“Molecular Symmetry Breakers” Generating Metal-Oxide-Based Nanoobject Fragments as Synthons for Complex Structures: \([\text{[Mo}_128\text{Eu}_4\text{O}_{388}\text{H}_{10}(\text{H}_2\text{O})_{81}]}_{20}\), a Giant-Cluster Dimer**

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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 \([\text{Mo}_{128}]\), \([\text{Mo}_{75}]\)[6, 7] and \([\text{Mo}_{28}]\)[1g] 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.[9] 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 MoVI and 4 EuIII centers and includes large fragments of the above-mentioned parent clusters. The interpretation would be that these dimers are formed by EuIII centers acting as symmetry breakers which prevent the corresponding highly symmetrical parent-ring closure.[1h, 6] Of general importance is that in systems showing growth, potential (abundant) agents, such as EuIII 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,[5] the generation of smaller species requires the presence of electrophiles, such as PrIII ions which increase the curvature by replacing the larger electrophilic \([\text{Mo}_3]\)-type building units (see below). In the presence of smaller EuIII ions, even ring closure to the parent clusters does not take place, which allows the isolation of compound I containing a novel cluster collective. Compound I 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 MoV 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 MoV centers, IR, and EXAFS spectroscopy (Eu-LIII 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,X,1a·ca. 600H₂O 1a[12]

\([\text{Mo}_{128}\text{Eu}_{4}\text{O}_{388}\text{H}_{10}(\text{H}_2\text{O})_{81}}]_{20}\)

The crystal structure of I 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 EuIII 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 \([\text{Mo}_{128}]\)≡\([\text{Mo}_{128}\text{O}_{36}\text{H}_{10}(\text{H}_2\text{O})_{70}}]_{20}\) (2a) parent-cluster archetype. The two cluster units of 1a are elliptical with an outer and inner ring diameter of about 38
three different building blocks \{Mo_1\}, \{Mo_2\}, and \{Mo_8\}.\[1b, 6\]  

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+} \equiv \{Mo_2^{2+}O_2(H_2O)_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_{135}\}- and \{Mo_{199}\}-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_7\}, \{Mo_9\}, and \{Mo_8\} type ((Mo_7^{IV}) \equiv \{Mo_7^{IV}O_2(H_2O)\}^{2+}):

- the fragments are (formally) cut, as shown in Figure 2, from the \{Mo_{135}\}-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_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_7\}

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_{135}\}-type ring-shaped system 2a, that is, the abundance of the typical \{Mo_1\} units which are part of the \{Mo_5O_6\} double-cubane-type compartments of the parent rings.\[1b, 6\] In the present case, ten of the twelve abundant compartments possess one \(\mu_3\)-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_5O_6\}-type double-cubane shows, 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_8\} 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_7\}\{Mo_5O_6\} segments. The overall building-block scheme for 1a can finally be presented as [[\{Mo_1\}]_6[\{Mo_2\}]_4[\{Mo_8\}]_2[\{Mo_9\}]_2[\{Mo_9\}]_2]_{Eu}^{III}.\[20\]

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 nanobject 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 \([\text{Mo}_{128}\text{Eu}_4]\) ring of \(\text{I}\) a can formally be constructed from a parent \([\text{Mo}_{75}]\)-type cluster by a “cutting” process giving the two large important fragments. Top left: A side view of the \([\text{Mo}_{128}]\) ring, the cutting positions are marked as large black spheres; top right: those units which have to be removed from the \([\text{Mo}_{128}]\) ring and those which have to be added to the resulting two large fragments (left and right) to generate the \([\text{Mo}_{128}\text{Eu}_4]\) cluster; bottom: the \([\text{Mo}_{128}\text{Eu}_4]\) cluster from a side and top view (color code as in Figure 1) with the new \([\text{Mo}_{*2}]\) units in brown which are shown in the side view together with the \(\text{EuO}_9\) polyhedron in ball-and-stick representation; the \(\text{MoO}_6\) octahedra of a selected \([\text{Mo}_7]\) and a \([\text{Mo}_9]\) group, respectively, as hatched violet polyhedra.

**Experimental Section**

1: A solution of \(\text{EuCl}_3 \cdot 6\text{H}_2\text{O} (6.0 \text{ g}, 16.4 \text{ mmol})\) in \(\text{H}_2\text{O} (500 \text{ mL})\) was quickly added under stirring to an aqueous solution of \(\text{K}_2\text{MoO}_4 (5.9 \text{ g}, 24.8 \text{ mmol})\) in \(\text{H}_2\text{O} (500 \text{ mL})\). After stirring for 30 min the practically colorless precipitate was collected by filtration, washed with ice-cold \(\text{H}_2\text{O}\), and dried at 120 °C for 5 h (yield: 6.3 g; IR (KBr; 1700–500 cm\(^{-1}\)): \(\nu = 1630\) (m), 935 (m), 858 (s), 758 (s), 700 cm\(^{-1}\) (m)). To the solution of this precipitate (1.5 g), in a mixture of \(\text{H}_2\text{O} (15 \text{ mL})\) and 1M \(\text{HCl} (12.5 \text{ mL})\), an aqueous solution (1.5 mL) of \([\text{N}_2\text{H}_6]\)\(\text{Cl}_2 (10 \text{ g L}^{-1})\) 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) plate-like crystals were collected by filtration, washed with ice-cold \(\text{H}_2\text{O}\), and dried at 120/56°C for 5 h (yield: 6.3 g; IR (KBr; 1700–500 cm\(^{-1}\)): \(\nu = 1618\) (m; \(\delta (\text{H}_2\text{O})), \ 990 \text{ (sh)}, 968 \text{ (m; } \delta (\text{Mo} = \text{O})), \ 905 \text{ (m)}, \ 830 \text{ (m)}, \ 740 \text{ (m-s), 630 (s), 561 cm}^{-1}\) (s).

The (corresponding) compound could be obtained, but not in pure form, using \(\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}\) 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 I: \(\text{H}_4\text{Eu}_4\text{MoO}_{256}\text{O}_{1538}\), \(M = 52854.45\), triclinic, space group \(P\bar{1}, a = 31.935(2), b = 32.869(2), c = 37.400(2) \AA, \alpha = 111.292(1), \beta = 110.325(1), \gamma = 99.30(1)\).
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I. D. Brown in Although the total number of molybdenum centers is certain, the unique (3.680 and \( R = 0.66 \)) and detector distance of 5.00 cm). A total of 371523 reflections (see above) and equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Egggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411984.


[11] EXAFS measurements were performed at the beamline A1 at HASYLAB (Hamburg) on samples ground together with suprapure polycrystalline and subsequently pressed into pellets with a thickness of 300 μm. Spectra were obtained in the transmission mode at the Eu-I\(\beta\) edge covering the range from 6.75–8.00 keV. The magnitude of the Fourier transform is significantly perturbed by ligand-field effects, the remaining six EuIII

[12] Although the total number of molybdenum centers is certain, the (formal) number of Mo\(\text{VI}\) centers has a slight uncertainty, though the comparison with previous related structures, that is, parts of the well(C118)/C105 ) containing the pyrophosphato groups have been structurally character-

(see formula). Based on the extremely small values of the potassium (and sodium) analyses this problem cannot be ruled out. The resulting problem is to explain the charge difference between


[16] Investigating the O-BVS values of the equatorial \( \mu_2 \)-O atoms it turns out that, firstly, (exactly only) one atom per compartment is protonated and, secondly, moving from one equatorial bridging ligand (H\(\text{O}_2\)) of the (new) [Mo\(\text{V}\)] unit to the corresponding other [Mo\(\text{V}\)] type bridging (H\(\text{O}_2\)) ligand and passing six compartments of half a cluster ring, the sequence of protonated (p) and unprotonated (u) equatorial \( \mu_2 \)-O atoms is: H\(\text{O}_2\)-p-u-p-u-p-u-p-H\(\text{O}_2\). 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\(\text{O}_2\)-p-u-p-u-p-u-p-H\(\text{O}_2\) or to a 50:50 distorted situation as in the parent cluster type is caused by two Eu\(\text{III}\) ions positioned close to the “u”-compartment. Our present results support our earlier conclusion (correct formula): one \( \mu_2 \)-OH group per compartment.[10, 11]


[19] The IR spectrum is practically identical to that of the related Pu\(\text{IV}\) molybdate educt used in ref.[15] and to that of a compound formulated there as Eu\(\text{3}^{\text{III}}\)-7MoO\(\text{3}\)-nH\(\text{2}^{\text{O}}\) (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).


Mo\(\text{V}\)/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.[31] Polyoxoanions containing phospho-

to groups constitute the largest class of heteropolyanions, with structures ranging from molecular complexes to extended frameworks.[2] In contrast, very few polyoxometalate-containing polyphosphate groups have been structurally characterized. In 1994, Kortz and Pope reported the first X-ray structure of a polyoxomolybdate(\(\text{VI}\)) containing the pyrophospho-

(P\(\text{O}_4\))\(\text{3}^{\text{II}}\) ligand.[33] Since then, only two other structures