Archimedean Synthesis and Magic Numbers: "Sizing" Giant Molybdenum-Oxide-Based Molecular Spheres of the Keplerate Type**

Achim Müller,* Sabyasachi Sarkar,
Syed Qaiser Nazir Shah, Hartmut Bögge,
Marc Schmidtmann, Shatarupa Sarkar, Paul Kögerler,
Björn Hauptfleisch, Alfred X. Trautwein, and
Volker Schünemann

Dedicated to Professor Sir Harold Kroto

It has long been the chemist's endeavor to vary the size of highly symmetrical molecular objects according to a predetermined plan ("sizing"). For spherical objects using, for example, different types of linkages between pentagons, this dream has now become reality. Pentagons play an important role in the cultural and intellectual history of mankind as well as in modern science—beginning with the Pythagoreans, then later from Archimedes, Kepler, and Dürer, to Goethe's Faust, and finally to Weyl and Penrose.[1, 2] For the chemist, pentagons are especially attractive, but it was not possible to control these units up to now. The most challenging task for us was to synthesize spherical objects (the most symmetrical objects in Euclidean space) from pentagons in accordance with the early geometric knowledge of Archimedes of Syracuse.[2] Here we report on the first construction of giant molecular spheres of the Keplerate type with different sizes which is achieved by varying the type of linkage between the pentagons by means of various spacers or linkers.[3–5] Incidentally, the linkers span an Archimedean solid with icosahedral symmetry.[13]

The yellow compound **1** was synthesized in high yield by the reaction of $FeCl_3$ with the $\{Mo_{132}\}$ cluster anion **2a**,[5] a Keplerate which contains the $\{(Mo)Mo_5\}$-type pentagons. The reaction is essentially based on the substitution of the $\{Mo^{V}_{2}\}$ spacers in **2a** by aqua-ligand-Fe^{III} polyhedra. Compound **1** was characterized by elemental analysis (including cerimetric titration to exclude the presence of Mo^{V} and Fe^{II} centers), thermogravimetry (to determine the amount of water of crystallization), magnetochemistry, spectroscopy (IR, Raman, UV/Vis, ESR, and ^{57}Fe Mössbauer spectroscopy), X-ray structure analysis, and bond valence sum (BVS) calculations (e.g. to differentiate between the positions of terminal oxygen atoms and H_2O ligands).[6–9] The starting compound, the Keplerate anion **2a**, is also readily accessible in high yield.[5, 10]

$$[\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}_5O_{21}L_6}\}_{12}\{\mathrm{B}\}_{30}]\cdot \mathrm{ca.}\ 150\,\mathrm{H_2O} \qquad \mathbf{1}$$

$$[\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}_5O_{21}L'_6}\}_{12}\{\mathrm{B'}\}_{30}]^{42-} \qquad \mathbf{2a}$$

spacers/linkers B, ligands L:
1: $B = \{Fe^{III}(H_2O)L\}^{n+}$ $(L = H_2O/CH_3COO^-/Mo_2O_{8/9}{}^{n-})$[7, 8]
2: $B' = \{Mo^{V}_2O_4(CH_3COO)\}^+$ $(L' = H_2O)$

Compound **1**, which crystallizes in the space group $R\bar{3}$,[9] contains discrete, neutral, spherical clusters **1a** (Figure 1). Each sphere contains twelve pentagonal fragments of the type $\{(Mo)Mo_5\}$, that is, $\{(Mo)Mo_5O_{21}\}$ with a central bipyramidal MoO_7 group which is linked by edge-sharing to five MoO_6 octahedra. These pentagonal fragments are connected by the

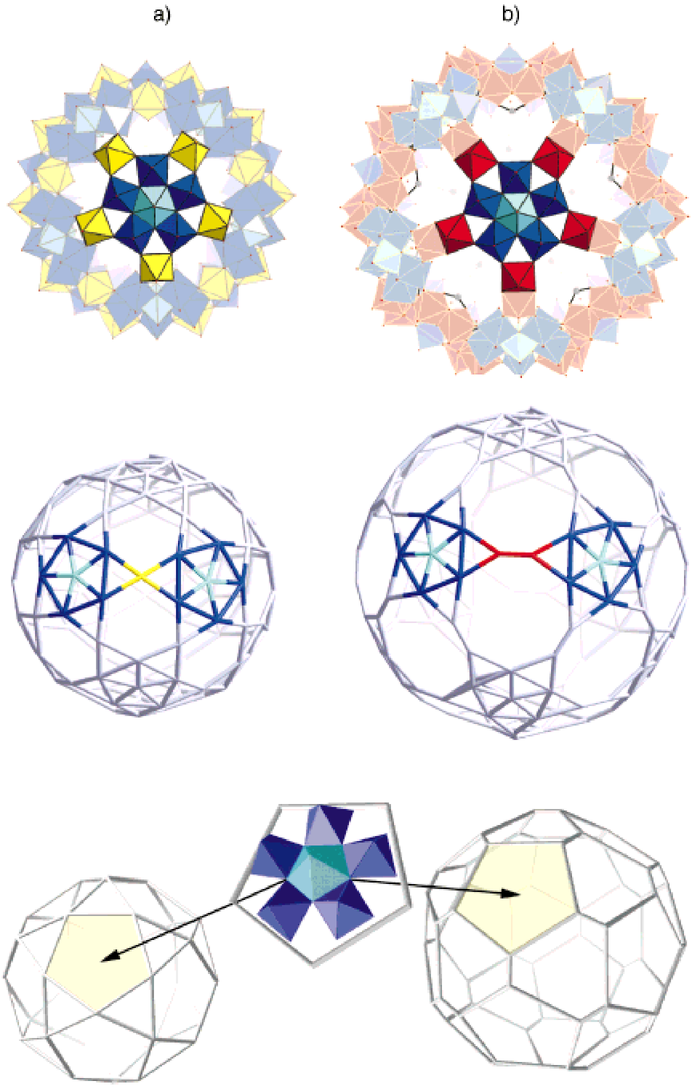

Figure 1. Top: polyhedral representation of **1a** (a) and **2a** (b) viewed along a C_5 axis showing five of the openings formed by the (Mo_9O_9) (accessible for very small molecules) and $(Mo_3Fe_3O_6)$ rings. ($\{(Mo)Mo_5\}$ units: blue; central MoO_7 unit: turquoise; linkers $\{Fe\}$ and $\{Mo^{V}_2\}$: yellow and red, respectively). Center: comparison of the spherical $\{Fe_{30}Mo_{72}\}$ fragment (**1a**) (a) and the $\{Mo_{132}\}$ fragment (**2a**) (b) with the corresponding basic fragments $\{(Mo)Mo_5\}$ and $\{Fe\}$ in **1a** (a) as well as $\{(Mo)Mo_5\}$ and $\{Mo^{V}_2\}$ in **2a** (b) (color code as above; viewed along a C_2 axis). Bottom: structures spanned by the fundamental spacer units (Archimedean solids) of **1a** and **2a** with one of the 12 capping $\{(Mo)Mo_5\}$ pentagons: the Fe_{30} icosidodecahedron (12 pentagons and 20 triangular faces) in **1a** and a truncated $\{Mo^{V}_2\}_{30}$ icosahedron (12 pentagons and 20 hexagons with trigonal symmetry) in **2a** (b).

---

[*] Prof. Dr. A. Müller, Prof. Dr. S. Sarkar, Dipl.-Chem. S. Q. N. Shah, Dr. H. Bögge, M. Schmidtmann, Sh. Sarkar, Dipl.-Chem. P. Kögerler, Dipl.-Chem. B. Hauptfleisch
Lehrstuhl für Anorganische Chemie I der Universität
Postfach 100131, D-33501 Bielefeld (Germany)
Fax: (+49) 521-106-6003
E-mail: a.mueller@uni-bielefeld.de

Prof. Dr. A. X. Trautwein, V. Schünemann
Institut für Physik, Medizinische Universität
Ratzeburger Allee 160, D-23562 Lübeck (Germany)

[**] We thank E. Krickemeyer, C. Kuhlmann, F. Peters, and Dr. S. K. Das for their help. S. Sarkar (permanent address: Department of Chemistry, IIT Kanpur 208 016 (India)) thanks the Alexander-von-Humboldt-Stiftung for financing his stay over several months in Bielefeld.

polyhedral Fe^{III} spacers so that the overall shape of **1a** has (approximately) icosahedral symmetry and the 102 metal atoms as well as their (terminal) ligands (O or H_2O), which are directed outwards, lie in two concentric spherical shells. Each Fe polyhedron is connected to two MoO_6 octahedra of two neighboring pentagons. While the centers of the 12 pentagons, that is, the central Mo atoms of the MoO_7 bipyramids, span an icosahedron, the 30 Fe centers span one of the 13 Archimedean solids, namely, an icosidodecahedron with 20 triangles and 12 pentagons (from this point of view these "open electrophilic" pentagons are capped by 12 nucleophilic $\{(Mo)Mo_5\}$ pentagons with a rotation of 360/10 = 36°; see Figure 1, bottom).

The Raman spectrum of **1** in concentrated aqueous solution (heating necessary!) corresponds approximately to the solid-state spectrum. (Interestingly, the solutions are acidic as a result of partial deprotonation of the H_2O ligands attached to the Fe centers.) The weak yellow color is in agreement with the presence of polyoxomolybdate(VI) fragments and Fe^{III} centers (the band at about 370 nm corresponds to that of $[Fe(H_2O)_6]Cl_3$) which are either nonabsorbing or only weakly absorbing in the visible region. The magnetic measurements also indicate the presence of a strong molecular magnet with high-spin Fe^{III} centers, between which, however, there are weak antiferromagnetic exchange interactions. The value of $\chi_{mol}T = 130\ \mathrm{emu\,K\,mol^{-1}}$ measured at room temperature corresponds to 30 nearly uncorrelated centers with $S = 5/2$—this is the largest number of paramagnetic centers found in a discrete cluster until now; furthermore the ^{57}Fe Mössbauer spectrum (4.2 K, $\delta = 0.52 \pm 0.01\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.70 \pm 0.01\ \mathrm{mm\,s^{-1}}$) also confirms these results: the presence of Fe^{III} centers in a weakly distorted octahedral environment of O atoms.

The structure of the spherical cluster anion **1a** (and correspondingly of **2a**) is remarkable, since it can be built up from the 12 pentagons characteristic for spherical polyhedral objects (Figure 1, bottom). The fact that the pentagons in **2a** are linked by the larger (binuclear) spacers (they give a truncated icosahedron) leads to the notable expansion of this spherical cluster relative to **1a**, which has correspondingly 20 large openings formed by the (Mo_9O_9) rings (Figure 1). Although the icosahedron more closely resembles the spherical construction than the other Platonic solids, one can nevertheless come to a better approximation of this spherical shape by a combination of hexagons and 12 pentagons. In general, spherical polyhedral structures (pseudoicosahedra) can be optimally constructed from exactly 12 pentagons and different sets of hexagons. In agreement with Euler's polyhedral law, the numbers of vertices, edges, and faces V, E, and F amount to $V = 20\,T$, $E = 30\,T$, and $F = 10\,T + 2$ (the latter is identical to the so-called "magic number" of Table 1); the "triangulation" number T ($T = h^2 + hk + k^2$), according to Caspar and Klug, is used to classify spherical viruses which are structurally similar to **1a** and **2a**.[5, 11] $60\,T$ corresponds to the number of protein units (in the strict sense of the term quasiequivalence a $T = n$ virus should contain n conformations of the capsid protein). The relationships between T or the magic number $10\,T + 2$ on the one hand, and the number of building blocks in these spherical clusters on the other (Table 1), could tempt one to speak of Pythagorean harmony following a related quotation by Aristotle (see ref. [11]).

The geometrical relationship between the five solids with icosahedral symmetry, that is the dodecahedron, the icosahedron, the two truncated (Archimedean) solids derived from these, and the (Archimedean) icosidodecahedron (Figures 2 and 3), is particularly interesting for the following reasons: 1) The 12 pentagons of **1a** can be formally assigned to the icosahedron (namely, its corners) as well as to the dodecahedron (namely, its faces). 2) In **2a** the 30 spacers of the type $\{Mo_2^V\}$ span a (distorted) truncated icosahedron ($T = 3$),[5] while in **1a** the 30 Fe^{III} spacers span an icosidodecahedron. 3) The two latter Archimedean solids can be differentiated by the fact that the pentagons "present" are either "condensed" (like in **1a**) or "isolated" (like in **2a**).[12] Remarkably, the spherical structural motif of both Archimedean solids is generated by the pentagonal units, in the sense of the title of this article.

Experimental Section

1: To a stirred orange-red solution of $FeCl_3 \cdot 6\,H_2O$ (1.1 g, 4.1 mmol) and $CH_3COONa \cdot 3\,H_2O$ (1.1 g, 8.1 mmol) in H_2O (75 mL), the NH_4^+ salt of **2a**[5] (1.4 g, 0.05 mmol) was added. The resulting mixture was vigorously stirred in an open 100-mL Erlenmeyer flask (wide-necked) for 24 h. After acidification with HCl (1 M, 1 mL) and addition of NaCl (2.0 g), the stirred reaction mixture was heated to 90–95 °C and then filtered whilst still hot. The golden yellow filtrate was cooled to 20 °C, and yellow, rhombic crystals of **1** formed over a period of 2–3 d (compare the space group $R\bar{3}$! which corresponds to the space-group relevant habit). The crystals were collected by filtration through a glass frit, washed twice with a little iced water (to remove the adhering NaCl), and dried in air. Yield: 0.5–0.6 g (33–39% based on **2a**). Characteristic IR bands for **1** (KBr pellet): $\tilde{\nu} = 1620$ (m, $\delta(H_2O)$), 1533 (m, $\nu_{as}(COO)$), 1406 (s-m, $\nu_s(COO)$), 968 (m, $\nu(Mo{=}O)$), 854 (m), 778 (s), 623 (m), 568 (s), 438 cm^{-1} (m); characteristic Raman bands ($\lambda_e = 1064$ nm): $\tilde{\nu} = 950$ (s), 908 (w) ($\nu(Mo{=}O)$), 835 (s), 510 (m), 445 (w),

Table 1. Relationship between the so-called magic numbers $10\,T + 2$ for spherical viruses and the structural units of polyhedral spherical objects of the Keplerate type, that is, in the present case with 12 pentagons and an Archimedean solid spanned by spacers.

Magic number $10\,T + 2$	Cluster/Molecule $\{Mo_{132}\}$ (20 hexagons)	 $\{Mo_{72}Fe_{30}\}$ (20 triangles)	Triangulation number $T = [h, k] = h^2 + hk + k^2$
12	12 central $\{(Mo)Mo_5\}$ pentagons (icosahedral structure)	12 central $\{(Mo)Mo_5\}$ pentagons (icosahedral structure)	1 [1, 0]
32	32 faces of the $\{Mo_2^V\}_{30}$–(spacer) polyhedron (truncated icosahedron)	32 faces of the $\{Fe_{30}\}$–(spacer) polyhedron (icosidodecahedron)	3 [1, 1]
42	42 (12 + 30) building blocks[a] (and charge of the cluster)	42 (12 + 30) building blocks[a]	4 [2, 0]
72	72 Mo^{VI} centers (and negative charge of the 12 pentagons[b])	72 Mo^{VI} centers	7 [2, 1]
132	132 Mo atoms	–	13 [3, 1]

[a] 12 $\{(Mo)Mo_5\}$ units + 30 $\{Mo_2^V\}$ or 30 {Fe} spacers. [b] $\{(Mo^{VI})Mo_5^{VI}O_{21}\}^{6-}$.

1433-7851/99/3821-3239 $ 17.50+.50/0

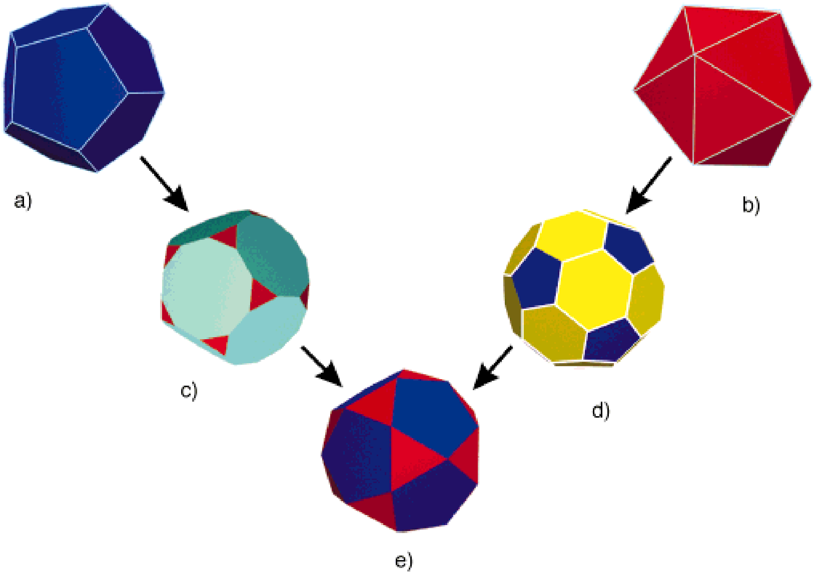

Figure 2. Relationships between solids with icosahedral symmetry: the dodecahedron (a) and icosahedron (b), the two corresponding truncated Archimedean solids (in c and d; as the $\{\mathrm{Mo}_2^{\mathrm{V}}\}_{30}$ fragment in the case of **2a**) as well as the Archimedean icosidodecahedron (e; corresponding to the $\{\mathrm{Fe}_{30}\}$ fragment in the case of **1a**).[13] It is interesting that the solids in (d) and (e) are distinguishable by a different degree of truncation and the related size. This corresponds to the relative sizes of **1a** and **2a**.

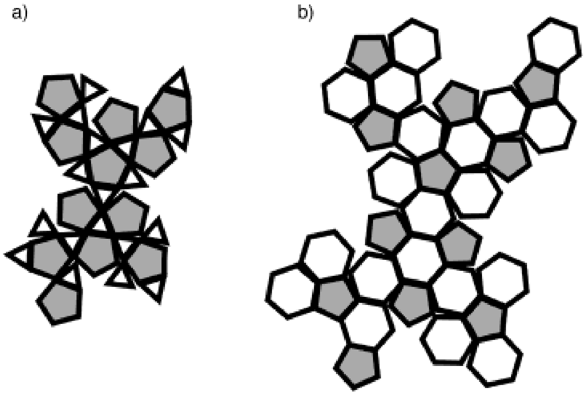

Figure 3. The nets ("Netzabwicklung") a) of the icosidodecahedron and b) of the "Ikosaedron truncum" (see ref. [1g]) to clarify the relationship between the two Archimedean solids of Figure 2d and 2e, which are spanned by the spacers.

370 (m), 238 cm^{-1} (m-w); UV/Vis (measured against cellulose as white-standard): $\lambda \approx 370$ nm. The IR and UV/Vis measurements of **2** were carried out under the same conditions and not under those given erroneously in ref. [5].

Received: March 5, 1999 [Z13123IE]
German version: *Angew. Chem.* **1999**, *111*, 3435–3439

Keywords: cage compounds · cluster compounds · polyoxometalates · supramolecular chemistry · topology

---

[1] Pentagons are of particular interest in numerous scientific areas: for the mathematician (to construct one of the five regular solids given in Euclid's famous work "Elements (Book XIII)", to which Dürer also refers), for the architect and the art theorist or felix aestheticus (in the sense of Fuller's geodesic domes and with respect to the "Golden Section"), for the solid-state physicist (with regard to the fascinating quasicrystals), for the virologist (because of the structure of spherical viruses), for the classical morphologist amongst the biologists (in particular because of the numerous plant organisms (blossoms) with fivefold symmetry), more recently for the cosmologist (because of a planetary nebula with a fullerene structure), and naturally for the chemist, who can use them to design harmonic molecular constructions. Pythagoras even associated physical well-being with the five-pointed star, which was the symbolic sign of his school, and he wanted—obviously with not very altruistic intentions—to keep secret the existence of the dodecahedron derived from it. a) A. L. Mackay, *Crystals and Fivefold Symmetry* in *Quasicrystals, Networks, and Molecules of Fivefold Symmetry* (Ed.: I. Hargittai), VCH, Weinheim, **1990**, pp. 1–18; b) H. W. Kroto, K. Prassides, A. J. Stace, R. Taylor, D. R. M. Walton in *Buckminsterfullerenes* (Eds.: W. E. Billups, M. A. Ciufolini), VCH, Weinheim, **1993**, pp. 21–57; c) K. Miyazaki, *Polyeder und Kosmos: Spuren einer mehrdimensionalen Welt*, Vieweg, Braunschweig, **1987**, pp. 69–75 (chap.: Fünfecke und Fünfsterne); d) R. Penrose in *Hermann Weyl, 1885–1985: Centenary Lectures* (Ed.: K. Chandrasekharan), Springer, Berlin, **1986**, pp. 23–52; e) H. S. M. Coxeter, *Regular Polytopes*, Macmillan, New York, **1963** (in particular the various chapters with "historical remarks"); f) H. Weyl, *Symmetry*, Princeton University Press, Princeton, NJ, **1952**, pp. 41–80 (chap.: Translatory, rotational, and related symmetries); g) E. Schröder, *Dürer, Kunst und Geometrie*: *Dürers künstlerisches Schaffen aus der Sicht seiner "Underweysung"*, Birkhäuser, Basel, **1980**; h) L. Liljas, *Prog. Biophys. Mol. Biol.* **1986**, *48*, 1–36; i) V. I. Arnol'd, *Huygens and Barrow, Newton and Hooke: Pioneers in mathematical analysis and catastrophe theory from evolvents to quasicrystals*, Birkhäuser, Basel, **1990**, pp. 62–66 (chap. 3, paragraph 16: The icosahedron and quasicrystals); j) S. Hildebrandt, A. Tromba, *Kugel, Kreis und Seifenblasen: Optimale Formen in Geometrie und Natur*, Birkhäuser, Basel, **1996**; k) A. Dress, D. Huson, A. Müller in *Muster des Lebendingen: Faszination ihrer Entstehung und Simulation* (Ed.: A. Deutsch), Vieweg, Wiesbaden, **1994**, pp. 183–202; l) A. Stückelberger, *Einführung in die antiken Naturwissenschaften*, Wiss. Buchgesellschaft, Darmstadt, **1988**, p. 12.

[2] Mackay states in the chapter: "What Is Special about Fivefold Symmetry?":[1a] "Five is, in a sense, the first "interesting" integer in that given five points in space all cannot be identically related to all the others […]". This has then the well-known consequences for the generation of structures in three-dimensional space or in a plane (cf. the tiling problem[1a]). Even Archimedes had recognized the importance of pentagonal patterns for the construction of spherical structures (cf. book 5 of the "Collectiones" of Pappos of Alexandria (around 320 AD), the last famous mathematician of that epoch).

[3] For the topologists under the mathematicians it is of particular interest that the Keplerates discussed here are based on the 12 pentagons essential for the construction of optimal spherical polyhedral structures; pentagons are present (in the "magic number" of 12), along with a variable but defined number of hexagons in all such formations, even in the largest known spherical polyhedral objects such as the Fuller domes. A Keplerate should define a spherical species—with part of its atoms located at the sphere spanning a Platonic solid—for example in which the 12 centers of the pentagonal units forming an icosahedron lie on a spherical shell, whereby the spacers span a relevant Archimedean solid (that is, with appropriate symmetry; see Table 1). In the first reported Keplerate there are 132 molybdenum atoms located on a spherical shell[5] and in the present Keplerate 102 metal atoms, and in both cases 12 of them span an icosahedron in an arrangement corresponding to Kepler's early speculative model of the cosmos.

[4] With regard to the synthesis of **1**, it is important to note that the $\mathrm{Fe^{III}}$ spacers used here, in addition to those of the $\mathrm{VO^{2+}}$ type, are particularly suitable for the linkage of nucleophilic molybdate fragments (see: A. Müller, W. Plass, E. Krickemeyer, S. Dillinger, H. Bögge, A. Armatage, A. Proust, C. Beugholt, U. Bergmann, *Angew. Chem.* **1994**, *106*, 897–899; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 849–851; A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Peters, M. Schmidtmann, P. Kögerler, M. J. Koop, *Chem. Eur. J.* **1998**, *4*, 1000–1006; A. Müller, W. Plass, E. Krickemeyer, R. Sessoli, D. Gatteschi, J. Meyer, H. Bögge, M. Kröckel, A. X. Trautwein, *Inorg. Chem. Acta* **1998**, *271*, 9–12).

[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: $0.25 \times 0.25 \times 0.15$ 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.

---

[*] 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