Giant Ring-Shaped Building Blocks Linked to Form a Layered Cluster Network with Nanosized Channels: $[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}]^{16-}$

Achim Müller,* Erich Krickemeyer, Hartmut Bögge, Marc Schmidtmann, Christian Beugholt, Samar K. Das, and Frank Peters[a]

Dedicated to Universitätskanzler Karl Hermann Huvendick on the occasion of his 60th birthday

Abstract: The synthesis of multifunctional inorganic materials from robust building blocks (synthons) that have a well-defined structure and can be linked together represents a constant challenge in crystal engineering. We report the synthesis of the deep blue mixed-valence (Mo^{VI}/Mo^{V}) compound $Na_{16}[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}] \cdot$ ca. $300\,H_2O$ (**1**), which consists of nanosized wheel-shaped building blocks with 152 Mo atoms. These discrete building blocks can be prepared easily by reduction of an acidified aqueous molybdate solution and, when linked together, they form a layered open framework with nanosized channels. The encapsulated water molecules can be partly replaced by organic molecules. The metal-oxide-based host lattice has altogether 28 4d electrons per ring. These can be assigned to 14 incomplete double-cubane-type compartments spanned by five Mo and six O atoms, which show negligible electronic interaction. The two electrons delocalized in each of these compartments give rise to the deep blue colour.

Keywords: inorganic rings · layered compounds · mixed-valent compounds · molybdenum blue · supramolecular chemistry

Introduction

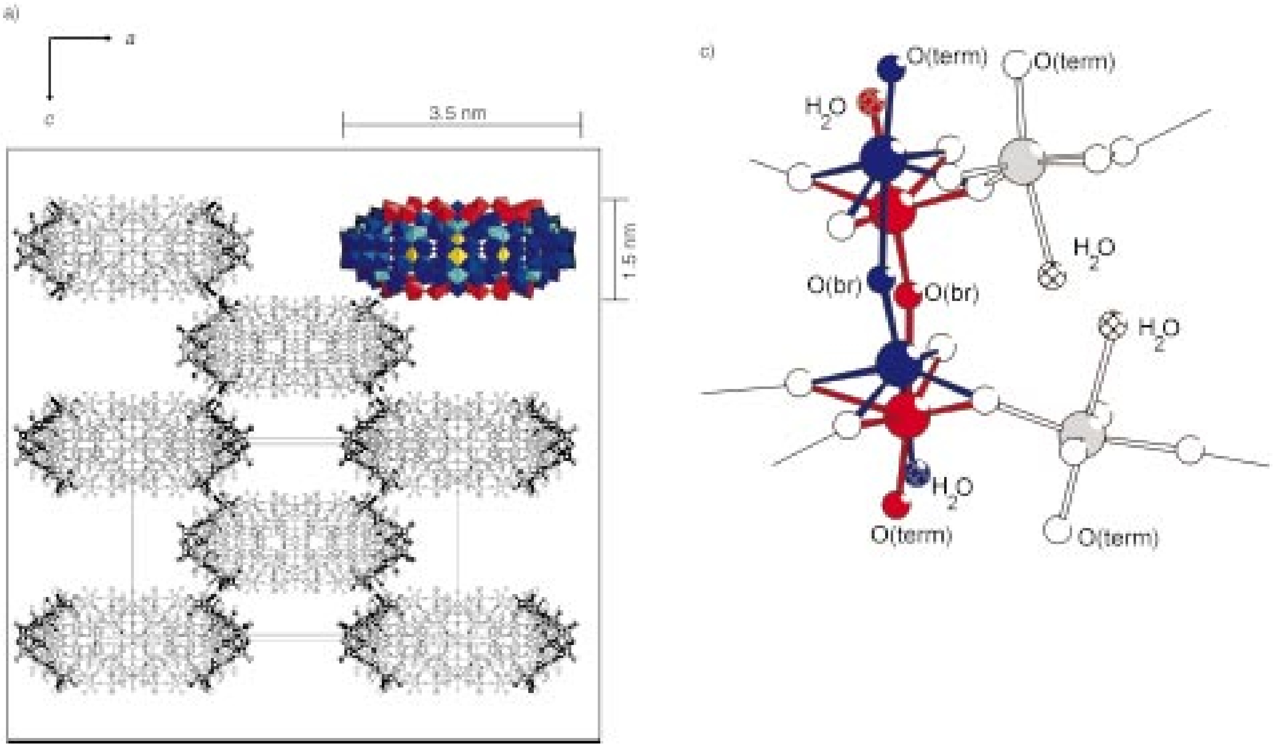
One of the most challenging problems in modern chemistry is the synthesis of multifunctional compounds and materials with desirable or predictable properties, such as mesoporosity (well-defined cavities or channels), electronic and ionic transport, ferro- as well as ferrielasticity, luminescence, and catalytic activity. In particular, deeply coloured, mixed-valence transition metal oxides,[1] including the hydrogen molybdenum bronzes[2] with their unusually high conductivity and wide range of composition, play an important role in both technology and materials science. Their large field of applications ranges from hydrogenation and dehydrogenation catalysts, superconductors, passive electrochromic display devices to 'smart' windows.[2] The synthesis of these compounds or solids from preorganized building blocks with well-defined geometries and desired chemical properties is therefore of special interest.[3] We have recently reported the synthesis of giant, reduced mixed-valence molybdenum-oxide clusters with nanosized cavities.[4] Reactions that allow these clusters to be linked to form open frameworks are of strategic interest. Here we report the synthesis of a layered solid-state structure with well-defined channels (diameter ca. 2 nm).

Results and Discussion

If, under special conditions (see Experimental Section), an aqueous solution of sodium molybdate is acidified and reduced with tin(II) chloride at room temperature, dark-blue rhombic-bipyramidal crystals of **1**, with the condensed cluster network **1a** ($[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}]^{16-}$), precipitate together with a certain amount of amorphous material.[5] The crystal structure of **1** (space group *Cmca*) shows the presence of nanosized, ring-shaped cluster fragments (crystallographic site symmetry $2/m$), which are linked to give a framework structure with nanosized channels (Figures 1 and 2). In the crystallographic *ac* plane, each cluster ring is surrounded by four further rings (Figure 1a) and is interconnected by covalent Mo–O–Mo bridges (Figures 1b, 1c), such that a layered structure is formed parallel to the *ac* plane (Figure 1a). The packing of these layers gives rise to nanosized channels; four neighbouring rings of one layer form a bipyramid with two rings from the adjacent layers. This corresponds formally to the observed shape of the crystals and

---

[a] Prof. Dr. A. Müller, E. Krickemeyer, Dr. H. Bögge, M. Schmidtmann, Dipl.-Chem. C. Beugholt, Dr. S. K. Das, Dipl.-Chem. F. Peters
Fakultät für Chemie der Universität Bielefeld
Lehrstuhl für Anorganische Chemie I
Postfach 100131, D-33501 Bielefeld (Germany)
Fax: (+49) 521-106-6003
E-mail: a.mueller@uni-bielefeld.de



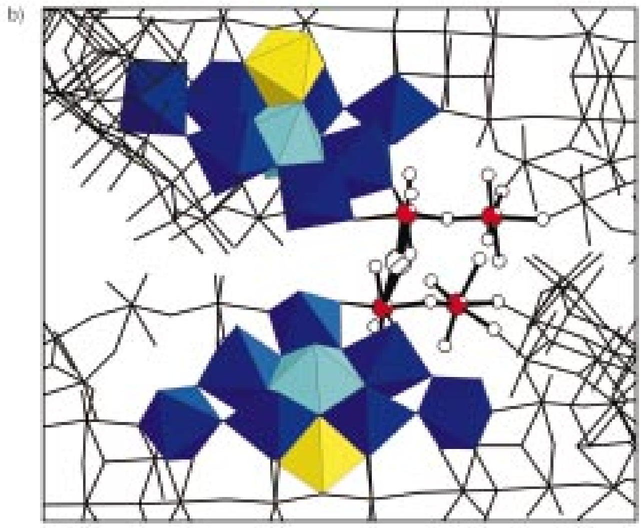


Figure 1. a) Ball-and-stick representation of the packing of the linked rings in crystals of **1** when viewed along the crystallographic *b* axis. Each ring is connected to surrounding rings by Mo–O–Mo bridges of the O=Mo–O–Mo–OH$_2$ units (b and c) to form layered networks parallel to the *ac* plane. One ring is shown as the basic unit in polyhedral representation ($\{Mo_2\}$ units, red; $\{Mo_8\}$, blue (central MoO_7 pentagonal-bipyramid, light blue); $\{Mo_1\}$, yellow). b) Detailed view of the bridging region between two cluster rings of **1**. One $\{Mo_8\}$ unit of each ring together with one $\{Mo_1\}$ unit is shown in polyhedral representation and one $\{Mo_2\}^{2+}$ ($\equiv\{Mo_2^{VI}O_5(H_2O)_2\}^{2+}$) unit per ring in ball-and-stick representation (Mo, red). The bridging (disordered) oxygen centres are depicted as large, hatched circles (for clarity, the disorder in the bridging positions is not shown here). c) Detailed view of the bridging $\{Mo_2\}$ units showing the disorder of the bridging Mo and O centres with the two orientations in blue and red respectively to indicate how the disorder could be resolved for the linking unit. In about 50% of the linking units the 'red positions' are occupied; in the other cases the 'blue positions' are occupied.

is in agreement with the 'correspondence principle' of crystallography.[6]

For a better understanding of the complicated structure of **1a**, its basic units are compared with those of related discrete clusters as follows. Each of the ring-shaped cluster fragments of **1a** comprises 14 $\{Mo_8\}$- linked by 14 $\{Mo_1\}$- and 13 $\{Mo_2\}$-type units (Figure 1a), whereas $\{Mo_8\}$ units, which occur in several polyoxomolybdates, can be considered as the fundamental building units.[4, 7–12] This scheme is applicable, for instance, to the related tetradecameric ($b = 14$) discrete anion with three sets of similar units (b = number of building units): $[Mo_{154}(NO)_{14}O_{420}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{70}]^{28-}$ ($\equiv [\{Mo_2^{VI}O_5(H_2O)_2\}_{14}\{Mo_7^{VI/V}(MoNO)O_{25}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{28-} \equiv [\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}]^{28-}$) **2a**.[4] (See Table 1, where several related compounds are given for comparison of their building units.) Starting formally with **2a**, the formulae can be obtained for the corresponding pure, discrete polyoxomolybdate $[\{Mo_2^{VI}O_5(H_2O)_2\}_{14}{}^{2+}(\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-})_{14}]^{14-}$ **3a** (based on the substitution $MoNO^{3+} \rightarrow MoO^{4+}$), as well as for the corresponding cluster $[\{Mo_2^{VI}O_5(H_2O)_2\}_{13}\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{16-}$ **3b** with one defect in the $\{Mo_2\}^{2+}$ group (which represents the building block of the layer system **1a**). Interestingly, both anions **3a** and **3b** occur in the recently isolated, mixed-crystal compound **3**[7] listed in Table 1. The main difference between the discrete cluster **3b** and **1a** is that the latter contains 1.5 H_2O ligands less per formula unit owing to the linkage of the ring-shaped building blocks; this is caused by a novel type of substitution reaction: $\{Mo_2\}$-type

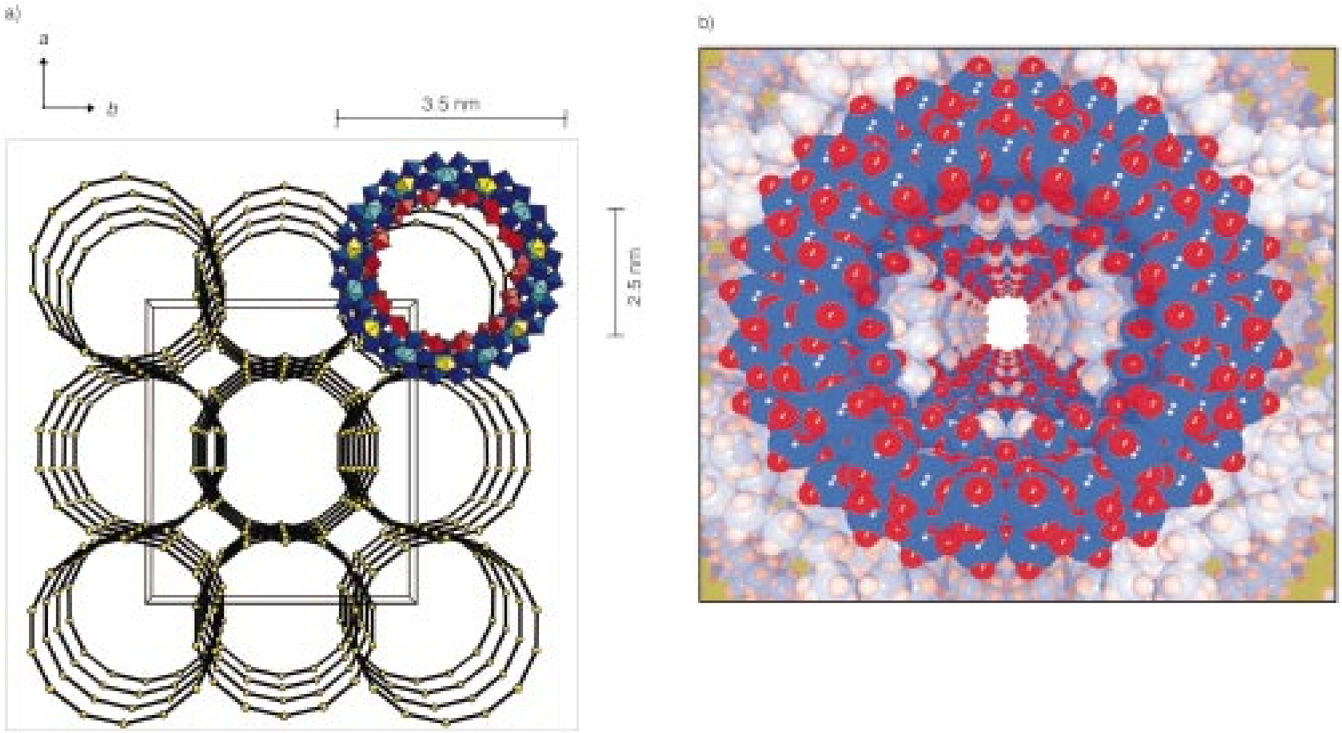


Figure 2. a) Perspective view along the crystallographic *c* axis showing the framework with nanotubes that are filled with H_2O molecules and Na^+ cations. For clarity, only one ring is shown completely in polyhedral representation. For the other rings, only the centres of the $\{Mo_1\}$ units are depicted and connected. The diameter of the central cavity inside a ring in the crystal is at least 1.9 nm. b) Space-filling representation of the central part of a nanotube.

Table 1. Compounds with nanosized rings: building units, molar extinction coefficients 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)	Vis/NIR (IVCT) λ [nm] (ε[$l\,mol^{-1}\,cm^{-1}$] $\times 10^5$)	Ref.
$Na_{16}[Mo_{152}O_{457}H_{14}(H_2O)_{66.5}]\cdot 300\,H_2O$ **1**	$\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	layer built up by rings with defects	5.6	1.2	750 (1.6)	this paper
$(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot 350\,H_2O$ **2**[a]	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings	5.7	1.2	750 (1.7)	[4a]
$Na_{15}\{0.5[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}\cdot$ **3a** $0.5[Mo_{152}O_{457}H_{14}(H_2O)_{68}]^{16-}\}\cdot 400\,H_2O$ **3b**	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$ + $\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	two different discrete rings, one of which possesses a defect	5.6 5.6	1.2 1.2	745 (1.8)	[7]
$Na_{16}[Mo_{176}O_{528}H_{16}(CH_3OH)_{17}(H_2O)_{63}]\cdot 600\,H_2O\cdot 30\,CH_3OH$ **4**	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	discrete rings	5.7	1.3	743 (2.1)	[8]
$Na_{14}[Mo_{154}O_{462}H_{14}(CH_3OH)_8(H_2O)_{62}]\cdot 400\,H_2O\cdot 10\,CH_3OH$ **5**[e]	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings	5.5	1.2	750 (1.7)	[9]
$Na_{24}\{0.5[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot$ **6a** $0.5[Mo_{144}O_{437}H_{14}(H_2O)_{60}]\}\cdot 350\,H_2O$ **6b**	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$ + $\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	discrete rings with defects and chains built up by rings with defects	[f]	[f]	744 (1.5)	this paper
$Na_{24}[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot 250\,H_2O$[a]	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	chains built up by rings with defects	5.8	1.2	745 (1.7)	[10]
$Na_{22}[Mo_{146}O_{442}H_{14}(H_2O)_{58}]\cdot 250\,H_2O$	$\{Mo_2\}_{10}\{Mo_8\}_{14}\{Mo_1\}_{14}$	chains built up by rings with defects	5.6	1.2	743 (1.6)	[7]
$Li_{16}[Mo_{176}O_{528}H_{16}(H_2O)_{80}]\cdot 400\,H_2O$[a]	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	discrete rings	5.6	1.3	740 (2.3)	[11]

[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 $[\{Mo_2^{VI}O_5(H_2O)_2\}^{2+}_{b-x}$-$(\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H_m(H_2O)_3Mo^{VI/V}\}^{(4-m)-})_b]^{(2b-bm+2x)-}\equiv[\{Mo_2\}_{b-x}\{Mo_8\}_b\{Mo_1\}_b]^{(2b-bm+2x)-}$ [b = number of building units per set = number of compartments (see Figure 3) = number of protonations at the equatorial μ_3-O atoms or in the $\{(\mu_3\text{-}O)_2O_2\}$ compartment (with $m=1$) = half of the (formal) number of Mo^V centres; x = number of defects or missing $\{Mo_2\}^{2+}$ units]. [c] Average BVS value for the Mo centres which span the b incomplete $\{Mo_5O_6\}$-type double cubanes, built up by (parts of) the $\{Mo_8\}$ and $\{Mo_1\}$ units (Figure 3). The (formal) number of Mo^V centres per ring is $2b$ (or two per compartment) for all compounds 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 3); this 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 according to the results of the numerous cation analyses. This value corresponds to a type of 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 $H\cdots H$ distance in the compartment (compare with ref. [13]). [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. [f] The structure is not sufficiently resolved to calculate reasonable BVS values.

0947-6539/99/0505-1498 $ 17.50+.50/0

Mo=O groups of rings (acting formally as ligands) replace the $\{Mo_2\}$-type H_2O ligands of neighbouring rings (Figure 1c). Consequently, each of these connections reduces the number of H_2O molecules in **1a** by 0.5 (three of the four possible linking positions are occupied statistically in the crystal lattice). The complex relationship between the described ring-shaped clusters is illustrated below.

$$\begin{array}{lr}
[\{Mo_2^{VI}O_5(H_2O)_2\}_{14}\{Mo_7^{VI/V}(MoNO)O_{25}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{28-} & \textbf{2a} \\
\quad +14\,\{MoO\}^{4+} \downarrow \; -14\,\{MoNO\}^{3+} & \\
[\{Mo_2^{VI}O_5(H_2O)_2\}_{14}\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{14-} & \textbf{3a} \\
\quad \downarrow \; -\{Mo_2^{VI}O_5(H_2O)_2\}^{2+} & \\
[\{Mo_2^{VI}O_5(H_2O)_2\}_{13}\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{16-} & \textbf{3b} \\
\quad \downarrow \; -1.5\,H_2O & \\
[\{Mo_2^{VI}O_5(H_2O)_{(26-1.5)/13}\}_{13}\{Mo_8^{VI/V}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{14}]^{16-} & \textbf{1a}
\end{array}$$

For the problematical determination of the actual charge of **1a** (or, in fact, of any known Mo-blue compound with ring-shaped cluster units), the difference between the (formal) number of Mo^V centres and the number of protons at μ_3-O positions must be considered. In this context the following observations are important: 1) According to the bond valence sum (BVS) values[14] of the Mo atoms (average value 5.6; see Table 1), 28 (= $2b$) 4d electrons [corresponding to the (formal) number of 28 Mo^V centres] are located within the *14 incomplete double-cubane-type compartments*, each of which is spanned by five Mo and six O atoms of the $\{Mo_8\}$ and $\{Mo_1\}$ units (see Figure 3). In other words, two 4d electrons are delocalized within each compartment. This is in agreement with the (formal) number of 28 (= $2b$) Mo^V centres determined by redox titrations, as well as with the measured ε value of the 750 nm band in the solution spectrum, which arises from an IVCT transition ($\varepsilon \approx 6 \times 10^3\,L\,mol^{-1}\,cm^{-1}/Mo^V$ centre[15]). 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, which can be assigned to *14 (= b) $\{(\mu_3\text{-}O)_2O_2\}$ related tetrahedral compartments* (Figure 3, Table 1). This BVS value indicates protonation and corresponds to one or two protons per tetrahedron. The 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. 20, some of which are displayed in Table 1). It follows therefore that the same number of relevant protons ($m = 1$ or 2, which means that one or both μ_3-O atoms in the tetrahedral compartments are protonated) as well as the same number of 4d electrons are present in each of the aforementioned compartments.

In the light of these results, the charge of the clusters (of all pure molybdenum-oxide based compounds without defects) is given by the difference between the (formal) number of Mo^V centres ($2b$) and the number of relevant protons (bm). On the other hand, the values obtained from sodium analyses, which could not be easily interpreted in the past because of the relatively small sodium content, have now gained greater significance because of the large number of known related compounds. According to these results we get $m = 1$, which also seems more plausible, as a degree of protonation $m = 2$ would lead to a rather small H ··· H distance in the tetrahedral compartments.

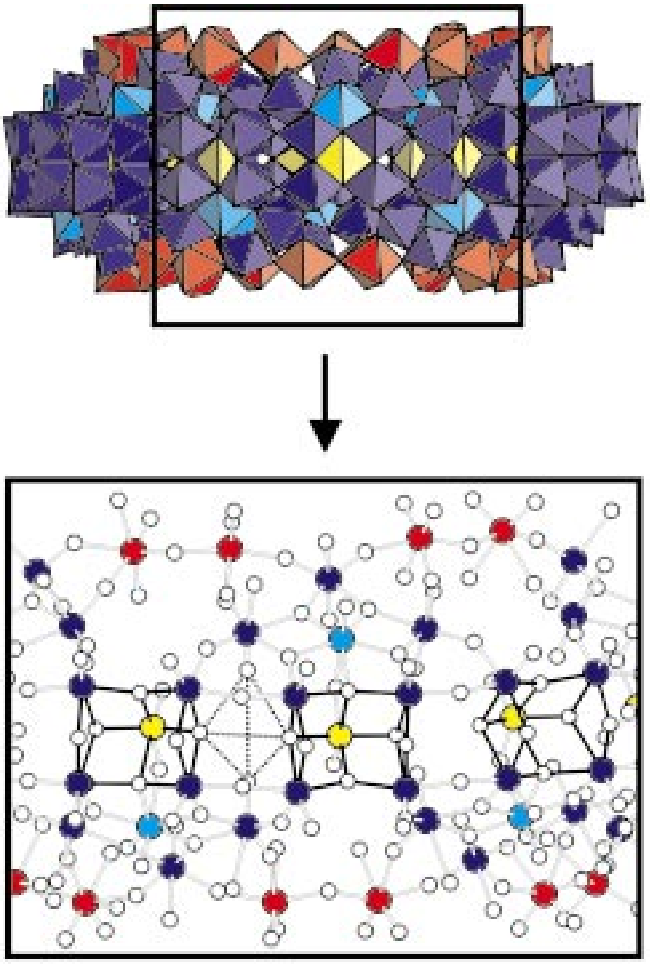


Figure 3. Structural details (bottom) of a typical ring-shaped cluster unit in polyhedral representation (top) with a view perpendicular to that depicted in Figure 2a. The detailed ball-and-stick representation highlights three of the 14 (incomplete) double-cubane-type compartments, each of which is spanned by five Mo centres that belong to $\{Mo_8\}$ as well as $\{Mo_1\}$ groups (Mo ··· Mo = 3.4–4.0 Å) and six O atoms [besides other experimental data, the lowered BVS values (average = 5.6) of the corresponding Mo atoms prove that two 4d electrons are trapped in each compartment]. It also highlights one of the 14 $\{(\mu_3\text{-}O)_2O_2\}$-type compartments (O ··· O = 3.07–4.0 Å, indicated by dotted lines); these are located between two double-cubane-type compartments [the two characteristic μ_3-O atoms (O ··· O = 3.07 Å) have an average BVS value of 1.2; see text].

The bond lengths in **1** are within the expected limits. Terminal Mo–O bonds have a length of about 1.67 Å, whereas terminal H_2O ligands, which are always located *trans* to terminal O atoms, have an Mo–O distance of about 2.4 Å. In some of the Mo-coordination polyhedra the terminal O and H_2O ligands change their positions. In these cases the Mo atom is shifted from the centre of its coordination polyhedron towards the terminal O atom and correspondingly is found disordered over two positions. All μ_2-O atoms possess one shorter ($\approx$1.85 Å) and one longer ($\approx$1.95 Å) bond to Mo atoms, the unprotonated μ_3-O atoms have three nearly equal Mo–O distances ($\approx$2.03 Å), while the μ_4-O atoms have three equally long (≈2.08 Å) and one much longer bond (≈2.5 Å). The characteristics of the μ_3-O atoms situated at the equator are one short (≈1.95 Å) and two long Mo–O bonds (≈2.3 and 2.45 Å). The O ··· O distance (3.08 Å) of the related 14 (μ_3-O) ··· (O-μ_3) pairs is significant for the proton localizations.

The following remarks are important with respect to the defects observed in **1a**. 1) The presence of the $\{MoO\}^{4+}$ groups in **1a**, instead of the $\{Mo(NO)\}^{3+}$ groups found in **2a**, causes a corresponding decrease in its negative charge by 14 units. This favours the release of the positively charged $\{Mo_2\}^{2+}$ units. 2) From a structural comparison of the tetradecameric ($b = 14$) with the corresponding larger hexadecameric ($b = 16$) ring system (such as in **4** with two additional sets of the $\{Mo_1\}$, $\{Mo_2\}$, and $\{Mo_8\}$ units), it can be seen that the $\{Mo_2\}$ units in the 'smaller' rings are less strongly bound.

Indeed, defects were not observed in the two types of cluster species mentioned, that is, either those with $\{MoNO\}^{3+}$ groups or those with three sets of $b = 16$ building units (Table 1). Regardless of this fact, we would expect, in principle, the number of defects observed and, consequently, the negative charge of one discrete, tetradecameric ring-shaped cluster to increase not only with increasing pH value of the solution, but also with decreasing molybdate concentration and reducing potential of the solution. This situation is roughly comparable with that of the (very much) smaller, lacunary polyoxometalate structures.[4b, 16] The actual charge of the system discussed here depends on the number of missing $\{Mo_2\}$ groups, x. Taking into consideration the different number of building units b ($b = 14$, tetradecameric; $b = 16$, hexadecameric ring) and the number of defects x, the general formula for the type of discrete ring unit that we are dealing with is $[\{Mo^{VI}_2O_5(H_2O)_2\}^{2+}_{b-x}(\{Mo^{VI/V}_8O_{26}(\mu_3\text{-}O)_2(H)(H_2O)_3Mo^{VI/V}\}^{3-})_b]^{(b+2x)-}$ ($\equiv [\{Mo_2\}_{b-x}\{Mo_8\}_b\{Mo_1\}_b]^{(b+2x)-}$). The term $2x$ represents the increase in charge because of x missing $\{Mo_2\}^{2+}$ groups; $2b$ is the formal number of Mo^V centres. For structure **1**, $x = 1$ and $b = 14$.

In accordance with the obtained Mo BVS values,[14] the 28 4d electrons of the deep blue mixed-valence (Mo^V/Mo^{VI}) compound **1** (class III in the Robin and Day classification[17]) are distributed over 70 Mo positions that belong to the $[\{Mo_8\}\{Mo_1\}]$ units. More precisely, these electrons are located within the 14 $\{Mo_5O_6\}$ compartments, each of which contains two delocalized electrons. This is equivalent to the situation in **2a** and also in all the other tetradecameric compounds listed in Table 1. An EHMO calculation for the discrete cluster **2a** reveals that the 28 4d electrons can be assigned to 14 MOs (molecular orbitals), which are mostly (>90%) spanned by the Mo(4d)-type atomic orbitals that belong to the Mo positions of the $\{Mo_5O_6\}$ compartment. Interestingly, these 14 MOs are nearly (accidentally) degenerate, but are separated from the LUMOs by a significant gap. Also, with increasing energy Mo(4d) functions of other Mo positions contribute to the lower lying unoccupied molecular orbitals. In principle, the electronic structure of this type of compound, though not the topology, shows some similarities to the transition metal-oxide bronzes. Of special interest in this context are the molybdenum bronzes and the hydrogen molybdenum bronzes, H_iMoO_3 ($i = 0-2$), which have a stoichiometric composition comparable with that of **1a**.[2] Remarkably, these function as both electron and proton conductors, can store hydrogen (in agreement with the given formula) and can show the other notable properties as mentioned in the introduction.

The lattice in **1** contains exchangeable, disordered H_2O molecules and Na^+ ions. (Additional, very small amounts of Na^+ together with Cl^- ions, present in the solution, can in principle be incorporated into the crystal lattice depending on the crystallization conditions and corresponding electrolyte concentration.) In vacuo, the compound slowly releases H_2O, which can be replaced reversibly by organic molecules, for instance, by formic acid. Interestingly the acid is partially deprotonated; this has been proven by infrared spectroscopy.

Conclusions

The occurrence of $\{Mo_2\}$-type defects within the ring-shaped structures leads to different reactivity and, at least, favours easier linkage of the clusters by Mo–O–Mo bonds to form not only compounds with layered structures as discussed above, but also, in the case of a larger number of defects, crystalline compounds with chains that have interesting anisotropic electronic properties. The linking is based on substitution of the H_2O ligands located in $\{Mo_2\}$ groups by the terminal O atoms of $\{Mo_2\}$ groups of neighbouring rings, which act formally as ligands. This is especially favoured if the electron density at the terminal O atom is increased.

In the compound type reported here, nanosized channels are present with basic properties (in contrast to the acidic channels in zeolites); these can incorporate small organic molecules such as formic acid.

One noteworthy aspect is that by linking the giant ring-shaped entities in different ways to form framework structures the significance of the current problem, the structure–property relationship, is increased; this fact can be correlated with the following properties of the cluster ring unit.

1) It exhibits a nanometre-sized cavity and thus presents new perspectives for novel host-guest chemistry.
2) It has an extended hydrophilic inner and outer surface due to the presence of a large number of H_2O ligands.
3) The periphery of the cluster ring has a rather high electron density.
4) It is possible to generate discrete structural defects on the inner surface of the cluster ring by the removal of positively charged $\{Mo_2\}$ groups, thereby increasing the negative charge or the nucleophilicity.
5) Different types of H_2O ligands at various sites can be substituted by other ligands.

The reaction pathway followed here is still relatively complex,[18] but this must be put into perspective against a background in which generations of chemists have attempted in vain to isolate crystals of the so-called soluble molybdenum-blue-type species from ill-defined solutions (see related remarks in ref. [5]). In the meantime we have succeeded, at least for compounds with discrete clusters[7–9, 12c] and for those with chain structures,[7] in developing synthetic methods that lead to the precipitation of pure and crystalline substances in high yield and without formation of any amorphous by-products, even after a few days (for instance, in the case of compounds with discrete clusters of the type $\{Mo_{154}\}$ **5**[7, 9] and $\{Mo_{176}\}$ **4**,[8, 12c] including those which have MeOH as well as H_2O ligands; see Table 1). Our future challenge will be to find conditions under which compounds with layered structures can also be prepared without amorphous material and in high yield.[18]

Experimental Section

$Na_{16}[Mo_{152}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}]\cdot$ ca. 300 H_2O (1): An aqueous solution of $Na_2MoO_4\cdot 2H_2O$ in H_2O (6.00 g, 2.48 mmol in 40 mL) was acidified with hydrochloric acid (10%, 15 mL) ($c_0(Mo) = 0.45\ mol\,L^{-1}$; $c_0(H^+) = 0.78\ mol\,L^{-1}$; $Z^+ = c_0(H^+)/c_0(Mo) = 1.74$). After the addition of $SnCl_2\cdot 2H_2O$ (0.58 g, 2.6 mmol; theoretically sufficient for the reduction of 20% of the Mo^{VI} to Mo^V) with stirring, the solution turned dark blue, and a dark blue precipitate was formed. The reaction mixture was allowed to stand at RT in a 100 mL Erlenmeyer flask (covered with a watch glass) undisturbed by vibration in order to initiate and improve the formation of crystals. Within 6 weeks, dark blue rhombic-bipyramidal crystals (crystal class *mmm*) of the diamagnetic compound **1** were precipitated from the reaction mixture. The crystals were separated mechanically from the amorphous part, washed quickly with a small amount of ice-cold water, and then dried under argon. The dry compound **1** is air-stable, but lost some water at 60 °C. IR (KBr pellet prepared under argon, 1100–400 cm^{-1}): $\tilde{\nu} = 971$, 912 (m, ν(Mo=O)), ca. 810 (sh), 750 (s), 634 (s), 559 cm^{-1} (s); (resonance) Raman (solid; $\lambda_e = 1064$ nm): $\tilde{\nu} = 799$ (vs), 534 (m), 463 (s), ca. 438 (sh), 323 (s), 215 cm^{-1} (s); UV/Vis (oxygen-free 0.1 M HCl): λ (ε_M $10^5\ L\,mol^{-1}\,cm^{-1}$) = 750 (1.6), 1065 nm (1.1) (electronic absorption spectrum of the 'solution' only measured for determination of the formal number of Mo^V centres; for the solid, $\lambda \approx 750$, 1050 nm). $Na_{16}Mo_{152}O_{523.5}H_{147}\cdot 300\,H_2O$ (28879.7): calcd Na 1.27, H_2O 18.7; found Na 1.6, H_2O 18.0 (Cl 0.5). The indirect cerimetric titration showed the presence of 28 4d electrons, which (formally) corresponds to 28 Mo^V centres.

If the precipitate was not filtered, additional dark blue triclinic pinacoidal plates of the compound $Na_{24}\{0.5[Mo_{144}O_{409}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{56}]\cdot 0.5[Mo_{144}O_{409}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{60}]\}\cdot$ ca. 350 H_2O (**6**) also precipitated. (Crystal data for **6**: space group $P\bar{1}$, $a = 29.271(14)$, $b = 33.604(12)$, $c = 44.781(18)$ Å, $\alpha = 91.40(3)$, $\beta = 91.44(4)$, $\gamma = 97.55(3)°$, $V = 43634$ Å^3, $Z = 2$.) The single-crystal X-ray structural analysis of the mixed-crystal compound shows the presence of discrete ring units as well as chains (built up from the rings) in the ratio 1:1 (see Table 1). Interestingly, both parts of the structure possess the same $\{Mo_2\}$-type defect. For further information on this latter chain structure see refs. [7, 10]. Compound **6** is formed after crystallization of **1**, which means it is synthesized under more dilute conditions.

Single-crystal X-ray structural analysis of 1: Several crystals were investigated by complete refinement procedures giving practically the same result, even with respect to the type of disorder. Data ($Mo_{K\alpha}$ radiation, graphite monochromator) were collected on a Siemens three-circle diffractometer with a 1K-CCD detector. The structure was solved by direct methods. Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407669. The formula is idealized in spite of the low R value. The error limit for the total number of $\{Mo_2\}$ groups is in agreement (±0.5) with the uncertainty in the determination of the occupation factors for disordered (under-occupied) atoms. Crystal data, data collection and refinement parameters are given in Table 2.

Table 2. Crystal data, data collection, and refinement parameters for compound **1**.

formula	$H_{747}Mo_{152}Na_{16}O_{823.5}$	Z	4
M_r [g mol^{-1}]	28879.69	ρ_{calcd} [g cm^{-3}]	2.276
colour	dark blue	$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.30
crystal dimensions [mm]	0.45 × 0.45 × 0.35	$2\theta_{max,\ measured}$ [°]	54
crystal system	orthorhombic	reflections measured	190090
space group	*Cmca*	unique reflect.	42001
T [K]	183 K	observed [$I > 2\sigma(I)$]	32335
a [Å]	49.836(3)	refined parameters	1841
b [Å]	56.022(3)	R_1[a] [$F_o > 4\sigma(F_o)$]	0.087
c [Å]	30.185(2)	wR_2[b]	0.234
V [Å^3]	84273(12)	$\Delta\rho$(max/ min) [e Å^{-3}]	3.93

[a] $R_1 = \sum \frac{||F_0| - |F_c||}{\sum |F_0|}$. [b] $wR_2 = \sqrt{\frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2}}$ with $\frac{1}{w} = \sigma^2(F_0^2) + \frac{0.1(F_0^2\ +\ 2F_c^2)}{3}$

Acknowledgments

We thank Dr. E. Diemann, P. Kögerler, B. Hauptfleisch, Dr. C. Lu and Dr. J. Meyer for their collaboration, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

---

[1] For some related aspects see *Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology, and Biology* (Ed.: D. B. Brown), Reidel, Dordrecht, **1980**; H. H. Kung, *Transition Metal Oxides: Surface Chemistry and Catalysis*, Elsevier, Amsterdam, **1989**; V. E. Henrich, P. A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, **1994**.

[2] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press/Clarendon, Oxford, **1984**, pp. 612–619; *Low-Dimensional Electronic Properties of Molybdenum Bronzes and Oxides* (Ed.: C. Schlenker), Kluwer, Dordrecht, **1989**; G. Schwitzgebel, St. Adams, *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 1426–1430; Cl. Ritter, W. Müller-Warmuth, R. Schöllhorn, *J. Chem. Phys.* **1985**, *83*, 6130–6138, and references cited therein.

[3] *Comprehensive Supramolecular Chemistry, Vol. 6, Solid-State Supramolecular Chemistry: Crystal Engineering* and *Vol. 7, Solid-State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn), Pergamon/Elsevier, Oxford, **1996**; *Multifunctional Mesoporous Inorganic Solids* (Eds.: C. A. C. Sequeira, M. J. Hudson), Kluwer, Dordrecht, **1993**.

[4] a) A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem.* **1995**, *107*, 2293–2295; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122–2124; b) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239–271; see also compounds listed in Table 1 with corresponding references.

[5] In addition to the crystals, amorphous material with identical spectroscopic properties was obtained; however, it cannot be clearly identified. In this context, it should be mentioned that generations of chemists have tried to isolate, without success, pure compounds from reduced molybdate solutions in order to grow crystals and to understand the unusual properties of the related molybdenum-blue species: *Gmelins Handbuch der Anorganischen Chemie, Molybdän*, VCH, Berlin, **1935**, pp. 134–147; *Gmelin Handbook of Inorganic Chemistry, Molybdenum Suppl., Vol. B3a*, Springer, Berlin, **1987**, pp. 61–68. Our earlier conclusion (A. Müller, J. Meyer, E. Krickemeyer, E. Diemann, *Angew. Chem.* **1996**, *108*, 1296–1299; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1206–1208) that soluble molybdenum blue consists of the linked or nonlinked ring-type species has now been confirmed.[18]

[6] B. K. Vainshtein, *Fundamentals of Crystals: Symmetry, and Methods of Structural Crystallography*, Springer, Berlin, **1994**.

[7] A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Z. Anorg. Allg. Chem.* **1999**, *625*, in press.

[8] A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.* **1998**, 1501–1502.

[9] A. Müller, E. Krickemeyer, S. Q. N. Shah, M. J. Koop, H. Bögge, M. Schmidtmann, *Inorg. Chem.*, in press.

[10] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, C. Menke, J. Meyer, *Angew. Chem.* **1997**, *109*, 500-502; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 484 – 486.

[11] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* **1998**, *110*, 1278 – 1281; *Angew. Chem. Int. Ed.* **1998**, *37*, 1220 – 1223.

[12] a) A. Müller, C. Beugholt, *Nature* **1996**, *383*, 296 – 297; b) A. Müller, H. Reuter, S. Dillinger, *Angew. Chem.* **1995**, *107*, 2505 – 2539; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328 – 2361; c) A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48 – 50.

[13] W. H. Baur, *Acta Crystallogr. Sect. B* **1992**, *48*, 745 – 746.

[14] I. D. Brown, in *Structure and Bonding in Crystals Vol. II* (Eds.: M. O'Keeffe, A. Navrotsky), Academic Press, New York, **1981**, pp. 1 – 30.

[15] R. I. Buckley, R. J. H. Clark, *Coord. Chem. Rev.* **1985**, *65*, 167 – 218.

[16] *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**; M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56 – 70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34 – 48.

[17] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247 – 422.

[18] Note added in proof: In the meantime we were able to obtain the layer-type compound in a facile synthesis in high yield and in pure and crystalline form in the presence of an electron-donating ligand; this changes the property of the cluster surface: A. Müller, S. K. Das, H. Bögge, C. Beugholt, M. Schmidtmann, *Chem. Commun.*, in press.

Received: June 29, 1998 [F1232]