the upper right, one $\{Mo_{17}\}$ building block consisting of one $\{Mo_1'\}$ (in the center) and two $\{Mo_8\}$ groups, and on the upper left one $\{Mo_8\}$ unit, is highlighted (gray with black outline). Also shown are the $\{Mo_2'\}$ groups built up from two face-sharing octahedra (gray). For comparison, the polyhedral representations of the $\{Mo_{36}\}$ cluster structure, consisting of two $\{Mo_{17}\}$ building blocks linked by two $\{Mo_1^\star\}$ units, are shown in the related views, also highlighting one $\{Mo_8\}$ (bottom left) and one $\{Mo_{17}\}$ building block (bottom right) ($\{Mo_8\}$, gray emphasized; $\{Mo_2'\}$, gray; and $\{Mo_1^\star\}$, hatched). (Cf.: Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239−271.)

Structure of the (Basic) Wheel-Type Unit and Formula Determination Problems

Compound **1** contains the two crystallographically independent discrete ring-shaped cluster anions, $\{Mo_{154}\}$ **1a** and $\{Mo_{152}\}$ **1b**, in the ratio 1:1.[13] The complete ring system **1a** shows 140 MoO_6 octahedra and 14 pentagonal MoO_7 bipyramids. According to our building-block principle, **1a** and **1b** can be formulated as $[\{Mo_2\}_{14-x}\{Mo_8\}_{14}\{Mo_1\}_{14}]^{(14+2x)-} \equiv [\{Mo^{VI}_2O_5(H_2O)_2\}^{2+}_{14-x}\{Mo^{VI/V}_8O_{26}-(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-}_{14}]^{(14+2x)-}$, where x denotes the number of defects, i.e., the number of missing $\{Mo_2\}$ groups, which is 0 for **1a** and 1 for **1b** (see Table 1). This means that the tetradecameric anion without defects contains 14 of the three different building blocks.

The ring-type unit of **1a** without defects can be schematically constructed: each of the 14 central MoO_7 pentagonal bipyramids is symmetrically connected to five MoO_6 octahedra by edge-sharing, resulting in a $\{(Mo)/Mo_5\}$ pentagon (Figure 5; this interestingly also occurs in novel-type spherical clusters as a building block[22]). Four of the mentioned MoO_6 octahedra are pairwise linked to two further MoO_6 octahedra via corners to form the important $\{Mo_8\}$-type unit. Starting from the $\{Mo_8\}$ units, the complete $\{Mo_{154}\}$-type ring is built up as follows: (i) The two MoO_6 octahedra which are not directly connected
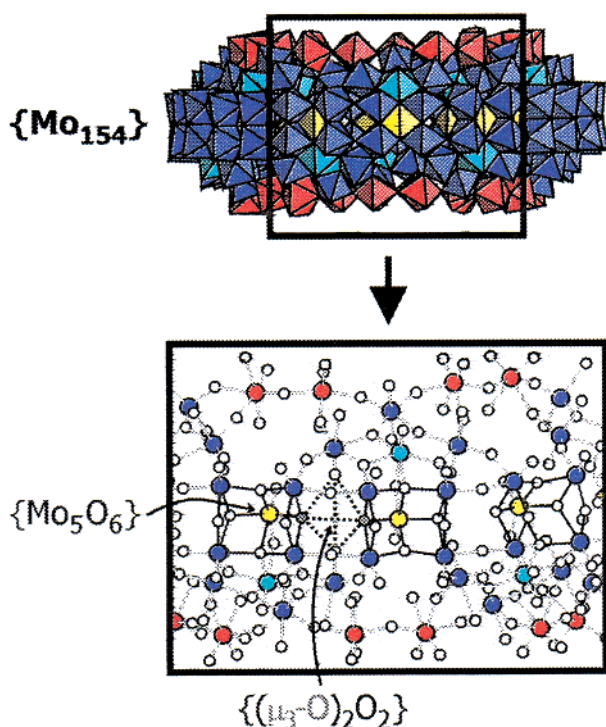

FIGURE 6. Ball-and-stick representation of the tetradecameric $\{Mo_{154}\}$-type cluster $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-}$, showing one $\{Mo_8\}$ unit with its central MoO_7 pentagonal bipyramid in polyhedral representation. For the purpose of size-comparison, a C_{60} fullerene molecule is shown.

to the central MoO_7 bipyramid are linked to two neighboring $\{Mo_8\}$ units through corners. (ii) Neighboring $\{Mo_8\}$ groups are additionally fused together via $\{Mo_2\}$ units, thus completing the inner-ring parts of the upper or lower half of the ring structure (Figure 6). (iii) The complete ring system is constructed when one half is rotated around 360/14° relative to the other and fused to it through $\{Mo_1\}$ groups which are correspondingly located at the equator of the (complete) ring.

A major problem was the determination of the charges and/or the formulas of the MB species (mixed-valent type III according to the classification of Robin and Day[23]). This was caused by (1) the difficulty in localizing/determining the Mo^V and protonation centers and (2) the very low count (near the error limits of the analytical methods) of cations which could not be localized by single-crystal X-ray structure analyses due to disorder problems.

For the determination of the actual charge of any known MB compound with ring-shaped cluster units, the difference between the (formal) number of Mo^V centers and the number of protons at μ_3-O positions must be considered. In this context, the following observations for compounds containing tetradecameric ($b = 14$) anions[16] are important:

(1) According to the bond valence sum (BVS) values of the Mo atoms (average value 5.6; see Table 1), 28 (=2b) 4d electrons (corresponding to the (formal) number of 28 Mo^V centers) are located within *14 incomplete double-cubane-type compartments,* each of which is spanned by five Mo and six O atoms belonging to the $\{Mo_8\}$ and $\{Mo_1\}$ units (see Table 1 and Figure 7). In other words, two 4d electrons are delocalized within each compart-

FIGURE 7. Polyhedral representation of the tetradecameric $\{Mo_{154}\}$-type cluster with view perpendicular to that depicted in Figure 6 (top) and structural details of cluster compartments in ball-and-stick representation (bottom). This representation highlights (1) three of the 14 (incomplete) double-cubane-type compartments, each of which is spanned by five Mo centers (Mo—Mo = 3.4—4.0 Å) belonging to $\{Mo_8\}$- as well as $\{Mo_1\}$-type groups and six O atoms (the lowered bond valence sum (BVS) values of the corresponding Mo atoms with an average value of 5.6 prove, besides other experimental data, that two 4d electrons are trapped in each compartment), and (2) one of the 14 $\{(\mu_3\text{-}O)_2O_2\}$-type compartments—indicated by dotted lines—which are located between two double-cubane-type compartments (the two characteristic μ_3-O atoms (dark gray, O—O = 3.07 Å) have an average BVS value of 1.2, proving a type of protonation) ($\{Mo_8\}$, blue (central MoO_7 pentagonal bipyramid, cyan); $\{Mo_1\}$, yellow; $\{Mo_2\}$, red).

ment. This is in agreement with the (formal) number of 28 ($=2b$) Mo^V centers determined by redox titrations, as well as with the measured ϵ value of the 750-nm band in the solution spectrum, which is due to an IVCT transition (ϵ per Mo^V center $\approx 5 \times 10^3$ L mol^{-1} cm^{-1}).[7]

(2) On the other hand, there are in total 28 ($=2b$) μ_3-O atoms located in the region of the ring equator with an average BVS value of 1.20 ± 0.05, which belong to *14 ($=b$)* $\{(\mu_3\text{-}O)_2O_2\}$-*type compartments* (see Figure 7 and Table 1). This BVS value basically indicates protonation and corresponds to one or two protons per tetrahedron, respectively.

As the average BVS values for μ_3-O (1.2 ± 0.05) and Mo (5.6 ± 0.1) are virtually identical in all of the known related tetradecameric ($b = 14$) and hexadecameric ($b = 16$) structures (ca. 50 until now, some of which are summarized in Table 1), it follows that the same number of protons ($m = 1$ or 2) as well as the same number of 4d electrons are present in each of the aforementioned compartments. On the other hand, the values of the cation

analyses have gained greater significance since a large number of related compounds have become known (Table 1). In accordance with these analytical results, we get *m* = 1 (for details and other arguments, see ref 16).

Interestingly, the results available so far imply that a particular species abundant in MB-type solutions corresponds to a reduced, protonated, hydrated "molecular molybdenum trioxide" with perhaps a varying degree of protonation (although the anions obtained in crystalline materials carry—at least preferably—a well-defined number of protons), but with the same degree of reduction or (formal) number of Mo^V centers. The corresponding formula should read $[(MoO_3)_{154}(H_2O)_{70}H_{(14+x)}]^{(14-x)-}$.

The Blue Color and Assembly of Electron Storage Elements (Electronic Necklace)

A careful investigation of a large number of different structures revealed that they comprise 14 (in the case of the hexadecameric species, 16) (practically) electronically uncoupled $\{Mo_5O_6\}$ incomplete double-cubane-type compartments, each of which carries two delocalized 4d electrons (Figure 7). This situation is comparable to an electronic necklace or electron-storage system where the uncoupled storage elements are threaded like pearls on a string. This can be nicely proven by Mo—BVS calculations (see Table 1 and ref 16) and is in agreement with the observation that the electronic absorption spectrum is, in principle, the same for the tetradecameric and hexadecameric clusters including several derivatives. The electronic transitions are of the IVCT ($Mo^V \rightarrow Mo^{VI}$) type with the ϵ-value correlating linearly with the number of Mo^V centers.

The Remarkable Properties of Giant Ring-Shaped Units

As in the meantime several compounds containing the nanostructured (tetradecameric) wheel-type building block, both linked and nonlinked, are known (Table 1), it seems worthwhile to summarize some its characteristic properties and potentials:

1. It exhibits a nanometer-sized cavity, presenting new perspectives for a novel host—guest chemistry.

2. It has an extended hydrophilic inner and outer surface due to the presence of a high number of H_2O ligands, causing the formation of a tremendous hydration shell, which explains the high solubility (see Figure 8).

3. It has a huge surface area, which explains in part the high affinity toward adsorbents, such as charcoal or silk.

4. It renders a molecular model for catalytically active metal oxides.

5. It is possible to generate discrete structural defects on the inner surface of the cluster ring (see Figure 9), e.g., by abstracting positively charged $\{Mo_2\}$ groups using special ligands such as formate which have a high affinity for these groups.
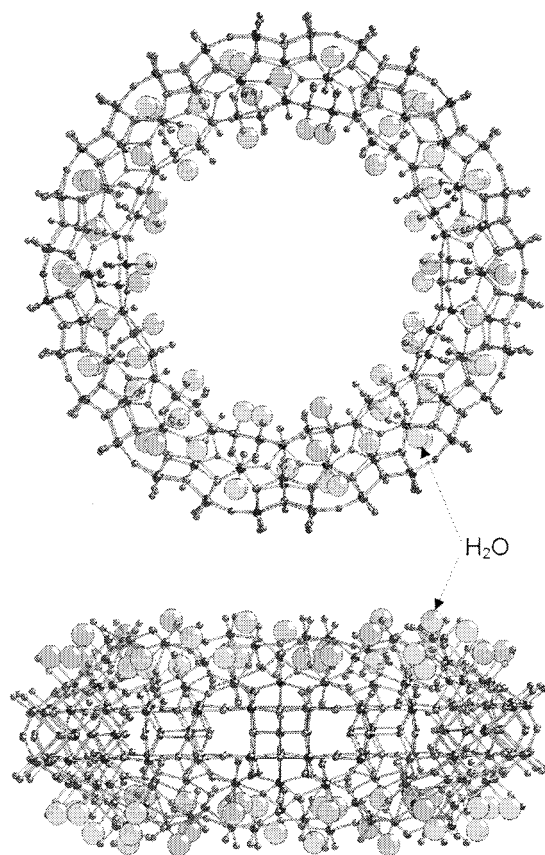
6. The ring-shaped units can get linked due to a type

FIGURE 8. Structure of the tetradecameric $\{Mo_{154}\}$-type cluster highlighting the 70 H_2O ligands.

of aging process in MB solutions but can also be connected according to a type of crystal engineering.

7. It is possible to place molecules at different sites of the cluster surface by replacing H_2O ligands (thereby subsequently changing the cluster properties, especially of its surface) and to study reactions between the molecules placed inside the cavity.

Aggregation of Giant Wheel-Shaped Building Blocks

An aspect of particular interest is the fact that large ring-shaped clusters can assemble in MB solutions to form chains (Figure 10) or layers (Figure 11). The assembly occurs after some time in solution according to a type of aging process and is based on the replacement of H_2O ligands at $\{Mo_2\}$ units (on rings) by oxygen atoms of terminal $\{Mo_2\}$-type Mo=O groups (on other rings). The linking can be accelerated if the nucleophilicity of these Mo=O groups is increased, for instance, by introducing electron-donating and linking-initiating ligands such as $H_2PO_2^-$ at relevant sites. In this special case, a mesoporous *layer compound* can be obtained.[18] As the process is based on reactions at the same type of amphiphilic O=MoL (L = H_2O, $H_2PO_2^-$) $\{Mo_2\}$-type units in different rings, the terminology "synergetically induced functional complementarity" seems to be justified.[18] The hypophosphoric acid acts in this case both as reducing agent *and* as H_2O-replacing ligand. Linking is, in principle, also supported

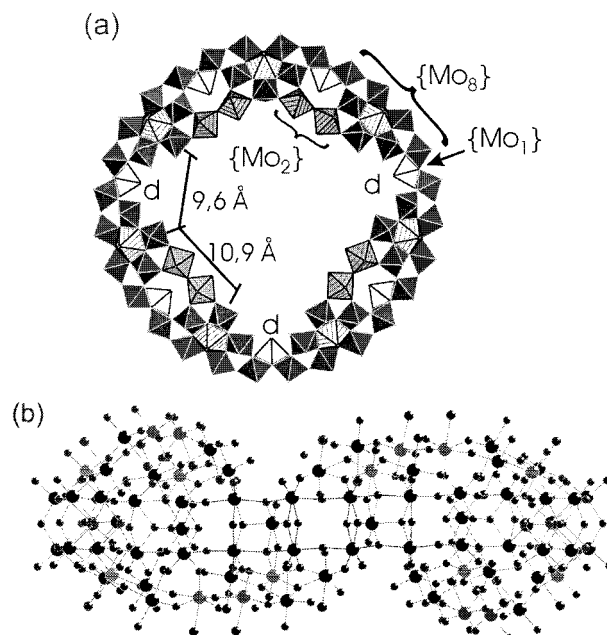
FIGURE 9. Structure of a $\{Mo_{142}\}$-type cluster ring with six well-defined missing $\{Mo_2\}$ groups: (a) in polyhedral representation showing only the upper half of the ring (view in the direction of the main axis) and (b) in ball-and-stick representation (view perpendicular to that in (a)) demonstrating the influence of the defects on the shape of the cluster.[10]
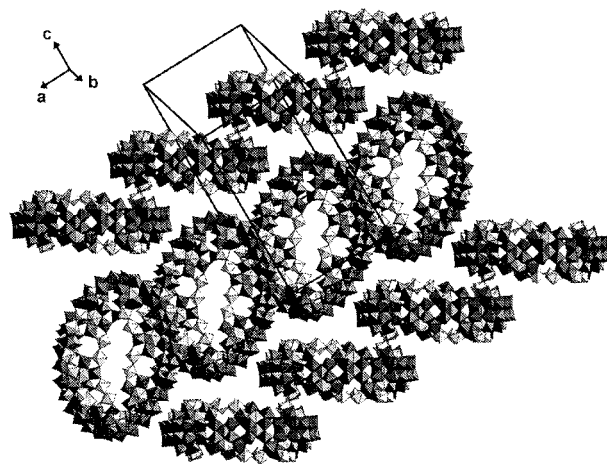

FIGURE 10. Polyhedral representation of polyoxomolybdate giant wheels linked by Mo—O—Mo bonds to form parallel chains in the crystal.

by abstracting some $\{Mo_2\}$-type fragments using high-affinity bidentate ligands (such as the formate anion) from the inner surroundings of the $\{Mo_{154}\}$-type cluster, which also causes a higher nucleophilicity at the O=Mo(H_2O) sites of $\{Mo_2\}$ units in the neighborhood. *Compounds with chains* having interesting electronic properties can be obtained in this way (see Figure 10).[13,17]

Such a type of linking to chains and layers, also occurring in pure MB solutions in the absence of other reagents, signifies that related types of species, besides the discrete wheel-type ones, have to be considered as possible MB solution constituents, at least according to the mentioned aging process. The same is true for the other species discussed in the next section.

(a)

(b)
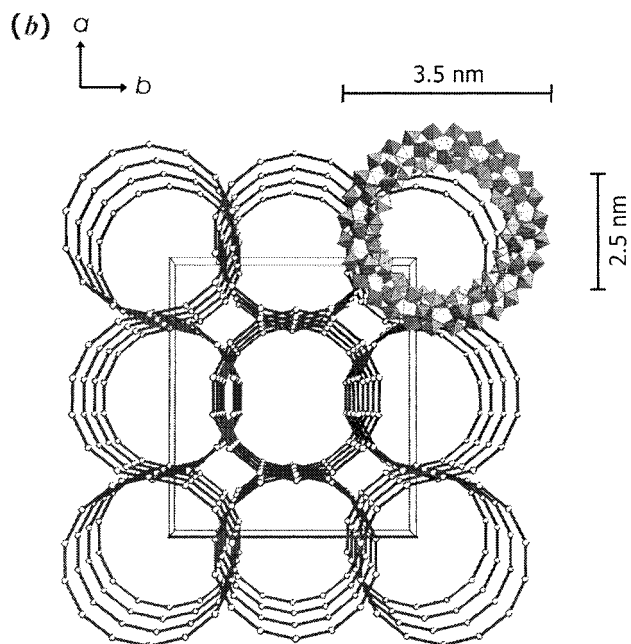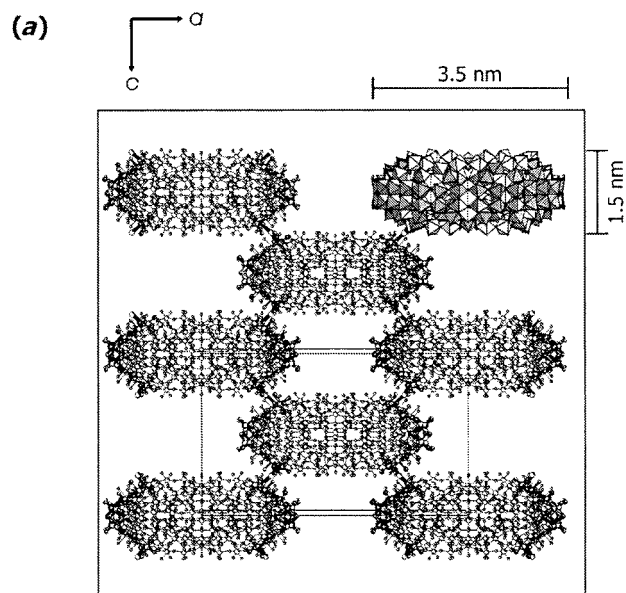
FIGURE 11. (a) Ball-and-stick representation of the "packing" of the covalently linked rings in crystals of $Na_{16}[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3$-$O)_{28}H_{14}(H_2O)_{66.5}]$·ca. 300H$_2$O ({Mo$_{152}$}) viewed along the crystallographic *b* axis. Each ring is connected to four surrounding rings via Mo−O−Mo bridges of the O=Mo−O−Mo−OH$_2$ units, thus forming layer networks parallel to the *ac* plane. (b) Perspective view along the crystallographic *c* axis showing the framework with nanochannels which are filled with H$_2$O molecules and Na$^+$ cations. For clarity, only one ring is shown completely in polyhedral representation.

Further Growth and Related Nucleation Processes, Cluster Encapsulation inside the Ring Cavities, and Additional Assembly to Much Larger Colloids

An even larger ring-shaped cluster than the tetradecameric {Mo$_{154}$} type with 176 molybdenum atoms ({Mo$_{176}$}), i.e., with the above-mentioned hexadecameric structure containing correspondingly 16 instead of 14 sets of each of
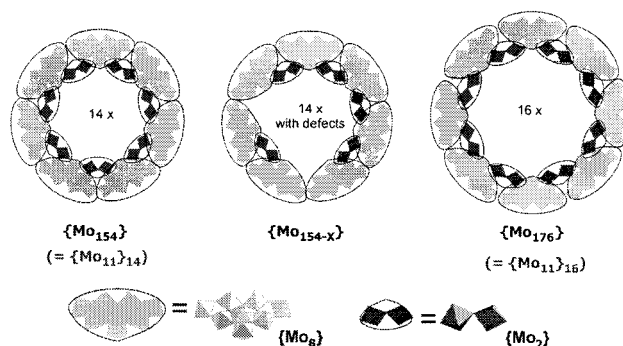
**FIGURE 12.** Schematic comparison of the tetradecameric {Mo$_{154}$}- (with and without defects referring to missing {Mo$_2$} groups) and hexadecameric {Mo$_{176}$}-type clusters showing the basic {Mo$_8$} and {Mo$_2$} units (the equatorial {Mo$_1$} units are not visible in this representation).
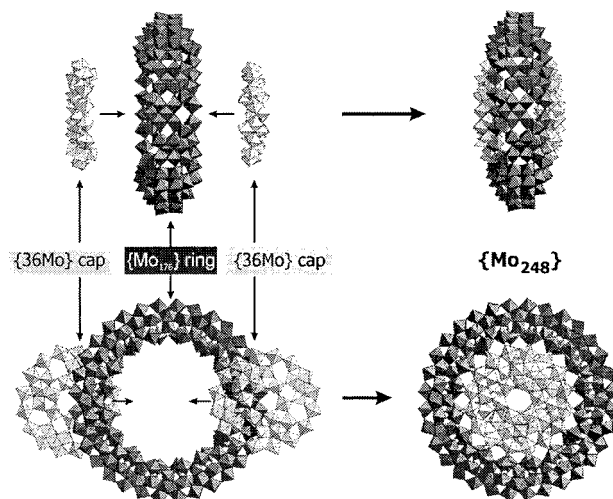
FIGURE 13. Schematic representation of the growth process {Mo$_{176}$} → {Mo$_{248}$}. The structure of a {Mo$_{248}$} cluster can formally be decomposed into a {Mo$_{176}$}-type ring and two {Mo$_{36}$O$_{96}$(H$_2$O)$_{24}$}- type hubcaps.

the three mentioned building blocks of the type {Mo$_8$}, {Mo$_2$}, and {Mo$_1$}, could also be obtained from MB solutions (Figure 12 and Table 1).[14,15,19] Under special reducing conditions, the hexadecameric cluster system even starts growing again, resulting finally in the situation that the two neutral (unstable) molybdenum oxide fragments of the type {Mo$_{36}$O$_{96}$(H$_2$O)$_{24}$} cover the cavity of the wheel-shaped cluster like hubcaps (Figure 13).[21] This is, in terms of the number of metal atoms, the largest known cluster anion that has been structurally characterized so far. Remarkably, the structure of the {Mo$_{36}$O$_{96}$(H$_2$O)$_{24}$}- type fragment is similar to a segment of the solid-state structure of the compound Mo$_5$O$_{14}$ (Figure 14).

The ring-shaped {Mo$_{154}$}-type clusters—if linked to chains—can also act as hosts for smaller polyoxometalate guests, such as the above-mentioned (nonreduced) {Mo$_{36}$}- type species (Figure 5). In this novel supramolecular system, the interaction between the host and the guest, which fits exactly into the cavity of the host, is due to 16 hydrogen bonds as well as the Coulomb interaction mediated by (at least) four sodium cations located be-
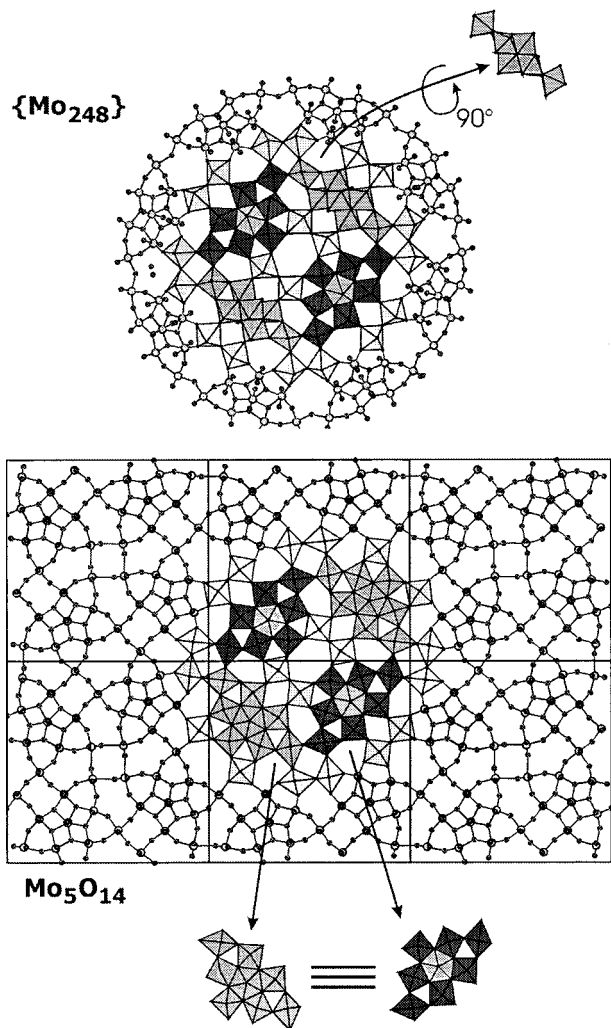
FIGURE 14. Structural comparison of the hubcap motif of the $\{Mo_{248}\}$ cluster and the related segment of the solid-state structure of Mo_5O_{14}. (Above) Schematic representation of one half of the $\{Mo_{248}\}$ cluster with a highlighted $\{Mo_{36}O_{96}(H_2O)_{24}\}$ hubcap in polyhedral representation. (Below) Structure of Mo_5O_{14} viewed along the *c* axis (cf.: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; Figure 22c-2, p 849). (Self-explanatory relations between the $\{Mo_8\}$, $\{Mo_8'\}$, and $\{Mo_2\}$ groups.)

tween the negatively charged host and negatively charged guest (Figure 15).

Conclusions and Perspectives: Novel-Type Reactions at Different Surface Sites and Inside the Cavity
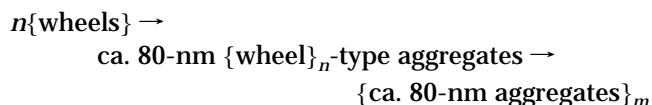
It is now clear that the reduction of acidified polyoxomolybdate solutions leads to different types of MB species, all of which have one common structural feature: giant wheel-shaped cluster units linked or in discrete form. Though details about the complex equilibria of the MB solutions are not known, it is nevertheless possible to isolate well-defined crystalline compounds, even in high yield. An important result is that crystalline precipitates can be obtained in the presence of high electrolyte concentrations which destroy the hydration shell of the
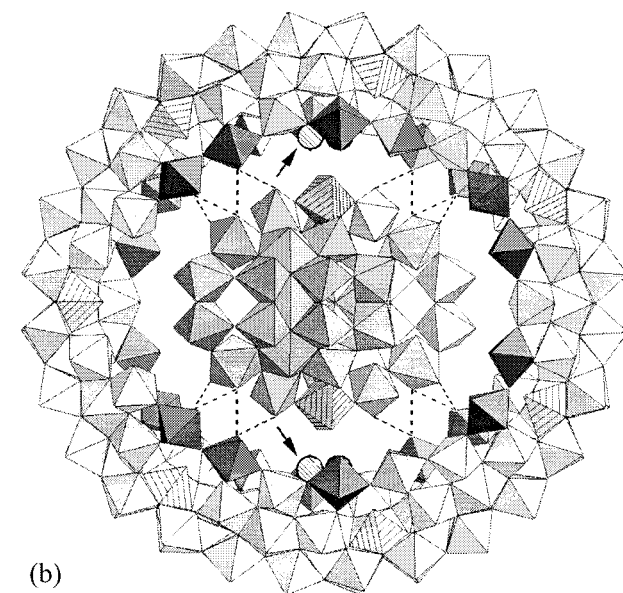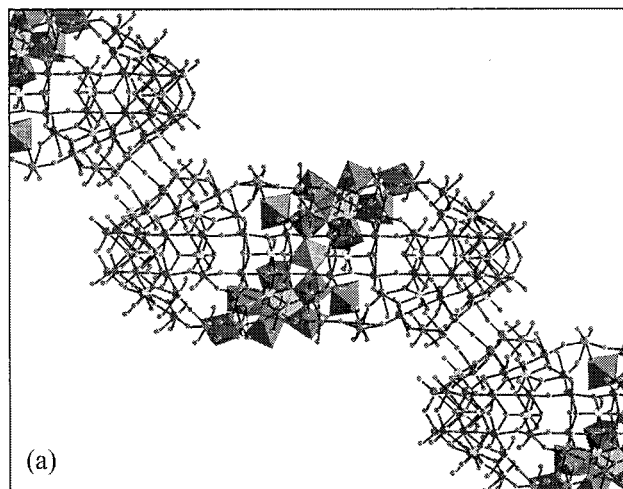
FIGURE 15. Some structural details of the novel supramolecular system $\{Mo_{36} \subset Mo_{148}\}$ (occupation of the cavities, ca. 20%). (a) Part of the chain structure is shown, which is built up by linking ring-shaped cluster units $\{Mo_{148}\}$ (i.e., based on the $\{Mo_{154}\}$ type with in sum three missing disordered $\{Mo_2\}$ groups; only the front halves of the rings are shown for clarity). (b) View perpendicular to (a): the interaction between host and guest is due to 16 hydrogen bonds (dotted lines) and (at least) four sodium cations (hatched circles, indicated by arrow; only two Na positions are visible in this perspective view).

clusters/colloids. Interestingly, the discrete anions themselves form very quickly, which can be nicely demonstrated by the corresponding resonance Raman spectrum using an excitation line λ_e within an absorption band being due to the IVCT of the type $Mo^V \rightarrow Mo^{VI}$ (see Figure 4).

A future challenge will be to understand the stepwise formation of very large colloids based on a type of structural hierarchy formulated schematically as[9]

$n\{\text{wheels}\} \rightarrow$

ca. 80-nm $\{\text{wheel}\}_n$-type aggregates $\rightarrow$

$\{\text{ca. 80-nm aggregates}\}_m$

Furthermore, a novel type of chemistry could develop as the unusual nanostructured wheel-type systems, which metaphorically speaking can be considered as structured landscape, have an enormous investigation and reaction potential with different reaction centers, for instance:

(1) Exchanging ligands at the (electron-rich) surface of a giant cluster.[15]

(2) Replacing H_2O ligands by the head of amphiphilic ligands, while the corresponding tail can create special characteristic (including electrophobic) sites inside the cavity.

(3) Filling the cavities with a variety of different covalently or noncovalently bound guests, which might show an altered reactivity compared to the discrete (isolated) ones.

(4) Filling well-defined cluster sites associated with defects with different electrophilic groups including new-coordinated cationic centers.

(5) Studying nucleation processes inside the cavity (Figure 15), not only those based on polyoxomolybdates[21] but also those based on other polyanions, e.g., tungstates (for fascinating giant polytungstates, see ref 24). Furthermore, the system provides optimal facilities to model the first steps of nucleation under boundary conditions. (This type of aggregation also has relevance for the metal-center assembly in biological systems, and for special types of biomineralization processes in compartments.)

All in all, we are dealing with nanostructured molecular systems with giant cavities which can, themselves, be used as building blocks for mesoporous network structures, as hosts (e.g., for rather large molecules), and as nanoreactors and nanosensors. Even larger ring-type systems can be anticipated, and in the presence of strong electrophiles also smaller rings than tetra- and hexadecameric ones should form.[25]

We thank Dr. E. Diemann for helpful discussions.

Note Added in Proof. When a chainlike compound is dissolved (Figure 10), discrete rings are initially formed; however, after a short time a new growth process takes place. As inferred from small-angle X-ray scattering (SAXS) measurements, the first steps consist of the formation of linear arrangements of a small number of rings (Knöchel, A.; Müller, A.; et al., unpublished results).

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