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"Molecular Symmetry Breakers" Generating Metal-Oxide-Based Nanoobject Fragments as Synthons for Complex Structures: [{Mo$_{128}$Eu$_4$O$_{388}$H$_{10}$(H$_2$O)$_{81}$}$_2$]$^{20-}$, a Giant-Cluster Dimer**

Leroy Cronin, Christian Beugholt, Erich Krickemeyer, Mark Schmidtmann, Hartmut Bögge, Paul Kögerler, T. Kim K. Luong, and Achim Müller*

Dedicated to Professor Karl Wieghardt on the occasion of his 60th birthday

The synthesis and manipulation of a huge variety of nanoscaled species of similar chemical nature under one-pot reaction conditions requires access to a potential "dynamic library" of appropriate building blocks.[1a] For instance, by exploiting a detailed knowledge of polyoxometalate chemistry, a variety of discrete clusters (see ref. [1b – g]) and related extended structures[2] can be formed by the linking of well-defined metal – oxygen building blocks. These types of compounds have been shown to exhibit unusual topological as well as electronic properties and, furthermore, are interesting for materials science.[3–5] A couple of years ago, we reported wheel-shaped mixed-valence molybdenum clusters of the type

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{Mo$_{154}$}, {Mo$_{176}$},[1b, 6, 7] and {Mo$_{248}$};[1f] of these, the first two parent species—exhibiting nanometer-sized cavities and therefore presenting fascinating perspectives for a new type of host – guest chemistry—can now be obtained in high yields in facile syntheses.[8] Herein, we describe for the first time a dimer of two giant clusters, that is, of structurally well-defined covalently linked nanoobjects with a rather high degree of complexity. The dimer contains two elliptical molybdenum oxide based units, linked together by two Eu-O-Mo bonds, each unit incorporates 128 Mo$^{VI/V}$ and 4 Eu^{III} centers and includes large fragments of the above-mentioned parent clusters. The interpretation would be that these dimers are formed by Eu^{III} centers acting as symmetry breakers which prevent the corresponding highly symmetrical parent-ring closure.[1b, 6] *Of general importance is that in systems showing growth, potential (abundant) agents, such as Eu^{III} centers, can act as "symmetry breakers" which results in the generation of structural complexity.* In any case, it is important to realize that large nanoobject fragments can, in principle, be used as synthons. The ability to connect or assemble clusters in a predefined manner may allow the design of nanoscopic devices using the "bottom up" method (that is, generating large objects from small units).

While the "classical" reduction of an acidified aqueous molybdate solution leads to the blue, wheel-shaped tetra- and hexadecameric parent-cluster anions mentioned above,[6] the generation of smaller species requires the presence of electrophiles, such as Pr^{III} ions which increase the curvature by replacing the larger electrophilic {Mo$_2$}$^{2+}$-type building units (see below). In the presence of smaller Eu^{III} ions, even ring closure to the parent clusters does not take place, which allows the isolation of compound **1** containing a novel cluster collective. Compound **1** was characterized by single-crystal X-ray structure analysis[9] (including bond valence sum (BVS) calculation to aid in the determination of the (formal) number of Mo^V centers and protonation sites),[10] elemental analyses ((K), Eu, Mo; see details in ref. [12]), thermogravimetric analysis, redox titration (to aid in the determination of the (formal) number of Mo^V centers), IR, and EXAFS spectroscopy (Eu-L$_{III}$ edge,[11] with the option to distinguish in principle between the different Eu centers in the lattice and cluster sites) as well as magnetic susceptibility measurements with a SQUID magnetometer.

Eu$_6$X$_2$**1a** · ca. 600 H$_2$O   **1**[12]

[{Mo$_{128}^{VI/V}$Eu$_4$O$_{388}$H$_{10}$(H$_2$O)$_{81}$}$_2$]$^{20-}$ **1a**[12]
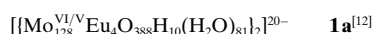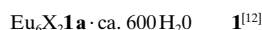
The crystal structure of **1** shows the dimeric unit **1a**, which comprises two linked nanosized clusters with 1202 non-hydrogen (including 264 metal) positions, of rather high structural complexity—regarding the versatility of different building blocks and protonation types—packed in a configuration that gives rise to channels incorporating Eu^{III} ions on the inner side of the cavities (Figure 1; see also ref. [12]). Compound **1a** can be geometrically related to fragments of the ring-shaped {Mo$_{154}$} ≡ [Mo$_{154}$O$_{462}$H$_{14}$(H$_2$O)$_{70}$]$^{14-}$ (**2a**) parent-cluster archetype. The two cluster units of **1a** are elliptical with an outer and inner ring diameter of about 38
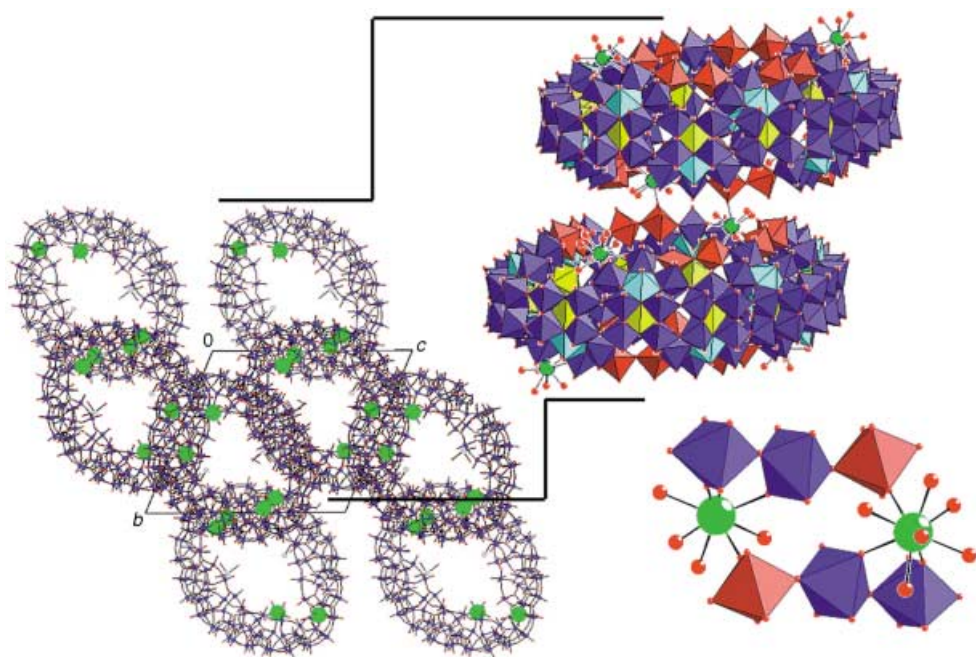
Figure 1. Left: a packing diagram of the cluster units of **1a** in ball-and-stick representation looking down the "cavities" (Eu[III] ions in green). Right: a representation of **1a** with the molybdenum oxide based units displayed as polyhedra ({Mo$_1$} yellow; {Mo$_2$} red; {Mo$_8$} blue with central pentagonal units in cyan; Eu[III] coordination spheres in ball-and-stick representation). Bottom right: an expanded view of the Mo-O-Eu groups linking the two cluster rings.

and 20 Å, respectively, at their most elongated points, and with an outer and inner ring diameter of approximately 30 and 12 Å, respectively, at their most compressed points (Figure 1). There is only one type of Mo-O-Eu bond in the linking region as the midpoint between the two Mo-O-Eu links is an inversion center which generates the dimeric unit (Mo−O 1.71 Å; Eu−O 2.43 Å).

The giant ring-shaped "parent" clusters (see above) obtained from molybdenum blue solutions are based on the three different building blocks {Mo$_1$}, {Mo$_2$}, and {Mo$_8$}.[1b, 6] These units are important for the related chemical versatility[1b, 6] in that the clusters can be considered as a "nanostructured-landscape" allowing characteristic reactions at different well-defined positions.[6] For instance some of the {Mo$_2$}$^{2+}$ ≡ {Mo$_2^{VI}$O$_5$(H$_2$O)$_2$}$^{2+}$ groups can be substituted by other electrophiles, such as Pr[III] ions. If the related electrophile is (significantly) smaller in size than the {Mo$_2$}$^{2+}$ group, an increase of the curvature in the substitution region is observed. This effect can lead—as in the Pr[III] case—to the formation of a smaller ring that exhibits an elliptical geometry[15] but which still shows practically the same building units as the parent tetra- and hexadecameric rings. The remarkable feature in **1** is that this is no longer the case in presence of Eu[III] ions as, besides larger basic fragments of **1a** corresponding to those of the parent ring, new structural features occur. This situation could be explained in that the presence of Eu[III] ions, which have a smaller ionic radius than Pr[III] ions, preventing ring closure to the parent ring type as the related dramatic increase of the curvature destabilizes the system.

The two ellipsoidal cluster entities of **1a** can be approximately described by the building-block scheme used for the

formation of the {Mo$_{154}$}- and {Mo$_{176}$}-type species, which comprise not only the building blocks {Mo$_1$}, {Mo$_2$}, and {Mo$_8$}, but also the additional "new" units of the {Mo$_2^*$}, {Mo$_7$}, and {Mo$_9$} type ({Mo$_2^*$} ≡ {Mo$_2^{VI/V}$O$_7$(H$_2$O)}$^{3-}$): the fragments are (formally) cut, as shown in Figure 2, from the {Mo$_{154}$}-type giant wheel at four positions. The "cutting" process takes place between those polyhedra showing the least number of bonds. The large fragments obtained (Figure 2) have the composition [{Mo$_1$}$_6${Mo$_2$}$_4${Mo$_8$}$_2${Mo$_7$}$_2$-{Mo$_9$}$_2$], that is, they include the two "new" {Mo$_7$} and {Mo$_9$} units which are formally generated by "cutting" asymmetrically two neighboring {Mo$_8$} units at the above-mentioned positions to produce the two major parts of the new ellipsoidal ring. The complete ellipsoidal ring unit is formed when the two fragments are combined with two new {Mo$_2^*$} units and four Eu[III] ions (Figure 2).

An examination of the equatorial plane of one ring unit of **1a** reveals the same basic type of construction principle as described for the {Mo$_{154}$}-type ring-shaped system **2a**, that is, the abundance of the typical {Mo$_1$} units which are part of the {Mo$_5$O$_6$} double-cubane-type compartments of the parent rings.[1b, 6] In the present case, ten of the twelve abundant compartments possess one μ_3-OH group,[16] which is in contrast to **2a** in which they show a symmetrical distribution of the respective O-BVS values caused by a related disorder of the H atoms.[16] The BVS of the Mo positions of the {Mo$_5$O$_6$}-type double-cubanes show, in comparison to those in the parent cluster **2a** (with two delocalized Mo(4d) electrons per compartment), higher values for just two of those four Mo atoms (see above) which are positioned next to the two {Mo$_2^*$} groups. As the latter show the correspondingly related lower Mo-BVS values, we have a situation that in these two special cases the two Mo(4d) electrons are delocalized over the two {Mo$_2^*$}{Mo$_5$O$_6$} segments. The overall building-block scheme for **1a** can finally be presented as [{Mo$_1$}$_{12}${Mo$_2$}$_8${Mo$_8$}$_4${Mo$_7$}$_4${Mo$_9$}$_4${Mo$_2^*$}$_2$Eu$_4$]$^{20-}$.

This "dimer" or "cluster collective" can be considered as the most complex discrete inorganic species structurally characterized to date while the results open new perspectives for nanochemistry. It seems possible to control the linking of certain types of polyoxometalate fragments, as in the present case in which the larger building units in **1a** can be considered as nanosynthons. The interesting related aspect is—formally speaking—that "molecular scissors" can be used to generate larger linkable nanoobject fragments. But the real interpretation is that the Eu[III] centers subsequent to their coordination at the fragments prevent, as "symmetry breakers", ring
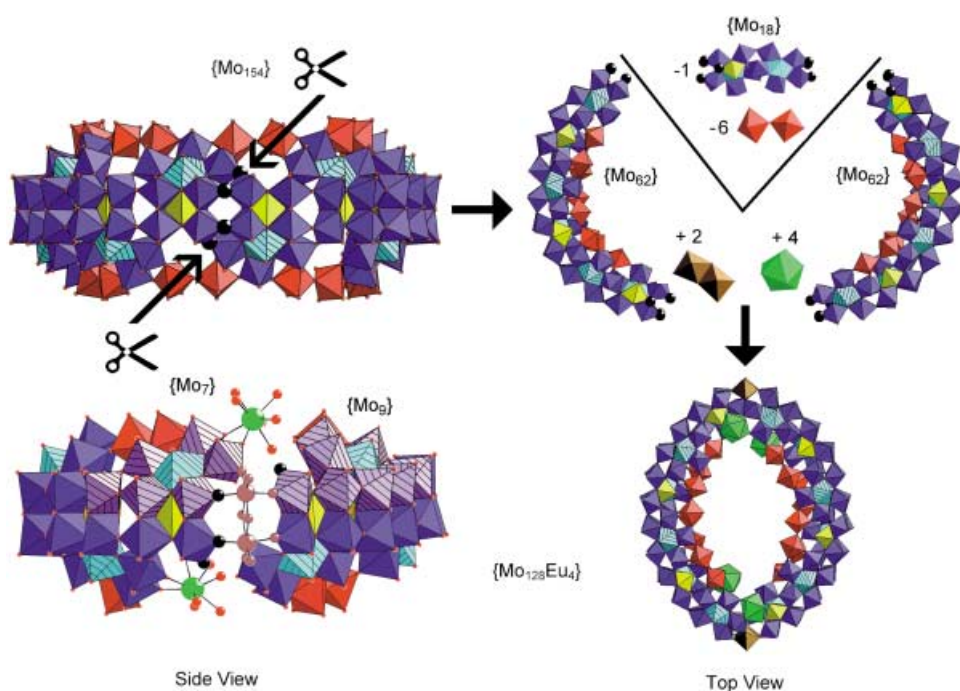
Figure 2. Demonstration of how an {Mo$_{128}$Eu$_4$} ring of **1a** can formally be constructed from a parent {Mo$_{154}$}-type cluster by a "cutting" process giving the two large important fragments. Top left: A side view of the {Mo$_{154}$} ring, the cutting positions are marked as large black spheres; top right: those units which have to be removed from the {Mo$_{154}$} ring and those which have to be added to the resulting two large fragments (left and right) to generate the {Mo$_{128}$Eu$_4$} cluster; bottom: the {Mo$_{128}$Eu$_4$} cluster from a side and top view (color code as in Figure 1) with the new {Mo$_2^*$} units in brown which are shown in the side view together with the EuO$_9$ polyhedra in ball-and-stick representation; the MoO$_6$ octahedra of a selected {Mo$_7$} and a {Mo$_9$} group, respectively, as hatched violet polyhedra.

closure which would lead to the parent-cluster type. They cause even further symmetry breaking, thereby avoiding the direct action of translational symmetry operation after ring closure. Furthermore, by controlling the structure of a nano-object such as **1a**, it may be possible to control linking/assembly which may not only result in extended structures but also in well-defined collectives of nanoclusters, the formation of which is as yet an unsolved problem in chemistry. These types of nanocluster assemblies/collectives might be of importance for the development of electronic devices (cf. ref. [17]). Interestingly, it could also be demonstrated that it is possible to position open-shell metal centers with, for example, different electronic and magnetic characteristics, on the well-defined sites of the nanoobjects.

The present situation again supports our previous statement and arguments: Molybdenum oxide based building blocks in acidic solutions under reducing conditions show a type of flexibility allowing—as components of a dynamic library—a linking versatility with the option of generating an overwhelming variety of structures which seems to be a unique situation in inorganic chemistry (for further arguments see ref. [18]).

Experimental Section

1: A solution of EuCl$_3 \cdot$6H$_2$O (6.0 g, 16.4 mmol) in H$_2$O (500 mL) was quickly added under stirring to an aqueous solution of K$_2$MoO$_4$ (5.9 g, 24.8 mmol) in H$_2$O (500 mL). After stirring for 30 min the practically colorless precipitate was collected by filtration, washed with ice-cold H$_2$O, and dried at 120°C for 5 h (yield: 6.3 g; IR (KBr; 1700–500 cm^{-1}): $\tilde{\nu}$ = 1630

(m), 935 (m), 858 (s), 758 (s), 700 cm^{-1} (m).[19]). To the solution of this precipitate (1.5 g), in a mixture of H$_2$O (15 mL) and 1M HCl (12.5 mL), an aqueous solution (1.5 mL) of [N$_2$H$_6$]Cl$_2$ (10 g L^{-1}) was added. The solution was heated (without stirring) in a 100-mL Erlenmeyer flask (wide necked; covered with a watch glass) in a preheated oil bath at 60–65°C for 45 min. The resulting deep-blue solution was then taken from the oil bath, cooled to room temperature, and kept in a closed flask for 16 h. After a small amount of a colorless precipitation was removed by filtration the filtrate was kept in a closed 100-mL Erlenmeyer flask (closed with a rubber stopper) for two weeks. The deep-blue (longish) platelike crystals were collected by filtration, washed with ice-cold H$_2$O, and dried under inert atmosphere over CaCl$_2$, yield: 0.48 g (39.4% based on Mo; for a detailed discussion of the analytical problem see ref. [12]). Characteristic IR bands (KBr; 1700–500 cm^{-1}): $\tilde{\nu}$ = 1618 (m; δ (H$_2$O)), 990 (sh), 968 (m; $\tilde{\nu}$ (Mo=O)), 905 (m), 830 (m), 740 (m-s), 630 (s), 561 cm^{-1} (s).

The (corresponding) compound could be obtained, but not in pure form, using Na$_2$MoO$_4 \cdot$2H$_2$O as starting material.[20]

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[8] It required more than 200 years and many generations of chemists to obtain these compounds from molybdenum blue solutions, which contain the parent-ring clusters, in a facile synthesis (see ref. [1b, 6]).

[9] Crystal data for **1**: H$_{1546}$Eu$_{14}$Mo$_{256}$O$_{1538}$, M_r = 52854.45, triclinic, space group $P\bar{1}$, a = 31.935(2), b = 32.869(2), c = 37.400(2) Å, α = 111.292(1),

$\beta = 97.542(1)$, $\gamma = 97.410(1)°$, $V = 35592(3)$ Å^3, $Z = 1$, $\rho = 2.466$ g cm^{-3}, $\mu = 2.907$ mm^{-1}, $F(000) = 25484$, crystal size $= 0.35 \times 0.20 \times 0.05$ mm^3. Crystals of **1** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three-circle goniometer with 1 K CCD detector, Mo$_{K\alpha}$ radiation, graphite monochromator; sphere data collection in ω at 0.3° scan width in four runs with 606, 500, 606, and 500 frames ($\phi = 0$, 88, 180 and 268°) at a detector distance of 5.00 cm). A total of 371523 reflections ($0.66 < \Theta < 27.05°$) were collected of which 153584 reflections were unique ($R_{int} = 0.0511$). An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined using SHELXL-93 to $R = 0.0559$ for 96134 reflections with $I > 2\sigma(I)$, $R = 0.1066$ for all reflections; max./min. residual electron density 3.680 and -2.844 e Å^{-3}. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1993/97; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001.) Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411984.

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[11] EXAFS measurements were performed at the beamline A1 at HASYLAB (Hamburg) on samples ground together with suprapure polyethylene and subsequently pressed into pellets with a thickness of 300 μm. Spectra were obtained in the transmission mode at the Eu-L$_{III}$ edge covering the range from 6.75 – 8.00 keV. The magnitude of the Fourier transform of the EXAFS after background and phase correction shows a distinct and symmetric maximum at 243 pm which is clearly a result of almost only (!) one kind of oxygen coordination to the Eu absorber. A second coordination shell at about 350 pm is assigned to Eu $\cdots$ Mo separations.

[12] Although the total number of molybdenum centers is certain, the (formal) number of Mo^V centers has a slight uncertainty, though the given number of 24 is the most reasonable one according to the comparison with previous related structures, that is, parts of the well known {Mo$_{154}$} and {Mo$_{176}$} clusters with respect to the related BVS values of comparable protonation sites and Mo$_5$O$_6$-type building blocks.[1b, 6] This assignment results in a charge of -20 per "dimer" **1a** by referring to the number of abundant protons and Mo^V centers (note: the related electron spins are paired here as in the reduced Keggin ions[13]). Despite the nonmagnetic $^7F_0$ ground state, the Eu^{III}-ions yield a temperature-dependent paramagnetism (TIP) since the weak spin-orbit splitting of the ^7F term ($\lambda \approx 300$ cm^{-1}) allows excited ^7F_J states ($J = 1, 2, \cdots$) to be thermally populated.[14] As the relevant states are not significantly perturbed by ligand-field effects, the magnetism of a system containing N Eu^{III} positions corresponds very well to N times the free Eu^{III} ion contribution (typical $\chi_{mol}T$ value for an Eu^{III} ion at room temperature: 1.53 emu K mol^{-1}[14b]). The observed paramagnetism of **1** ($\chi_{mol}T = 23.2$ emu K mol^{-1} at 290 K, corrected for diamagnetism and an estimated TIP value of the polyoxomolybdate ring) corresponds to 15($\pm$1) individual Eu^{III} centers per formula unit which is in agreement with the Eu analysis (calcd (%) for **1** with X = H: Eu 4.03; found: Eu 3.9). While eight of these are definitely constituents of the {Mo$_{256}$}-type cluster dimer, the remaining six Eu^{III} cations per formula unit are strongly disordered in the crystal lattice and cannot be localized exactly. (The observed temperature dependence of $\chi_{mol}T$ for **1** also rules out the presence of Eu^{II} centers.) Thus, the resulting problem is to explain the charge difference between -20 (see above) and -18 corresponding to the presence of six Eu^{III} lattice cations. This might be a result of the (corresponding) presence of two alkali cations (found (%) ca. 0.07) or two H$^+$ ions which is a more reasonable explanation (see formula). Based on the extremely small values of the potassium (and sodium) analyses this problem cannot be solved without doubt. Location of the water ligands was by comparison with previous structures while the related oxygen BVS indicate the presence of two "new type" water ligands per ring of **1a** on the building blocks adjacent to the new {Mo$_2^*$} groups (see, Figure 2). The given crystal-water content corresponds to the maximum number with respect to the unit-cell volume according to our usual procedure (note: the rapid release of crystal water!).

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[16] Investigating the O-BVS values of the equatorial μ_3-O atoms it turns out that, firstly, (exactly only) one atom per compartment is protonated and, secondly, moving from one equatorial bridging ligand (H$_2$O1) of the ("new") {Mo$_2^*$} unit to the corresponding other {Mo$_2^*$} type bridging (H$_2$O2) ligand and passing six compartments of half a cluster ring, the sequence of protonated (p) and unprotonated (u) equatorial μ_3-O atoms is: H$_2$O1 u-p u-p u-p u-p u-p u-u H$_2$O2. The alternating occupation of these positions is caused by the repulsive forces between the H atoms of adjacent compartments. That the above sequence is favored over the other possible sequence H$_2$O1 u-u p-u p-u p-u p-u p-u H$_2$O2 or to a 50:50 disordered situation as in the parent cluster type is caused by two Eu^{III} ions positioned close to the "u-u" compartment. Our present results support our earlier conclusion (correct formula): one μ_3-OH group per compartment.[1b, 6]

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[19] The IR spectrum is practically identical to that of the related Pr^{III} molybdate educt used in ref. [15] and to that of a compound formulated there as Eu$_2$O$_3 \cdot$ 7 MoO$_3 \cdot n$ H$_2$O ($n = 6$ and 8) and obtained according to a preparation method given in the literature (*Gmelin Handbook of Inorganic Chemistry, Mo Suppl., Vol. B4*, Springer, Berlin, **1985**, p. 262 and *Chem. Abstr.* **1973**, *78*, 10950).

[20] See C. Beugholt, *Dissertation*, Fakultät für Chemie, Universität Bielefeld, **2001**, with a preliminary formula.

Mo^V/Pyrophosphate Polyoxometalate: An Inorganic Cryptate

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Polyoxometalate chemistry continues to be a subject of great interest, since the wide and fascinating variety of structures and properties of these objects gives rise to numerous applications.[1] Polyoxoanions containing phosphato groups constitute the largest class of heteropolyanions, with structures ranging from molecular complexes to extended frameworks.[2] In contrast, very few polyoxometalate-containing polyphosphato groups have been structurally characterized. In 1994, Kortz and Pope reported the first X-ray structure of a polyoxomolybdate(VI) containing the pyrophosphato (P$_2$O$_7$)$^{4-}$ ligand.[3] Since then, only two other structures

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