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Influencing the Size of Giant Rings by Manipulating Their Curvatures: $Na_6[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]\cdot(\sim200H_2O)$ with Open Shell Metal Centers at the Cluster Surface

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The deliberate and efficient synthesis of mesoscopic systems with multifunctional properties, such as mesoporosity, perhaps in combination with other types of desired qualities, reveals a challenge for modern chemistry. Reduced highly nucleophilic giant polyoxomolybdates, which show a variety of structures—even with the ability to link them differently together—are promising species for this approach.[1] In particular, the tetra- and hexadecameric giant wheel-type structures, which can be used as synthons for the construction of mesoporous materials, possess a variety of structural features including related reaction centers and allow a derivatization on their inner surface.[2] The aim of the work presented here is to incorporate strong electrophilic open shell metal centers.[3] Herein, we report the synthesis of a mixed-valent molybdenum-blue-type polyoxomolybdate $Na_6[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]\cdot(\sim200H_2O)$ (**1**) (Robin−Day type III[7]) containing a new type of wheel-shaped anion $[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]^{6-}$ (**1a**) where the six 9-fold-coordinated Pr^{3+} centers linked to the inner (cavity) surface of the cluster have a tremendous influence on the shape and even the size of the giant ring.

1 was prepared by reducing an acidified suspension of sodium praseodymium polymolybdate in H_2O and characterized by elemental analysis,[8] single-crystal X-ray structure analysis[9] (including bond valence sum (BVS) calculations for the determination of the positions of the H atoms and the (formal) number of 24 Mo^V centers; for details, see ref 2a), vibrational as well as visible−NIR spectroscopy,[10] redox titrations (for the (additional) determination of the (formal) number of Mo^V centers), and thermogravimetry. The precipitate, obtained by rapidly combining aqueous solutions of $Na_2MoO_4\cdot2H_2O$ (3 g, 12.4 mmol, in 50 mL) and $Pr(NO_3)_3\cdot5H_2O$ (6 g, 14.4 mmol in 50 mL) under stirring, was filtered, washed carefully with water, dried for 6 h at 120 °C, and afterward suspended in 80 mL of hydrochloric acid (0.4 M) while a solution of hydrazinium dichloride (3.5 mL, 0.1 M) was added. After the suspension was heated for 45 min at 70 °C in an oil bath the resulting blue solution was cooled to room temperature, filtered after 1 day, and stored in a stoppered Erlenmeyer flask for 12 days. The precipitated dark-blue, poorly water-soluble pinacoid-shaped crystals of **1** were filtered, washed with water, and subsequently dried in an argon stream. Yield: 250 mg (11% based on Mo).

The single-crystal X-ray structure analysis[9] of compound **1** shows in the unit cell four of the novel-type dodecameric ring-shaped clusters **1a** packed parallel to the crystallographic *bc* plane. Each cluster has a diameter of ca. 32 Å and is strongly distorted/twisted with respect to an ideal circular structure (see Figure 1). The architecture of **1a** can be compared to that of the "symmetrical" tetradecameric ring-shaped molybdenum-blue species insofar as it shows the same type of the three different characteristic building blocks,[1] but they are less in number. (All structures of the so-called soluble molybdenum-blue species known so far are either tetra- or hexadecamers of the three mentioned building blocks $\{Mo_2\}$,$\{Mo_8\}$, and $\{Mo_1\}$.[1,2]) **1a**, however, consists of only 12 sets of these but with six of the $\{Mo_2\}^{2+}$ groups replaced by $\{Pr(H_2O)_5\}^{3+}$ units, which have a strong structural influence on the type of ring formed. Because of the exchange of $\{Mo_2\}^{2+}$ groups by $\{Pr(H_2O)_5\}^{3+}$ fragments and the smaller number of building blocks, the negative charge of **1a** is, compared to the (normal) tetradecameric anion mentioned above, correspondingly decreased.[11] Since the BVS calculations[12] show no significant divergence with respect to the corresponding O and Mo (BVS) values of several molybdenum-blue compounds, it was possible to determine—together with the other data—the analogue formula $[\{Mo_2\}_6\{Pr\}_6\{Mo_8\}_{12}\{Mo_1\}_{12}] \equiv [\{Mo^{VI}{}_2O_5(H_2O)_2\}_6\{Pr^{III}(H_2O)_5\}_6\{Mo^{VI/V}{}_8O_{26}(\mu_3{-}O)_2H(H_2O)_3Mo^{VI/V}\}_{12}]^{6-}$

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(3) It has been demonstrated that lanthanide cations, which show large coordination numbers as well as different coordination geometries, can link polyoxometalate-based fragments,[4−6] for example, of the lacunary type even with the possibility of generating giant clusters with 16 Ln and 148 W atoms. Wassermann, K.; Dickman, M. H.; Pope, M. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1445.

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(8) Anal. Calcd for $Na_6Mo_{120}Pr_6O_{644}H_{568}$ (M = 23372.4 g/mol): Na, 0.6; H_2O, 15.4 (crystal H_2O), 6.0 (coordinated H_2O); (formal) *number* Mo^V, 24.0. Found: Na, 0.6; H_2O (TG), 21.6; (formal) *number* of Mo^V, 24.1 (cerimetric redox titration).

(9) Crystal data for **1**: monoclinic space group $P2_1/c$ (No. 14), $a = 27.720(1)$ Å, $b = 38.557(1)$ Å, $c = 65.349(2)$ Å, $\beta = 99.937(1)°$, $V = 68797(8)$ Å^3, $Z = 4$, $D_{calcd} = 2.344$ mg/mm^3, μ(Mo Kα) = 2.65 mm^{-1}. The data were collected at 163(2) K using a Siemens AXS three-circle diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, graphite monochromator) with 1K-CCD detector (ω scan frames). Of the 352 528 reflections measured ($1.52° \leq \theta \leq 25.0°$), 120 947 unique reflections were used to solve the structure by direct methods (SHELXTL, version 5). The structure was refined on F^2 by least-squares techniques. At convergence, R1 equals 0.0884 and the goodness of fit on F^2 is 1.082. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-411093.

(10) Spectroscopic data (main characteristic bands) for **1**. IR (KBr pellet; ν(cm^{-1})): 1613 (m, δ(H_2O)), 974 (vs), ν(Mo = 0), 803 (s), 746 (m), 636 (s), 555 (s), 482 (sh). Resonance Raman (KBr dilution matrix; λ_e = 1066 nm; ν(cm^{-1})): 809 (m), 793 (s), 536 (s), 466 (s), 326 (m), 217 (s).

(11) There seems to be an equilibrium in solution between higher soluble "classical" molybdenum-blue species (without $\{Mo_2\}$ replacement) and **1a**, which is less soluble. A synthetic method favoring the replacement by activating the $\{Mo_2\}$ group would increase the rather low yield obtained here (investigations are in progress).

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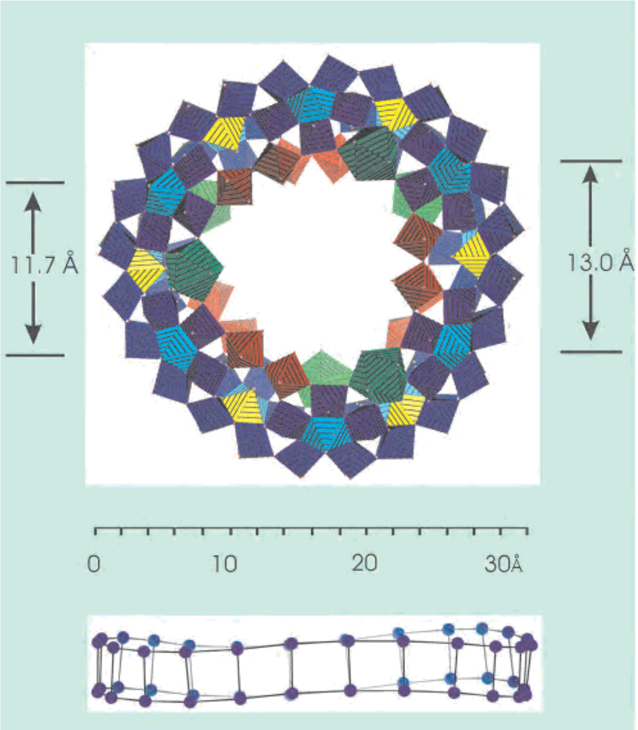

Figure 1. Structure of the anion of **1** in polyhedral presentation with the $\{Mo_1\}$ units in yellow, the $\{Mo_2\}$ in red, the $\{Mo_8\}$ units including the pentagonal bipyramids (light blue) in dark-blue, and the $\{PrO_4(OH_2)_5\}$ polyhedra in green (constituents of the lower half of the ring are more pale in color). The two marked distances between two equivalent pentagonal bipyramids are a measure of the curvature, which is greater if an $\{Mo_2\}$ unit is replaced by a Pr^{3+} cation. The lower part shows the molybdenum centers forming the rim of the wheel.

(**1a**) (for related details see refs 1c and 2a where the problem of the formula determination of these types of giant clusters has been discussed).

Each Pr^{III} center is bound to the cluster surface by four bridging oxygen atoms and exhibits, in total, a 9-fold coordination geometry including five H_2O ligands that are mostly found to be disordered over two positions. If the disorder is ignored, the resulting polyhedron can be described as a tricapped distorted prism. It is possible, therefore, that **1a** exhibits new possibilities for further functionalization with more complex ligands via exchange of the coordinated H_2O ligands. The $\{Pr(H_2O)_5\}^{3+}$ fragment, which is significantly smaller than the $\{Mo_2\}$ units, has, as mentioned above, a significant influence on the curvature, i.e., on the size as well as the shape of the cluster (see Figure 1). A good measure of the curvature is the distance between two equivalent pentagonal bipyramids of the $\{Mo_8\}$ groups with either an $\{Mo_2\}$ unit (distance 13 Å) or a Pr^{III} center (distance 11.7 Å) in between (see Figure 1). The shortest Pr−Pr distance is 12.2 Å.

The work presented here shows that it is possible to functionalize giant molybdenum oxide species having transferable building blocks and to influence their size. Important in context is that they have a variety of different reaction centers comparable to a mesoscopic surface, for instance, those of the electron-rich type. It is possible to place (strongly interacting) open shell metal centers including those with an odd number of electrons on the inner surface. Our future work in this field will include the incorporation of other lanthanide cations in order to study their influence on the ring-type structures and the functionalization of these by replacing H_2O with appropriate (e.g., amphiphilic) ligands, which should allow interesting creations of inner-cavity surfaces. Further fascinating possibilities would be to study different types of (magnetic/electronic) interactions of open shell metal centers at different positions of the cluster surface.

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Supporting Information Available: Tables listing crystal data and structure refinement details, atomic coordinates, bond lengths and bond angles, and anisotropic displacement parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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