range of 10–30 nm. Nanoprobe EDXS and EELS analysis revealed a composition of Pd_3P for most of the particles. Above 500°C the initial 2 nm clusters reacted only with the phosphorus atoms of the ligand shell, since neither boron nor carbon could be detected in the larger particles. The samples containing the palladium phosphide colloids were supported on lacy carbon film on a copper grid and investigated in a JEM-4000EX electron microscope, which was operated at 400 kV and a structural resolution of about 0.16 nm ($C_s = 1.0$, $C_c = 2.5$ mm, spread of focus about 60 Å, and semiconvergence angle 0.50 mrad). The crystal structure images were recorded at magnification of about 300000 × (3.4 pixels per 1.7 Å) with a slow-scan CCD camera (Gatan 694). Two particles imaged along different directions are shown in Figure 1. All images were recorded in the linear range of the CCD camera (0–12000 gray levels). The particles are too small to be oriented by stage tilting when the microscope is in diffraction mode, so correctly aligned particles must be sought among randomly oriented particles.

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Formation of a Ring-Shaped Reduced "Metal Oxide" with the Simple Composition $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$**

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Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday

Two years ago, we reported on the ring-shaped polyoxometalate ion **1**.[1a–c] We have now succeeded in obtaining crystals which contain an even larger ring-shaped cluster formed by a conservative self-organization process. Remarkably, it represents a simple reduced, protonated, and hydrated molecular metal oxide, built up from 176 molybdenum and 608 oxygen atoms.[2] Based upon the number of metal atoms, it seems to be the largest discrete inorganic species characterized by single-crystal X-ray structure analysis.[3] Its large cavity (diameter 2.3 nm) opens new perspectives for host–guest and supramolecular chemistry.

$[Mo_{154}(NO)_{14}O_{448}(H_2O)_{70}H_{28}]^{14-}$ **1**

$[(MoO_3)_{176}(H_2O)_{80}H_{32}]$ **2**

After acidifying an aqueous solution of lithium molybdate (about 1 M) followed by reduction with tin(II) chloride at room temperature, dark blue rhombic-bipyramidal crystals (crystal class *mmm*) of a compound containing cluster **2** precipitate together with chemically identical amorphous material from the dark blue reaction mixture. The blue compound contains cluster **2** together with additional, partly disordered lattice components (crystal water as well as small amounts of Li^+ and Cl^- ions; see Experimental Section). The compound was characterized by elemental analyses, cerimetric titration of the formal number of Mo^V centers, thermogravimetric analysis (to determine the crystal water content), bond valence sum calculations (to determine the number and position of protonated oxygen atoms as well as the formal number of Mo^V centers[4]), spectroscopic methods (IR, Raman, UV/Vis and NIR spectroscopy), EHMO calculations, and single-crystal X-ray structure analysis.[5]

Remarkably, **2** shows the stoichiometry of a protonated reduced molecular molybdenum trioxide with coordinated H_2O ligands. Despite the significantly different properties of **1** and **2**, a structural comparison shows striking similarities. According to a related building-block scheme for the cluster types $[\{Mo_2\}\{Mo_8\}\{Mo_1\}]_{\underline{n}} \equiv [\{Mo_2^{VI}O_5(H_2O)_2\}\{Mo_8^{VI/V}XO_{25}(OH)_2(H_2O)_3Mo^{VI/V}\}]_n$, **1** can be formulated as a tetradecamer (with $n = 14$ and X = NO) and **2** as a hexadecamer (with $n = 16$ and X = O; Figure 1).[1b, 6–8] This confirms that the $\{Mo_8\}$ units, connected by building units of the type $\{Mo_1\}$ and $\{Mo_2\}$ in **1** and **2**, represent a special type of building block that occurs in several polyoxometalate structures.[1a,b, 6–8] A more detailed structural comparison of both systems shows that the inner regions of the rings, which are mainly built up by $\{Mo_2\}$ units, are less tightly bound in **1**. This causes the rings to be slightly domed in the corresponding regions and can—upon decreasing the negative charge of the ring—easily lead to a release of $\{Mo_2\}^{2+}$ groups with further consequences for the reactivity in the case of **1**.[7, 8] Further unusual condensation reactions in the case of **2** can occur at the relatively tightly bound $\{Mo_2\}$ groups result in the formation of polyoxometalate fragments in the inner regions of the rings. These condensations lead to the formation of structures with a kind of "hubcap" caused by a novel type of molecular growth. In general however, the growth of polyoxometalates by condensation is only observed if the overall ion charge increases with a concomitant, approximately constant charge per molybdenum center. This ensures the solubility of the clusters and prevents not only the molecular units from forming the oxidic solid (showing translational

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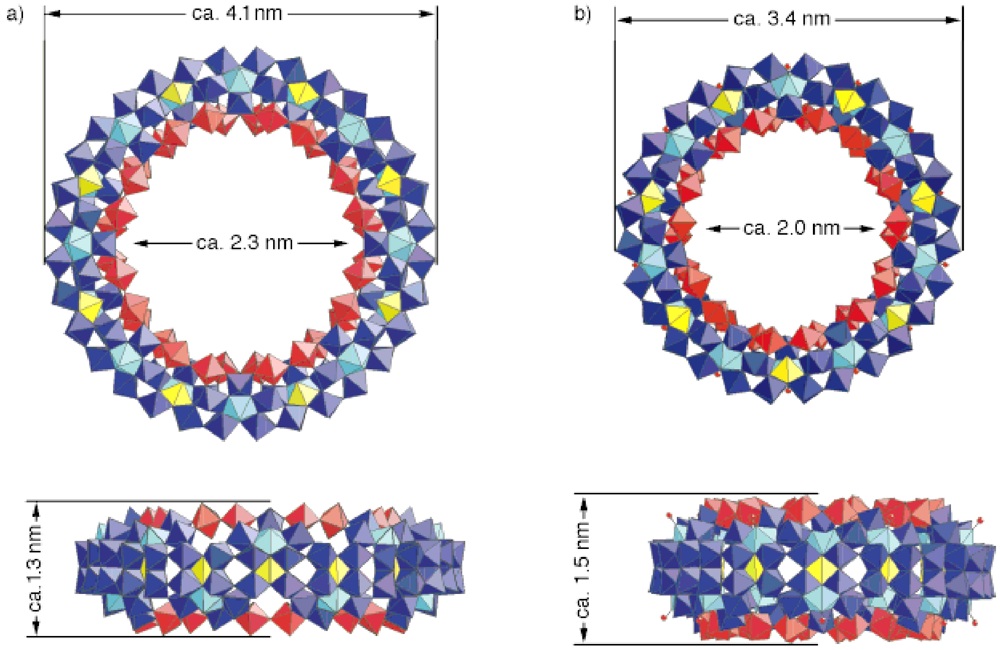

Figure 1. a) Polyhedral representation of the structure of **2** (view along the approximate C_8 axis (top) and perpendicular to it (bottom)). Compound **2** consists of sixteen $\{Mo_8\}$ units (blue, with a central pentagonal MoO_7 bipyramid in light blue), which are linked by the sixteen units of the $\{Mo_2\}$ type (red) as well as sixteen $\{Mo_1\}$ units located at the equatorial ring plane (yellow). b) Polyhedral representation of **1** (top: view from the top; bottom: side view) to show the structural similarities and differences: The ring of **2** is distinctly less thick than that in **1** because of the smaller ring tension and looser bonding in the flexible $\{Mo_2\}$ groups.

invariance) but also hydrolysis to smaller species or uncontrolled linking. In the special case considered here, however, the solubility in protic solvents is achieved by the extremely hydrophilic surface of the cluster, arising from the presence of numerous water and hydroxyl ligands.

A comparison of the electronic structures of **1** and **2** calculated by EHMO methods[9] shows a clear ordering of the molybdenum-centered molecular orbitals in the HOMO region for both ring systems. A first set of 14 (for **1**) or 16 (for **2**) molecular orbitals, which contain mainly (around 90 %) 4d orbitals of the 56 (or 64) molybdenum atoms located on the peripheral near equatorial positions[8] (mainly, in agreement with the results of the bond valence sum calculations of the molybdenum atoms with corresponding values between 5 and 6[4]), is followed by an energetically separated second set of molecular orbitals. This second set of orbitals contains contributions of increasing energy stemming from 4d orbitals of molybdenum atoms located in the central cluster regions. The energetic structuring of the considered molecular orbitals is strongly dependent on the protonation of the species (that is, the number of hydroxyl groups). With respect to the given degree of protonation (28 OH and 70 H_2O in **1** or 32 OH and 80 H_2O ligands in **2**) the EHMO calculation favors a charge of 14^- for **1** and zero for cluster **2**. These charges correspond to 28 or 32 Mo^V centers, respectively. Thus in both cases the first set of mainly molybdenum-centered MOs is fully occupied resulting in a distinct HOMO–LUMO separation. The exchange of the $\{MoNO\}^{3+}$ (in **1**) by $\{MoO\}^{4+}$ groups (in **2**) in the $\{Mo_8\}$ units scarcely influences the predominantly Mo^V-centered frontier orbitals, as expected, but influences considerably the ion's charge with substantial consequences (see above as well as references [7, 8, 10]). Our calculation shows that the $\{MoNO\}^{3+}$-centered molecular orbitals, which due to their energy do not interact with other molecular orbitals, are concentrated around an energy level of about −12 eV.

A general problem arises with the characterization of these types of compound.[12] Since the spectroscopic data (for example, vibrational spectra[13, 14]) and the analytical data do not differ significantly, extremely large clusters can in principle often only be distinguished from similar large clusters of the same type (but with a different number of building blocks) by single-crystal X-ray structure analyses or, as in the present case, by the crystal shape. In an earlier article about molybdenum blue, this problem was addressed as follows:[14a] "Principally, also the presence of different and larger ring-shaped species with the general composition $\{(MoO_3)_m(H_2O)_nH_p\}^{x-}$ cannot be totally excluded, neither by X-ray powder diffraction nor by IR and Raman spectroscopy alone." In this context, it is interesting that the new cluster **2**, which belongs to the class of the soluble molybdenum-blue compounds, indeed possesses the composition $\{(MoO_3)_m(H_2O)_nH_p\}$ (here with $m = 176$, $n = 80$, $p = 32$), which has been predicted to be characteristic for this type of compound.[14a, 17]

If the intention is to create ever larger species, the fundamental question is whether the present type of cluster synthesis in polyoxometalate chemistry leads to a dead end. This question is difficult to answer. Under normal preparative conditions, extremely large clusters of the type in question according to our present knowledge, preferentially form amorphous materials that cannot be characterized unambiguously (see also reference [15]). Though the relationship between certain reaction conditions and the size of emerging clusters is not yet understood in detail, the requirements for the formation of extremely large systems like **2** are observed to be very low pH values and high molybdate concentrations. In this context, the influence of the cluster charge (or the degree of reduction) on the growth process, for instance due to a successive exchange of $\{MoNO\}^{3+}$ by $\{MoO\}^{4+}$ groups, represents an interesting aspect for further research. Our aim for the future is to concentrate on the simplification of the syntheses in order to get uniform crystalline material in high yields and reasonable time.

Experimental Section

2$\cdot$ca. 400 $H_2O\cdot$ca. 20 $Li^+\cdot$ca. 20 Cl^-: Li_2MoO_4 (4.50 g, 25.9 mmol; Johnson Matthey) was dissolved in H_2O (25 mL) as far as possible, and HCl (14.8 mL of a 10% solution) was then added to the stirred reaction mixture, which nearly led to the complete dissolution of the lithium molybdate. Finely ground $SnCl_2\cdot 2H_2O$ (p.A.; 0.61 g, 2.7 mmol, an amount theoretically sufficient for the reduction of 20% of the Mo^{VI} to Mo^{V} centers) was then added in small portions while stirring, whereby a dark blue precipitate formed. The reaction mixture was stored at 20°C in a wide-necked 100 mL Erlenmeyer-flask covered by a watch glass without further disturbance (to facilitate the crystallization) for about six weeks. Dark blue rhombic-bipyramidal crystals of the above-mentioned composition precipitated. In addition to less crystalline or amorphous material (see ref. [15]) minor amounts of dark blue pinacoidal[16] and rhombic plates[16] were formed subsequently, due to the lower molybdate concentrations in the reaction medium as material precipitates. Furthermore, a small amount of a colorless precipitate of a salt containing the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ anion was formed. The rhombic-bipyramidal crystals were separated mechanically in the mother liquor, washed several times with the filtered mother liquor and dried on filter paper in air (yield: ca. 0.2–0.3 g corresponding to 4–6% relative to the initial molybdate quantity). The mechanical separation is necessary as the rhombic-bipyramidal crystals, which lose some of their crystal water upon storage in air, do not differ sufficiently in solubility from the pinacoidal and rhombic plates.[17]

Characterization of **2**$\cdot$ca. 400 $H_2O\cdot$ca. 20 $Li^+\cdot$ca. 20 Cl^-: Cerimetric titration yields 32 ± 2 Mo^{V} per formula unit. Elemental analyses: ca. 0.4% Li and ca. 2.0% Cl.[12] Thermogravimetry: ca. 20% weight loss or ca. 400 H_2O. Some characteristic bands in IR (KBr pellet, prepared under argon): $\tilde{\nu}$ [cm^{-1}]: 1616 (m, $\delta(H_2O)$), ca. 991(sh) 972(m), 911(w–m) (ν(Mo=O)), ca. 820(sh) 742(s), ca. 675(sh) 632(s), 558(s). Solid-state Vis/NIR spectrum (KBr pellet, in transmission): λ [nm]: ca. 700 and ca. 1000 due to intervalence charge-transfer transitions.

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[2] The term (conservative) self-organization seems to be justified for an aggregation process that leads to extremely large and/or complicated molecular structures under one-pot conditions. However, the prerequisite should be that an intermediate formed during the self-aggregation process possesses such a directing effect on the following processes that the complex structure cannot be synthesized in a stepwise fashion by the chemist. In this sense, the formation of a crystal showing translation invariance from a nucleus cannot be described as complex as it is due to the operation of translation symmetry.

[3] Cf. K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem.* **1997**, *109*, 1513–1516; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445–1448.

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

[5] Space group *Cmcm*; $a = 53.317(4)$, $b = 31.146(2)$, $c = 66.830(4)$ Å, $V = 110979(12)$ Å^3; $Z = 4$; solved with direct methods, $R = 0.104$ for 22845 independent reflections ($F_0 > 4s(F_0)$); (Siemens)AXS-Smart diffractometer (173240 reflections obtained at −100°C of 1271 records, which cover 0.3° in ω each, $2\theta_{max} = 45°$). The crystals of **2** were taken directly out of the mother liquor and measured immediately to prevent weathering through loss of crystal water. The measurements of individual crystals always led to the same result. The structure was solved with the programme SHELXS-96 and refined with the programme SHELXL-93 (G. M. Sheldrick, University of Göttingen, **1996** and **1993**). Further details of the structure investigations can 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 number CSD-408508.

[6] A. Müller, H. Reuter, S. Dillinger, *Angew. Chem.* **1995**, *107*, 2505–2539; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328–2361, and references therein.

[7] The formulation based on the building blocks $\{Mo_2\}$, $\{Mo_8\}$ and $\{Mo_1\}$ is useful for the following reasons: In the ring of **1**, defects in the $\{Mo_2\}^{2+}$ units can easily be produced, for example, by a formal exchange of $\{MoNO\}^{3+} \rightarrow \{MoO\}^{4+}$. The resulting decrease of the cluster charge supports the repulsion of the $\{Mo_2\}^{2+}$ units. The defects obviously favor a linking of the rings to chains[8a] and layer structures[8b] but generally speaking cause a change in reactivity.

[8] a) 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; b) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, C. Lu, C. Beugholt, unpublished results; c) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239–271.

[9] The EHMO calculations are based on the positions of the atoms obtained from the X-ray structure analysis. Standard atomic parameters of the program were used (G. A. Landrum, YAeHMOP 2.0: "Yet Another Extended Hückel Molecular Orbital Package"; URL: http://overlap.chem.cornell.edu/yaehmop). The positions of the H atoms were obtained on the basis of bond valence sums of the oxygen positions by molecular modeling calculations (generic UFF-plus force-field) using the CERIUS 3.2 software (CERIUS 3.2, Molecular Simulations, Cambridge **1993**).

[10] The reduction of aqueous molybdate solutions with hydroxylamine,[11a] which is important in this context, has been known for about 100 years and has often been described misleadingly in the literature. It leads preferentially to the formation of $\{MoNO\}^{3+}$ units[11b] and in general to polynuclear molybdates.[11c,d] In addition to the formation of the $\{MoNO\}^{3+}$ group, hydroxylamine can also give rise to the reduction of further molybdenum centers.[1a] The $\{MoNO\}^{3+}$ groups can be linked by molybdate fragments[11d] but also under special conditions by sulfide/polysulfide ions,[11c] which in both cases results in the formation of polynuclear chalcogenomolybdates. The synthesis and a relatively good characterization of the large, red polyoxomolybdate cluster $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ was most likely carried out already in 1931.[11e] On the other hand, the structure of the yellow precipitate (an important starting material[11e]) which is always formed at the initial phase of the reaction between molybdate and hydroxylamine, has not yet been characterized. Obviously, it is a polymolybdate with "(NO)" groups, but containing no (reduced) Mo centers.[11f] Our investigations show that hydroxylamine is *not* essential for the synthesis of the considered type of ring species. However, the possible substitution steps of the type $\{MoNO\}^{3+} \leftrightarrow \{MoO\}^{4+}$, as pointed out above, can have major consequences for the reaction pathways.[8]

[11] a) K. von der Heide, K. A. Hoffmann, *Z. Anorg. Chem.* **1896**, *12*, 279–292; V. Kohlschlüter, K. A. Hoffmann, *Justus Liebigs Ann. Chem.* **1898**, *307*, 323; Übersicht: E. Lassner, *J. Less Common. Met.* **1968**, *15*, 143–150; b) see, for example, A. Müller, S. Sarkar, *Angew. Chem.* **1977**, *89*, 189–190; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 183–184; *ibid.* **1977**, *89*, 479–480 or **1977**, *16*, 468–469; A. Müller, W. Eltzner, S. Sarkar, H. Bögge, P. J. Aymonino, N. Mohan, U. Seyer, P. Subramanian, *Z. Anorg. Allg. Chem.* **1983**, *503*, 22–36, and references therein; c) see, for example, A. Müller, W. Eltzner, H. Bögge, S. Sarkar, *Angew. Chem.* **1982**, *94*, 555–556; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 535–536; A. Müller, W. Eltzner, N. Mohan, *ibid.* **1979**, *91*, 158–159 or **1979**, *18*, 168–169; d) P. Gouzerh, Y. Jeannin, A. Proust, F. Robert, *ibid.* **1989**, *101*, 1377–1378 and **1989**, *28*, 1363–1364; S. Zhang, Y. Wei, Q. Yu, M. Shao, Y. Tang, *J. Am. Chem. Soc.* **1997**, *119*, 6440–6441, and references therein; e) W. F. Jakob, B. Jezowska, *Roczniki. Chem.* **1931**, *11*, 229–253; f) K. Wieghardt, G. Backes-Dahmann, W. Swiridoff, J. Weiss, *Inorg. Chem.* **1983**, *22*, 1221–1224; A. Müller, W. Eltzner, unpublished results.

[12] The determination of the exact formula and especially the charge of extremely large mixed valence clusters by single-crystal X-ray

structure analysis presents a general problem, in particular if further charged lattice components of the relevant compound (small amounts of cations as well as anions located in cavities and channels) and large amounts of crystal water molecules cannot be clearly located, for instance due to disorder. In these cases, the formula including the charge can in principle only be determined if analytical data and the (formal) charges of all ingredients are taken into account. The analytical data, however, cannot be very accurate as firstly, the concentration of the mentioned charged lattice components is generally very small (but not the number of ions in the formula unit) and secondly, the large crystal water content varies to some extent. The isolated compound with cluster **1**, for instance, shows in addition to NH_4^+ ions, an "uptake" of small amounts of Na^+ and Cl^- ions which complicate the determination of the cluster charge by elemental analysis as the difference in the number of cations and anions is of relevance here. The real charge of **1** is smaller as mentioned earlier, namely 14 − which is in agreement with the average BVS (bond valence sum) values of 5.60 for the 70 (**1**) and 80 (**2**) molybdenum centers located in the peripheral incomplete double cubes, which are built up from four Mo atoms of the $\{Mo_8\}$ units as well as one $\{Mo_1\}$-type center and six oxygen atoms. Each of the double-cube compartments contains two 4d electrons. Remarkably, the absolute divergence of the BVS values for the 56 (**1**) or 64 (**2**) outer peripheral ring positions from the $\{Mo_8\}$ units is only ±0.05 and for the 14 (**1**) or 16 (**2**) equatorial positions ($\{Mo_1\}$-type centers) only ±0.10 for six different cluster structures. This corresponds (formally) to the 28 (for **1**) and 32 (for **2**) Mo^V centers and is (for the $\{Mo_8\}$ part) also in agreement with the conclusions from the EHMO calculations and the redox titrations. A related problem in charge determination was also stressed by Pope and coworkers in an important publication,[3] though the determination of the charge of their particular cluster anion—as was also pointed out—is not so difficult. This is due to the fact that the oxidation states of the metal centers are clearly known.

[13] The IR spectra of large clusters (of the type $\{Mo_{36}\}$,[6] $\{Mo_{57}\}$,[6] and partly $\{Mo_{154}\}$[1a–c]) can be modeled by superposition of (weakly coupled) characteristic vibrations of different $\{Mo_mO\}$ fragments.[14b] This simplifies of course the proof of functional groups on the one hand, but on the other complicates the differentiation of species with different numbers of these fragments, as in the case of **1** and **2**.

[14] A. Müller, J. Meyer, E. Krickemeyer, E. Diemann, *Angew. Chem.* **1996**, *108*, 1296–1299; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1206–1208; b) A. Müller, M. Ohm, H. Bögge, unpublished results.

[15] A. Müller, E. Diemann, B. Hollmann, H. Ratajczak, *Naturwissenschaften* **1996**, *83*, 321–322.

[16] The pinacoidal plates contain in the crystal lattice the smaller tetradecameric ring-type clusters corresponding to **1** with a 1:1 ratio of rings of composition $[\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}]$ and $[\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}]$; the latter have a defect. Structural data: space group $P\bar{1}$; $a = 31.007(2)$, $b = 32.818(2)$, $c = 47.325(3)$ Å; $\alpha = 90.59(1)$, $\beta = 90.11(1)$, $\gamma = 96.70(1)^\circ$; $V = 47826$ Å^3; $Z = 2$; $R = 0.110$ for 57819 independent reflections ($F_o > 4\sigma(F_o)$). The rhombic plates contain in the crystal lattice the larger $\{Mo_{176}\}$-type rings as in **2** but with different packing and with a substantially higher amount of crystal water molecules (ca. 600 H_2O). Structural data: space group $P2_1/n$; $a = 29.205(2)$, $b = 64.040(4)$, $c = 74.622(3)$ Å; $\beta = 99.81(1)$; $V = 137522$ Å^3; $Z = 4$; $R = 0.192$ for 63952 independent reflections ($F_o > 4\sigma(F_o)$).

[17] Note added in proof: The resulting product mixture obtained here is still relatively complex, but this must be put into perspective against the background that generations of chemists have attempted in vain to isolate crystals from solutions of molybdenum blue type species. The investigation of these products is also complicated due to the fact that the lattice energy is very low resulting in a series of isolated compounds with different packing of the clusters. We have succeeded in developing synthetic methods in which crystalline substances can be isolated in a few days without amorphous coprecipitation. This synthesis refers to the mentioned cluster of the type $\{Mo_{154}\}$ ($R = 0.057!$) and $\{Mo_{176}\}$, which have MeOH ligands as well as H_2O ligands. (A. Müller, M. J. Koop, H. Bogge, M. Schmidtmann, *Chem. Commun.* submitted; A. Müller, E. Krickemeyer, M. J. Koop, S. Q. N. Shah, H. Bogge, M. Schmidtmann, *Z. Anorg. Allg. Chem.* submitted.).

Expression of Chirality by Achiral Coadsorbed Molecules in Chiral Monolayers Observed by STM[**]

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Pasteur discovered almost 150 years ago the three-dimensional separation of the sodium ammonium salt of racemic tartaric acid in enantiomorphous crystals.[1] Since then, chemists have been intrigued by the concept of chirality. The development of the scanning probe techniques, such as scanning tunneling microscopy (STM)[2] and atomic force microscopy (AFM),[3] made it possible to locally probe monolayers. Only a few reports have dealt with the direct observation of supramolecular chirality in two dimensions by use of scanning probe techniques. Spontaneous breaking of chiral symmetry by achiral molecules in a Langmuir–Blodgett (LB) film was determined by Viswanathan et al. with AFM.[4] Enantiomorphous monolayer domains from achiral liquid crystalline molecules,[5] achiral purine molecules,[6] and didodecylbenzene molecules[7] on graphite have been observed by STM. Eckardt et al. reported the separation of chiral phases in monolayer crystals of racemic amphiphiles in LB films by AFM.[8] The direct observation of enantiomorphous monolayer crystals from liquid crystalline enantiomers and the formation of coexisting enantiomorphous domains from a racemate by STM have been described by Stevens et al.[9] Spontaneous resolution in two dimensions was recently demonstrated by grazing-angle X-ray diffraction.[10]

We have used small chiral organic molecules with hydrogen-bonding potential to self-assemble chiral physisorbed monolayers on a graphite surface. The *S* enantiomer of the chiral isophthalic acid derivative 5-[10-(2-methylbutoxy)-decyloxy]isophthalic acid (ISA, Figure 1 A) was dissolved in 1-heptanol, and a small droplet was applied to the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG). Figure 1 B shows a STM image of the resulting monomolecular layer of (*S*)-ISA adsorbed to the basal plane of HOPG. The image reveals a closely packed arrangement of molecules on the graphite surface with submolecular resolution. The aromatic isophthalic acid head groups of (*S*)-ISA molecules can clearly be recognized as bright spots. Bright and dark refers to the black/white contrast in the images;

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