[5] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem.* **1998**, *110*, 3567–3571; *Angew. Chem. Int. Ed.* **1998**, *37*, 3360–3363.

[6] See, for example: A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48–50; A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239–271; 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 elemental analyses show that **1a** is, within the error limit of our data, a neutral cluster (uncertainty only exists in the number and/or kinds of ligands/fragments). Compound **1** contains, according to numerous analytical values and also, according to the IR spectrum, no Cl^-, Na^+, and NH_4^+ ions; however there are 12 CH_3COO^- ligands and "additionally" three negatively charged $Mo_2O_{8/9}$ "ligand" fragments with a total charge of −6, which are necessary for the neutrality of the cluster. Clearly, the positively charged hypothetical cluster formed by the complete replacement of the spacers in **2a** by those in **1a** is not stable under the present conditions. (The $\{(Mo^{VI})Mo^{VI}_5O_{21}\}_{12}Fe^{III}_{30}$ cluster fragment, structurally unambiguously identified, has a charge of +18.) The $Mo_2O_{8/9}$ fragments, which are derived from the $\{Mo_2\}$ units of the starting compound and which function as a type of ligand on the inside of the cluster (in a similar manner to H_2O and CH_3COO^-), are strongly disordered due to the highly symmetrical space group, whereby the occupation factors of the Mo positions of the $Mo_2O_{8/9}$ fragments, found in the X-ray structural analysis add up to about six. The position of the twelve strongly disordered acetate ligands could not be unambiguously determined, mainly because of the numerous possible positions (≥ 120). However, this problem did not arise in a related compound (*Cmca*; $a = 36.8148$, $b = 34.4029$, $c = 35.0556$ Å) which crystallizes in a space group of lower symmetry and in which the clusters **1a** are linked by Fe-O-Fe bonds into layers. Because of the markedly less disorder, the positions of the $\{Mo_2\}$ fragments as well as (some) of the acetate ligands were resolved.[8]

[8] The $Mo_2O_{8/9}$ "ligand" fragments in this compound have the following structures: $\{(O_{br})_2O{=}Mo^{VI}(OH)_2(H_2O)Mo^{VI}{=}O(O_{br})_2\}^{2-}$ and $\{(O_{br})_2O{=}Mo^{VI}O(H_2O)Mo^{VI}{=}O(O_{br})_2\}^{2-}$ with octahedral and square-pyramidal coordination of the Mo centers, respectively, whereby the atoms of the $\{Mo^{V}_2\}$ ligands designated formally as $(O_{br})_2$ (br = bridging) are coordinated to the Mo atoms of the spherical shell in a similar manner to those of the H_2O and CH_3COO^- ligands. Correspondingly, in the above formula all three types of ligands are denoted as L.

[9] Crystal structure analysis of **1**: Space group $R\bar{3}$, $a = 55.1306(14)$, $c = 60.193(2)$ Å, $V = 158439(8)$ Å^3, $Z = 12$, $\rho = 2.346$ g cm^{-3}, $\mu = 2.70$ mm^{-1}, $F(000) = 108744$, crystal dimensions: 0.25 × 0.25 × 0.15 mm^3. Crystals of **1** were removed from the mother liquor and immediately measured at 153(2) K on a Bruker-axs-SMART diffractometer (three-circle goniometer with a 1K-CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator). Measurements were performed on a hemisphere with 0.3° ω-scans in three runs with 606, 435, and 230 frames ($\phi = 0$, 88, and 180°) based on a detector distance of 5 cm. Of the 274226 reflections measured ($1.57 < \Theta < 24.99°$), 61998 were independent ($R(\text{int}) = 0.0659$) and were used in the refinement. An empirical absorption correction on the basis of symmetry-equivalent reflections was carried out with the help of the program SADABS. The structure was solved and refined with the programs SHELXS-97 and SHELXL-97 to $R = 0.082$ for 34204 reflections with $I > 2\sigma(I)$; max./min. residual electron density: 2.97 and −3.26 e Å^{-3} (SADABS, SHELXS/L by G. M. Sheldrick, Universität Göttingen, Germany, **1997**; structural graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, **1999**). Several individual crystals were measured in which the same type and number of strongly disordered $Mo_2O_{8/9}$ fragments bound to the inside of the spherical shell could be localized. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132027. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Some basic comments on the synthesis of giant clusters based on polyoxomolybdates: in contrast to the synthesis of the Keplerate clusters, which can be readily obtained in high yield, the synthesis of the extremely soluble molybdenum blue compounds based on giant ring-type structures caused considerable problems in the past. However, these are now also readily accessible in the presence of a high electrolyte concentration which destroys the hydration shell that stabilizes the structures in solution (A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.* **1998**, 1501; A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1187–1192; A. Müller, S. K. Das, H. Bögge, C. Beugholt, M. Schmidtmann, *Chem. Commun.* **1999**, 1035–1036; A. Müller, C. Beugholt, M. Koop, S. K. Das, M. Schmidtmann, H. Bögge, *Z. Anorg. Allg. Chem.* **1999**, *625*, in press).

[11] H. S. M. Coxeter in *A Spectrum of Mathematics: Essays Presented to H. G. Forder* (Ed.: J. Butcher), Oxford University Press, Oxford, **1967**, pp. 98–107; I. Stewart, *Spiel, Satz und Sieg für die Mathematik*, Birkhäuser, Basel, **1990**, pp. 95–114.

[12] Within the context of the Pythagorean knowledge of geometry (from about 500 BC) and the knowledge given in the first book written on natural philosophy, the epochal *Timaios*, it is demonstrated very impressively that the elementary building blocks of nature, such as these polygons, have to "find" each other, metaphorically speaking, in Euclidean space for the joint construction of complex, and in particular, unusual and harmonic structures (see, for example, ref. [1k]).

[13] Further information on Archimedean solids in chemistry can be found in a recent review: L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080–1096; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018–1033.

"Open and Shut" for Guests in Molybdenum–Oxide-Based Giant Spheres, Baskets, and Rings Containing the Pentagon as a Common Structural Element

Achim Müller,* Sebastian Polarz, Samar K. Das,
Erich Krickemeyer, Hartmut Bögge,
Marc Schmidtmann, and Björn Hauptfleisch

In memory of Frank Hellweg

The synthesis of very large molecular containers[1] or host systems—for problem-solving use—presents an enormous challenge for modern chemistry. Here, we report on the formation of a giant molecular basket which is generated by "opening" a giant molybdenum–oxygen sphere ("Keplerate"),[2] and on the option of exchanging the contents of the spheres in a variable and controlled manner. Our prediction—based on the isolation of the first giant molecular Keplerate spheres[2]—that a novel supramolecular chemistry, or in other words a defined Keplerate chemistry would develop[2] has now been confirmed with this article. A kind of Pythagorean harmony[3] is evident in this type of chemistry and is of particular interest in this context since the structural unit which is responsible for the curvature in the spherical and ring-shaped giant clusters, to which the common formula $\{Mo_{11}\}_n$ can be given, is the same.

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[*] Prof. Dr. A. Müller, Dipl.-Chem. S. Polarz, Dr. S. K. Das,
E. Krickemeyer, Dr. H. Bögge, M. Schmidtmann,
Dipl.-Chem. B. Hauptfleisch
Lehrstuhl für Anorganische Chemie I
Fakultät für Chemie der Universität
Postfach 100 131, D-33501 Bielefeld (Germany)
Fax: (+49) 521-106-6003
E-mail: a.mueller@uni-bielefeld.de

1433-7851/99/3821-3241 $ 17.50+.50/0

Compound **1**, with the aforementioned giant molecular basket **1a** as its anion, which is clearly important for the understanding of the exchange reaction of the ligands in the spherical Keplerate clusters described here, precipitates from solutions that contain the Keplerate anion **2a**[2] on standing for some time in air (Figure 1). (Compound **1** has not yet been isolated free of side products.) The addition of anions with (bidentate) ligand function (e.g. perchlorate, sulfate, sulfite, phosphate, hypophosphite, or phenylphosphonate ions) to freshly synthesized solutions of **2** gave compounds with the correspondingly substituted Keplerate clusters, which have identical spherical shells, in a pure form and in relatively high yield. In the resulting compounds, the CH_3COO^- ligands, which were originally coordinated to the $\{Mo^V_2O_4^{2+}\} \equiv \{Mo^V_2\}$ groups of **2a**,[2] have been either completely exchanged (as in the case of the phosphate and hypophosphite) or partially exchanged (as in the case of the sulfate). Compounds **3** and **4** are described here.[4]

$Na_{46}[Mo^{VI}_{66}Mo^{V}_{50}O_{331}(CH_3COO)_{30}(H_2O)_{56}] \cdot ca.\ 300\,H_2O$ **1**

$(NH_4)_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COO)\}_{30}] \cdot ca.\ 300\,H_2O \cdot ca.\ 10\,CH_3COONH_4$ **2**

$(NH_4)_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(H_2PO_2)\}_{30}] \cdot ca.\ 300\,H_2O$ **3**

$(NH_4)_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(HSO_4)\}_{18}\{Mo^V_2O_4(CH_3COO)\}_{12}] \cdot ca.\ 300\,H_2O$ **4**

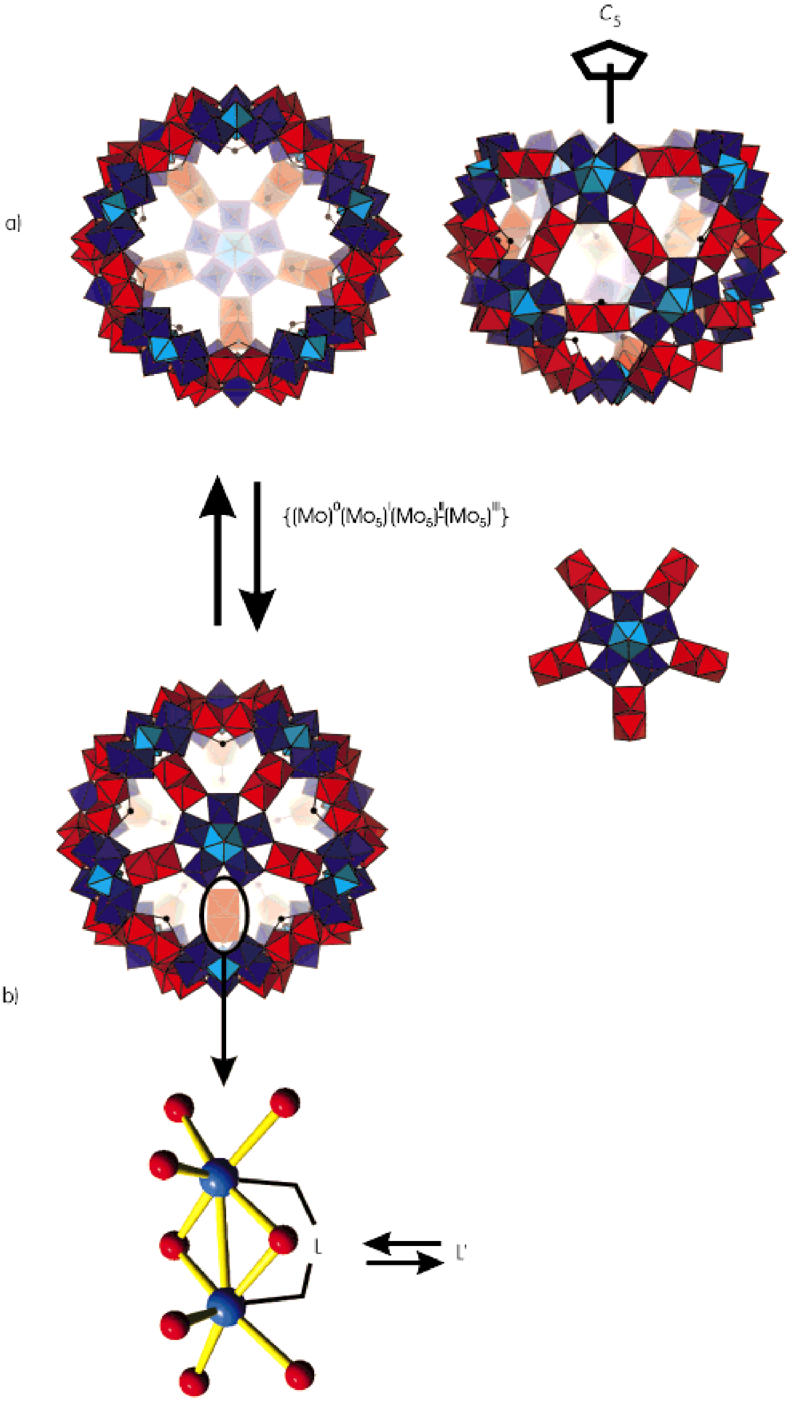

Figure 1. Structure of **1a** (viewed along the C_5 axis and perpendicular to it) a) and **2a** b). The position where the ligand exchange reactions take place in **2a** is circled and a separate $\{Mo^V_2L\}$ unit is given below. The $\{Mo_{16}\}$ motif ("lid" of the basket **1a**) is separately represented ($\{(Mo)Mo_5\}$ pentagons: blue; $\{Mo^V_2\}$ fragments: red).

Compounds **1**, **3**, and **4** were characterized by elemental analysis (including cerimetric titration to determine the number of Mo^V centers), thermogravimetry (to determine the amount of water of crystallization), spectroscopy (IR, Raman, UV/Vis), single-crystal X-ray structure analysis,[5] and bond valence sum (BVS)[6] calculations (to determine the positions of the H_2O molecules as well as to differentiate between the Mo^{VI} and Mo^V centers).

Compound **1**, which has a basket-shaped anion, crystallizes in the space group $Pmn2_1$.[5] Compounds **3** and **4** are isostructural or pseudoisostructural, respectively, to the corresponding compounds with a giant spherical structure of the type $\{Mo_{132}\}$, which contain acetate[2] (space group $Fm\bar{3}$) or formate ligands,[7] respectively (space group $R\bar{3}$) at the $\{Mo^V_2\}$ groups. The structure of the basket-shaped giant cluster **1a** can be formally derived from the giant sphere **2a**[2] (Figure 1) ($\{Mo_{11}\}_{12} \equiv \{(Mo)^0(Mo_5)^I(\{Mo^V_2\}_{5/2})^{III}\}_{12}$) by the "removal" of a $\{(Mo)^0(Mo_5)^I\{(Mo^V)^{II}\text{-}(Mo^V)^{III}\}_5\}$ motif (Figure 1). During the reaction, however, the distribution of the acetate ligands concentrated at the "edge of the basket" changes somewhat—including their coordination to the $\{(Mo)Mo_5\}$ units, which are not abundant in **2a**. The relative number of Mo^V centers in **1a** is less than that of **2a**, so that the reaction (with regard to **1a** and **2a**) can formally be considered as a partial oxidation.

Product **1**, with its basket-shaped anion **1a**, which is formed after "opening" the giant molecular sphere **2a**, is much more soluble in H_2O than **2**, whose anion **2a** has mainly terminal oxygen ligands on the surface of the sphere. The reason for this difference in solubility lies in the easy access of the solvent to the hydrophilic interior of **1a**, which has a large number of H_2O ligands positioned *trans* to the terminal O atoms. Therefore, crystallization of **1** only takes place after the equilibrium has shifted extensively in the direction of the basket-type species, whereby the solution must be kept diluted in order to ensure that the less soluble spherical cluster **2a** remains long enough in solution. But if the work is carried out in the presence of a high sodium acetate concentration (this causes salting out as a result of the destruction of the hydrate shell) or even in the presence of NH_4^+ ions, which reduce the solubility of the relevant salt, then our goal to obtain **1** will not be achieved and **2** precipitates instead.

To understand the remarkable guest/ligand exchange in the reaction of **2a** to **3a** or **4a**, the following points should be considered:

1) The ligand exchange should not occur through the "molecular windows" found on the C_3 axes of **2a** (at least when dealing with rigid $\{Mo_9O_9\}$ rings), since these are too small for the negatively charged ions.

2) The isolation of **3** and **4** takes place at a time when the reaction medium still contains a considerable amount of spherical anions.

3) It follows from (1) that either the ligands which "approach" the sphere **2a** lead to its "opening" or that in solution there is an equilibrium between the corresponding basket-shaped object and "closed" spherical-shaped species–with the possibility of direct ligand exchange. In the latter case, one can easily understand the facile crystallization of the compounds **3** and **4** (i.e., after ligand exchange and equilibrium readjustment) which contain the corresponding cluster spheres **3a** and **4a**, since they are—due to the lower hydrophilicity of the surface of the sphere relative to **1a**—less soluble than the corresponding basket species, with which they are in equilibrium. Further evidence for the presence of an equilibrium is provided by the fact that from a solution which was produced exclusively from the basket compound **1** the spherical cluster anion **2a** (corresponding to **2**) can be isolated (the reverse is also valid). In these considerations, one cannot assume that the $\{Mo_{16}\}$ fragment/lid is present as a relatively stable unit in solution.

The fact that during the transformation sphere → basket a fragment of the type $\{(Mo_{11})Mo_5\}$ is "dislodged" stimulates ideas concerning the relevance of pentagonal building blocks in structural chemistry. The star-shaped basic motif $\{(Mo)^0\text{-}(Mo_5)^I(Mo_5)^{II}\text{-}(Mo_5)^{III}\}$ (cf. Figure 2b), comprising several formal (motif-)"generations", can be clearly recognized in Figure 1, which shows the structure of **2a** along the direction of the fivefold axis. The existence of the pentagonal pattern clearly correlates with the controlling/symmetry-determining influence of the central pentagonal MoO_7 bipyramid ("zero generation") which is connected to the five MoO_6 octahedra of the "first generation". The five MoO_6 octahedra of the "second generation" are then connected to those of the first by corners, whereby the former build up the neighboring relatively stable Mo^V–Mo^V dumbbells of the $Mo_2^VO_4^{2+}$ type with further MoO_6 polyhedra.

It must be emphasized that this motif-related view does not correlate directly with the real formation process of these structures; however, it is very useful to elucidate the structural chemistry.

In this context it is certainly remarkable that, on the one hand the $\{Mo_{11}\} \equiv \{(Mo)^0(Mo_5)^I(Mo_5)^{II}\}$ fragments/motifs can generate not only the giant spheres, but they are also the basic motif for various ring-shaped polyoxomolybdate structures of the type $\{Mo_{11}\}_n$ ($n = 14, 16$) (Figure 2 and 3). Only in the case of stronger reducing conditions, as in the present case, are the $\{(Mo_5)^{II}\}$ centers equivalent and this ultimately leads to an arrangement with C_5 symmetry. (The above-mentioned bidentate ligands are, however, necessary for the formation of the present type of spherical structures that are produced by linking 12 of these regular $\{Mo_{11}\}$ pentagons). If this is not the case—that is, under less reducing conditions—then a shift of a MoO_6 octahedron and a C_s-$\{Mo_{11}\}$ fragment with lower symmetry results, (Figure 2a and 3), and consequently ring-shaped species of the $\{Mo_{154}\}$ and $\{Mo_{176}\}$ type[8, 9] (related stoichiometry $(Mo_{11})_{14}$ and $(Mo_{11})_{16}$) are formed, respectively.

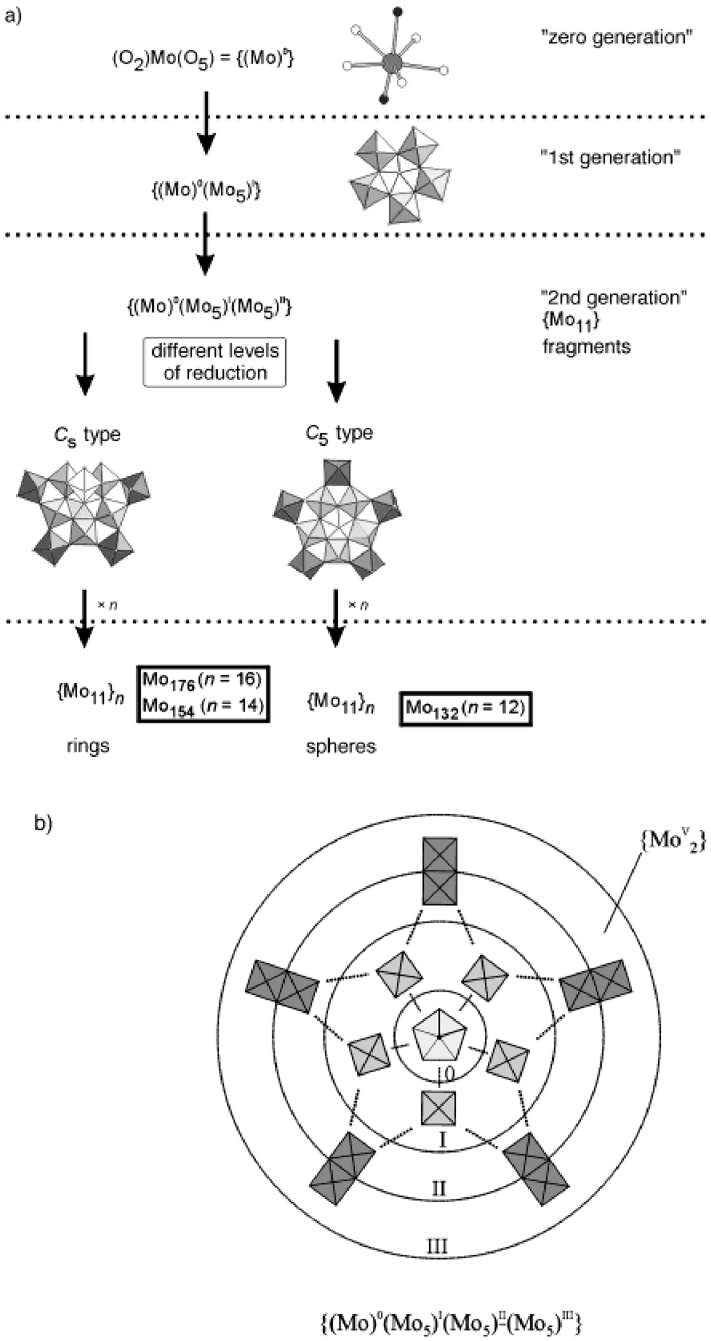

Figure 2. a) Schematic (formal) relationship between the basic structural elements and/or the motifs of giant molecular spheres and rings as well as b) the formal relationship to the $\{(Mo)^0(Mo_5)^I(Mo_5)^{II}\text{-}(Mo_5)^{III}\} \equiv \{Mo_{16}\}$ motif ("lid" of the giant sphere).

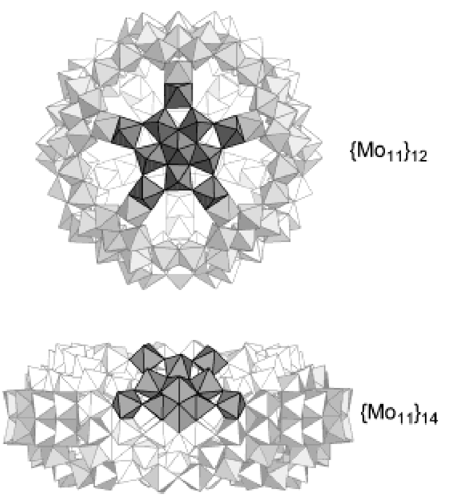

Figure 3. Structural comparison of the ring-shaped and spherical clusters $\{Mo_{11}\}_{14}$ and $\{Mo_{11}\}_{12}$, respectively, each with a highlighted $\{Mo_{11}\}$ unit.

We believe that the results reported here point the way towards a novel type of supramolecular nanochemistry. The synthesized "vessels" allow not only the inclusion but also the common (!) transport of various molecular and/or ionic collectives. Since the exchange of acetate ligands described here is also possible with many other guests/ligands—for example, those with even larger organic groups—it is possible to construct new tailored surface structures on the inside of the sphere, particularly with amphiphilic ligands. Additionally, by the control of the reaction conditions, such as by the use of ligands that do not coordinate too strongly, the extent of substitution of the acetate ligands can be varied. With a smaller ligand than that used in **2a** (e.g. $HCOO^-$ instead of CH_3COO^-) it is even possible to generate an onion-shaped arrangement of the enclosed van der Waals clusters, for example with a $(H_2O)_n$ collective or cluster.[7] In this case only the spherical cluster shell influences the type of organization of the central guest collective in the hollow interior of the Keplerate clusters. Additionally, there is the possibility that smaller guests, such as very small organic molecules, can be "smuggled" into **2a** through the 20 openings formed by the $\{Mo_9O_9\}$ rings, which have a diameter of about 0.35 nm. Corresponding investigations are currently underway.

In any case, there are still many exciting novelties to be discovered in the field of polyoxometalate chemistry (see also refs. [8, 9]), and certainly we can expect a (topological) variety comparable to that of the fullerenes.[10]

Experimental Section

1: A stirred solution of $Na_2MoO_4 \cdot 2H_2O$ (7.67 g, 31.7 mmol) and $CH_3COONa \cdot 3H_2O$ (12.50 g, 91.9 mmol) in H_2O (250 mL) was treated with $N_2H_4 \cdot H_2SO_4$ (0.80 g, 6.2 mmol) and 50% CH_3COOH (65 mL). The mixture was stirred for 10 min (gradual color change to green whilst $N_2H_4 \cdot H_2SO_4$ slowly reacted; pH value ca. 4.0). After addition of NaCl (5.00 g, 85.6 mmol), the reaction solution was left in an open beaker (400 mL, wide-neck) for 3–4 weeks (under the fume hood), whereby the volume of the solution reduced to about 50 mL. During this time the initial product **2a** was partially oxidized: within the first hours the color of the solution slowly changed to dark brown with simultaneous evolution of gas. On concentration of the mixture, several fractions precipitated: first, a dark brown precipitate (filtration at a volume of about 150 mL), then orange-brown crystals of $Na_{10}[H_4Mo^{VI}_{10}Mo^{V}_{8}O_{56}(CH_3COO)_2] \cdot$ ca. $34H_2O \cdot 3CH_3COONa$,[11] followed by a mixture of colorless crystals and black-brown, columnar crystals of **1**. The mixture of crystals was separated from the oily dark brown mother liquor by filtration through a glass frit (D2). The mixture was washed several times with an aqueous sodium acetate buffer solution (see below) followed by 2-propanol, and finally dried over $CaCl_2$. The individual crystal fractions could only be separated mechanically from one another. Total yield: ca. 3.5 g (ca. 35% **1**, ca. 15% $Na_{10}[H_4Mo_{18}O_{56}(CH_3COO)_2] \cdot$ ca. $34H_2O \cdot 3CH_3COONa$, and ca. 50% colorless crystals). Compound **1** is very soluble in H_2O. Characteristic IR bands (KBr pellets; 1800–500 cm^{-1}): $\tilde{\nu} = 1628$ (m, $\delta(H_2O)$), 1543 (s, $\nu_{as}(COO)$), 1447 (m), 1412 (m) ($\delta(CH_3)$, $\nu_s(COO)$), 971 (s), 937 (w-m) ($\nu_{as}(Mo{=}O)$), 854 (s), 795 (vs), 724 (s), 627 (w), 566 cm^{-1} (s); characteristic Raman bands (solid and solution; $\lambda_e = 1064$ nm; 1000–200 cm^{-1}): $\tilde{\nu} = 953$ (w-m), 934 (w-m) ($\nu(Mo{=}O)$), 874 (s), ca. 845 (sh), 371 (m), 313 cm^{-1} (w-m); UV/Vis (solid-state spectrum measured against cellulose as white-standard: $\lambda =$ ca. 440 (br), ca. 600 nm (br). The spectroscopic data are almost identical with those of **2** (the same sample techniques were also used in ref. [2] and not those given there erroneously).

Preparation of the sodium acetate buffer solution for washing: A stirred and cooled aqueous solution of CH_3COOH (50%; 500 mL) was treated with an aqueous solution of NaOH (20%) until the pH was 4.0–4.2.

3: A stirred solution of **2**[2] (1.0 g, 0.04 mmol) in H_2O (50 mL) was treated with $NaH_2PO_2 \cdot H_2O$ (1.0 g, 9.43 mmol) and 50% H_3PO_2 (ca. 0.8 mL, pH = 2.0). The mixture was stirred for 24 h at 20 °C, NH_4Cl (2.0 g, 37.4 mmol) was added, and the mixture was cooled to 15 °C. The dark brown, rhombohedral crystals of **3** slowly precipitated from the dark brown solution over a period of 4 d, were filtered over a glass frit and dried in air. Yield: 0.55 g (56% based on **2**). Characteristic IR bands (KBr pellets; 1800–500 cm^{-1}): $\tilde{\nu} =$ 1620 (m, δ (H_2O)), ca. 1425 (sh), 1402 (s) (δ_{as} (NH_4^+)), 1118 (m), 1075 (w), ca. 1033 (w) (H_2PO_2), 973 (s), ca. 940 (w) ($\nu(Mo{=}O)$), 857 (s), 801 (s), 724 (vs), 630 (m), 572 cm^{-1} (s); characteristic Raman bands (solid and solution; $\lambda_e = 1064$ nm; 1000–200 cm^{-1}): $\tilde{\nu} = 939$ (m, $\nu(Mo{=}O)$), 881 (s), ca. 850 (sh), 374 (m), 304 cm^{-1} (m); UV/Vis (solid-state spectrum measured against cellulose as white-standard): $\lambda =$ ca. 450 (br), ca. 600 nm (br).

4: A stirred solution of **2**[2] (0.50 g, 0.018 mmol) in H_2O (25 mL) was treated with Na_2SO_4 (0.35 g, 2.5 mmol) and hydrochloric acid (15%, ca. 1 mL). The stirred reaction solution ($pH \approx 4.5$) was kept in an oil bath at 30 °C for 48 h. (The crystals used for the data collection were obtained in suitable quality by heating the solution to 90 °C for a short time prior to the addition of NH_4Cl.) After addition of NH_4Cl (0.4 g, 7.5 mmol) and cooling to 18 °C, dark brown, rhombohedral crystals of **4** slowly precipitated from the dark brown solution over a period of 4 d. These crystals were collected by filtration using a glass frit and dried in air. Yield: 0.2 g (40% based on **2**). Compound **4** is very soluble in H_2O and moderately soluble in EtOH. Characteristic IR bands (KBr pellet; 1800–500cm^{-1}): $\tilde{\nu} = 1625$ (m, $\delta(H_2O)$), 1540 (w, $\nu_{as}(COO)$), ca. 1425 (sh), 1401 (s) ($\delta_{as}(NH_4^+)$), 1187 (m), 1132 (m), 1044 (w-m) ($\nu_{as}(SO_3)$), 970 (s), 936 (w-m) ($\nu(Mo{=}O)$), 855 (s), 798 (s), 726 (m), 632 (w-m), 572 cm^{-1} (m); characteristic Raman bands (solid and solution; $\lambda_e = 1064$ nm; 1000–200 cm^{-1}): $\tilde{\nu} = 942$ (m) ($\nu(Mo{=}O)$), 879 (s), ca. 845 (sh), 375 (m), 312 cm^{-1} (w-m); UV/Vis (solid state spectrum measured against cellulose white-standard): $\lambda =$ ca. 450 (br), ca. 600 nm (br).

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Keywords: cage compounds · cluster compounds · polyoxometalates · structure elucidation · supramolecular chemistry

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[1] The title of this article refers to an interesting contribution by P. C. H. Mitchell ("Open and shut case for anions", *Nature* **1990**, *348*, 15–16; section: News and Views), which in turn refers to one of our earlier publications on a related host/guest chemistry (A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer, J. Döring, *Angew. Chem.* **1990**, *102*, 927–929; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 926–927). In our opinion,

the given title is now completely justified in the present work, because only closed hosts were described in our work at that time. The term "open and shut" can also be applied to the giant wheel-type clusters (A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48–50).

[2] a) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem.* **1998**, *110*, 3567–3571; *Angew. Chem. Int. Ed.* **1998**, *37*, 3360–3363; b) see also: A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. H. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein, V. Schünemann, *Angew. Chem.* **1999**, *111*, 3435–3439; *Angew. Chem. Int. Ed.* **1999**, *38*, 3238–3241 (previous article).

[3] The Pythagoreans believed that the world order, its harmony, and symmetry could be defined by numbers: Aristotle wrote in his famous book Metaphysics that according to the Pythagoreans—contrary to his own beliefs—the elements of numbers are the elements of all things and various types of structures could be differentiated by different numbers (see: A. Stückelberger, *Einführung in die antiken Naturwissenschaften*, Wiss. Buchgesellschaft, Darmstadt, **1988**, p. 12).

[4] The extent of the exchange of the acetate ligands depends on the nucleophilicity of the added ligand and the pH value of the solution. The exchange with the phosphate and hypophosphite ions (at least at low pH values) is complete at room temperature; however, only partial exchange with the sulfate ion was observed under the present conditions. We will not report any details here on the phosphate-Keplerate since our investigations have indicated an interesting result which must be discussed separately: the relative uptake of HPO_4^{2-} and $H_2PO_4^-$ ions can be nicely controlled by changing the pH value.

[5] **1**: Space group $Pmn2_1$; $a = 49.117(4)$, $b = 34.898(3)$, $c = 25.223(2)$ Å, $V = 43234(7)$ Å^3; $Z = 2$; 207015 reflections obtained at 183 K from 1271 frames, each of which covered 0.3° in ω scans ($2\theta_{max} = 50°$); structure solution with direct methods, $R = 0.0896$ for 35329 independent reflections ($F_o > 4\sigma(F_o)$). **3**: Space group $R\bar{3}$; $a = 32.719(1)$, $c = 73.567(2)$ Å, $V = 68205(3)$ Å^3; $Z = 3$; 134487 reflections obtained at 183 K from 1271 frames, each of which covered 0.3° in ω scans ($2\theta_{max} = 54°$); structure solution with direct methods, $R = 0.0457$ for 24569 independent reflections ($F_o > 4\sigma(F_o)$). **4**: Space group $R\bar{3}$; $a = 32.695(1)$, $c = 73.529(3)$ Å, $V = 68069(3)$ Å^3; $Z = 3$; 134980 reflections obtained at 183 K from 1271 frames, each of which covered 0.3° in ω scans ($2\theta_{max} = 54°$); structure solution with direct methods, $R = 0.0409$ for 23684 independent reflections ($F_o > 4\sigma(F_o)$). The crystals were taken directly from their reaction solutions and measured immediately on a Bruker-axs-SMART diffractometer to prevent the loss of water of crystallization. The measurement of several individual crystals led to the same results. The structures were solved with the program SHELXS-97, refined with the programs SHELXL-93 and SHELXL-97, and the absorption corrections were performed with the program SADABS (G. M. Sheldrick, Universität Göttingen, **1997** and **1993**). Disorder problems occurred in the following cases: 1) all of the smaller lattice components, 2) the acetate ligands at various positions in **1** and **4**, 3) terminal MoO groups with the appended *trans*-positioned H_2O ligands in **4**, 4) the $H_2PO_2^-$ ligands in **3** and HSO_4^- ligands in **4**. Problems (1) and (4) give rise to a related error limit in the formulae. The structural graphics were generated with the program DIAMOND 2.1 (K. Brandenburg, Crystal Impact GbR, **1999**). Further details of the crystal structure investigation of **3** 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-410885. Crystallographic data (excluding structure factors) for the structures of **1** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132028 and CCDC-132029, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] 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.

[7] A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge, M. Schmidtmann, *Chem. Commun.* **1999**, 927–928.

[8] a) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239–271; b) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, S. K. Das, F. Peters, *Chem. Eur. J.* **1999**, *5*, 1496–1502.

[9] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**; c) A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.* **1999**, 1347–1358.

[10] a) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163; b) *Buckminsterfullerenes* (Eds.: W. E. Billups, M. A. Ciufolini), VCH, Weinheim, **1993**; c) *Von Fuller bis zu Fullerenen: Beispiele einer interdisziplinären Forschung* (Eds.: W. Krätschmer, H. Schuster), Vieweg, Braunschweig, **1996**.

[11] Space group $P\bar{1}$; $a = 12.1293(5)$, $b = 15.2523(6)$, $c = 15.2852(6)$ Å, $\alpha = 114.911(1)$, $\beta = 94.227(1)$, $\gamma = 101.647(1)°$, $V = 2471.4(2)$ Å^3; $R = 0.0358$ for 12491 independent reflections ($F_o > 4\sigma(F_o)$).

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