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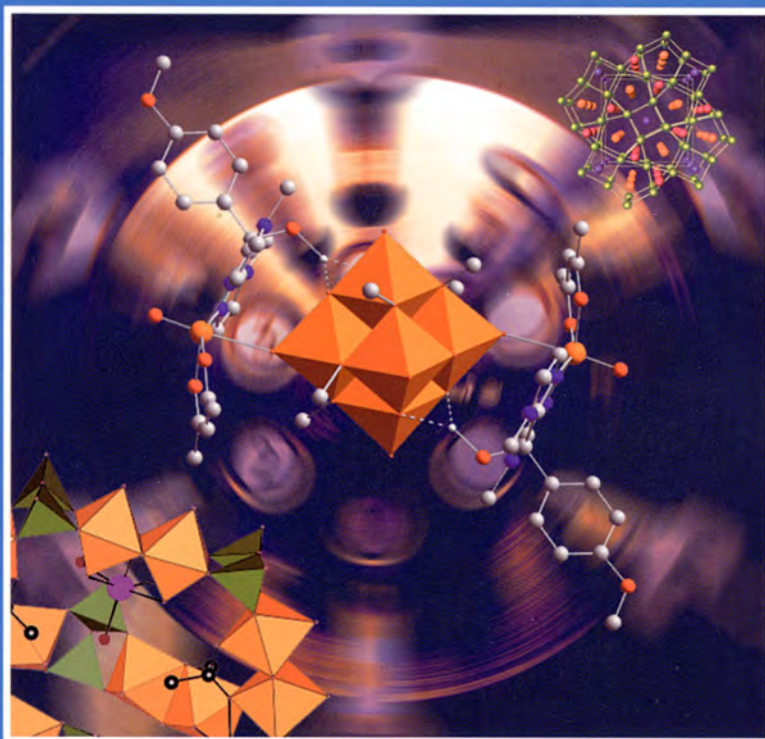
Inorganic Experiments

Second, Completely Revised and Enlarged Edition

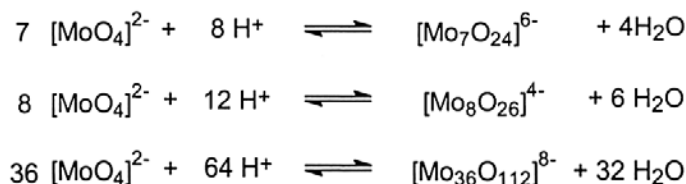Edited by J. Derek Woollins

4.27

Polyoxomolybdate Clusters: Nanoscopic Wheels and Balls

LEROY CRONIN, EKKEHARD DIEMANN and ACHIM MÜLLER

Inorganic metal-oxygen cluster anions form a class of compounds that is unique in its topological and electronic versatility and is important in several disciplines. Names such as Carl Wilhelm Scheele, Jöns Jakob Berzelius, Alfred Werner and Linus Pauling appear in the early literature of this field. These clusters, socalled isopoly- and heteropolyanions, contain highly symmetric core assemblies (coordination polyhedra) of MO_x units (M = V, Mo, W) and often adopt spherical structures based on Achimedean and Platonic solids of considerable topological interest. Understanding the driving force for the formation of high-nuclearity clusters is still a formidable challenge.

Polyoxometallates are especially common amongst the group VIA metals. In aqueous solution they have a rich pH dependent chemistry where the ions are able to polymerise through sharing of edges and/or corners of the metal oxygen polyhedra. For example, the acidification of a solution of molybdate gives rise to fragments which increase in nuclearity as the pH of the solution decreases (Scheme 4.27-1).

$$7\ [MoO_4]^{2-} + 8\ H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$$

$$8\ [MoO_4]^{2-} + 12\ H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6\ H_2O$$

$$36\ [MoO_4]^{2-} + 64\ H^+ \rightleftharpoons [Mo_{36}O_{112}]^{8-} + 32\ H_2O$$

Scheme 4.27-1 Formation of polyoxomolybdates at low pH in aqueous solution.

The molybdenum polyoxometallates (polyoxomolybdates) are particularly interesting because they exhibit a vast number of structures due to the various sharing and linking of co-ordination polyhedra. This is especially the case under reducing conditions as these support protonation due to related increase of higher electron density at the O atoms. Note: The largest polymolybdate under non-reducing conditions is $[Mo_{36}O_{112}]^{8-}$.

Figure 4.27-1 depicts a set of polyhedra or related building groups like {Mo_8} present in the $[Mo_{36}O_{112}]^{8-}$ anion. The central polyhedron is a pentagonal bipyramid which is linked via edges with five octahedral polyhedra.
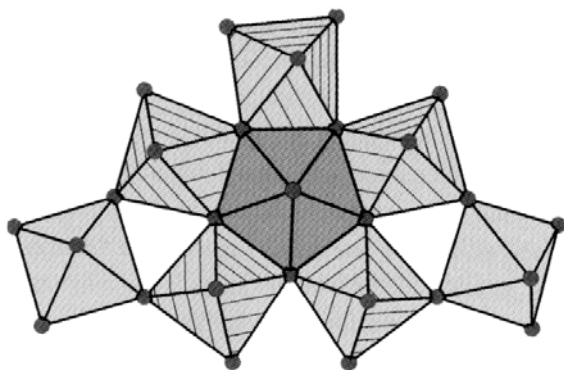
Fig. 4.27-1 A polyhedral representation of a section of aggregated polyhedra found in the $[Mo_{36}O_{112}]^{8-}$ anion while the $\{Mo_8\}$ building group shown is also present in the larger wheel system. The Mo(VI) ions (not shown) are at the centres of the polyhedra with the oxygen ligands at the corners, represented by black spheres.

Considering the number of potential combinations of polyhedra it is not surprising that such systems form a bewildering number of anions (Mathematicians would call it combinatorial explosion). The main control parameters in the synthesis of such anions appear to be pH, ionic strength, molybdate concentration, type of electrolyte, and, particularly important for the compounds reported here, the concentration and type of the reducing agent. By reduction the overall negative charge of the anion is increased which results in an increase of the charge density mainly on some of periphery type oxygen atoms which might then be protonated and thus get susceptible for a further condensation step. Another choice could be spin-pairing between two reduced, neighboured metal atoms, thus forming a metal-metal bond. It can be imagined that the situation opens a vast number of possibilities for linking and growing new exciting structures and even more if hetero atoms are included. Carl Wilhelm Scheele first documented solutions of strongly acidified reduced molybdate, so called *molybdenum blue* solutions, already in 1783. However the true nature of the system eluded scientists for well over two hundred years. In one of the following two experiments material will be crystallised from a *molybdenum blue* solution – this was first achieved in experiments by the group in Bielefeld in 1995. In the second experiment a giant polyoxomolybdate is obtained on the base of a higher pH value.

We report here the syntheses of two aesthetically beautiful nanoscale polyoxomolybdates of the type $\{Mo_{11}\}_n$ which have spherical (n = 12) or circular (n = 14) shape, i.e. molybdenum blue type which were highlighted worldwide in newspapers and magazines. In spite of their completely different structure (see Fig. 4.27-2), they have similar $\{Mo_{11}\}$ type building blocks which results in an almost equivalent stoichiometry. In the ball type cluster the $\{Mo_{11}\}$ group has necessarily the high C_5-symmetry, as 12 of these span an icosahedron. It should be mentioned that it is a difficult task to determine the complete formula of a compound like the wheel type species with a protonated, mixed-valence anionic species of the class II or III type (classification according to Robin and Day) with rather high molar masses, mainly if a very low concentration of (crystallographically) disordered cations in the lattice complicates additionally the determination of the correct anion charge. The accuracy of the usual analytical determinations often does not suffice to answer this question directly.

In the case of the circular 'molybdenum blue' compound the general synthetic strategy involves the strong acidification (pH ~1) of an aqueous molybdate(VI) solu-
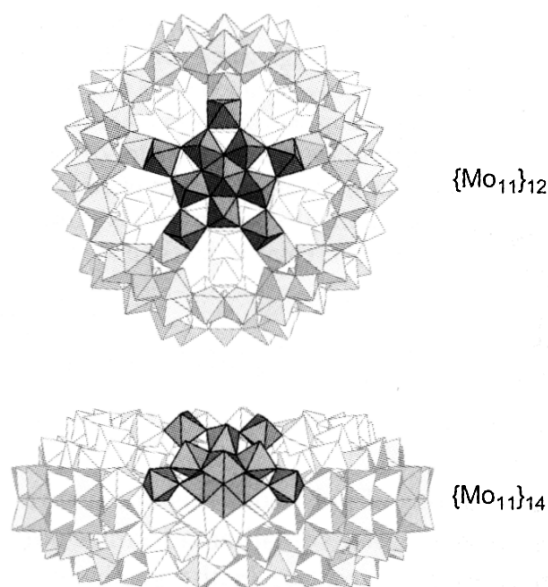
{Mo$_{11}$}$_{12}$

{Mo$_{11}$}$_{14}$

Fig. 4.27-2 Comparison of the {Mo$_{11}$}$_{14}$-type "Giant Wheel" (side view) with the {Mo$_{11}$}$_{12}$-type "Giant Ball" cluster.

tion and its subsequent treatment with an reducing agent like iron powder, tin(II) chloride, molybdenum(V) chloride, ascorbic acid, cysteine, hydroxylamine, hydrazine, hypophosphite, dithionite etc.. On the other hand, an icosahedral ball-shaped cluster can be formed in an aqueous molybdate(VI) solution at higher pH values ranging from 2–4 in the presence of an appropriate bridging ligand, e.g., acetate which in effect stabilises the dinuclear {Mo$_2^V$} units (see below) formed upon reduction.

Special Safety Precautions

1. Sodium molybdate salts: irritant.

2. Sodium dithionite: irritant, can liberate toxic gas (handle in fume hood).

3. Ce(IV)(SO$_4$)$_2$: corrosive (handle with gloves).

4. Hydrochloric and sulfuric acid: toxic, corrosive (handle with gloves in fume hood).

5. Hydrazinium sulfate is assumed to be carcinogenic (handle with gloves in fume hood).

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Experimental

a) Preparation of the "Giant Wheel" Type Compound

Dissolve 3.0 g (12.4 mmol) of Na$_2$MoO$_4$ · 2H$_2$O in 13 ml water (use 100 ml Erlenmeyer flask) and then add *freshly powdered* Na$_2$S$_2$O$_4$ (0.2 g, 1.15 mmol) to the solu-

tion under continuous stirring (hint: be sure to use fresh $Na_2S_2O_4$). The colour changes to light yellow. Under continuous stirring 30 ml of hydrochloric acid (1 M) are added dropwise (use a burette). The resulting solution should turn to dark blue colour. After stirring for 10 more minutes flush the flask through with either nitrogen or argon for 5 minutes before removing the stirrer and closing the flask with an airtight stopper. Be sure to leave the flask in a place undisturbed at *ca.* room temperature for minim. 24 hours. After this time the solution should have precipitated a quantity (*ca.* 1 g) of blue, slightly oblique, rectangular crystals. Carefully isolate the crystalline material by filtration and wash the crystals with a small amount of cold water (care, these crystals are highly soluble in water!). Note the yield and store the crystals in a closed flask under nitrogen or argon.

Analysis of the "Giant Wheel" type compound

Deduction of the unit cell of the crystals gives the space group of P-1 with $a = 30.785(2)$, $b = 32.958(2)$, $c = 47.318(3)$ Å, $\alpha = 90.53(1)$, $\beta = 89.86(1)$, $\gamma = 96.85(1)$, $V = 47665(6)$ Å^3. Determination of the structure of the crystals reveals that the unit cell comprises two non-equivalent cluster rings with 154 and 152 Mo atoms (Fig. 4.27-3). (The last one has a defect, with one $\{Mo_2\}$ group less, while the minor difference between both species will not be considered here.) The giant anion ring is *ca.* 34 Å wide (outer width) with an inner cavity of *ca.* 20 Å and is *ca.* 15 Å thick, being mostly composed by octahedrally coordinated Mo centres with Mo in either the VI or V metal oxidation state and different functionalities of the oxygen atoms. The formal aggregation of these units can be rationalised by dividing the system into repeating building blocks as shown in Figure 4.27-3. The building block principle adopted in Figure 4.27-3 means that the overall anion can be described as being composed of fourteen $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$ fragments. The top half of the ring is shown as a cartoon (right-hand-side) and can be clearly seen to comprise seven $\{Mo_8\}$ and $\{Mo_2\}$ groups on the top side with the fourteen $\{Mo_1\}$ groups (not shown in the cartoon) occupying the equator of the ring. The complete ring is constructed when the bottom half (also comprising seven $\{Mo_8\}$ and $\{Mo_2\}$ groups) is rotated around 360/14° relative to the first and fused to it through the fourteen $\{Mo_1\}$ groups. The formula of the compound is: $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5} [Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5} \cdot$ *ca.* 400 H_2O. The positions of the coordinated water molecules and bridging hydroxides can be determined from a single-crystal X-ray structure analysis especially by bond-valence calculations, but it is not possible to determine the number of sodium ions present in the cell due to disorder of these ions.

The IR spectrum shows peaks (in cm^{-1}) at 1616 (m) (d(H_2O)), 975 (m), 913 (w-m) (ν(Mo=O)), 820 (sh), 750 (s), 630 (s), 555 (s) (s = strong, m = medium and w = weak intensity; sh = shoulder). The electronic absorption spectrum is dominated by two bands characteristic for all *molybdenum blue* species (in H_2O/HCl, pH = 1): λ_{max} [nm] ε_{max}[$M^{-1}cm^{-1}$] = 745 (1.8 · 10^5), 1070 (1.4 · 10^5). These bands have to be assigned to intervalence Mo^V/Mo^{VI} charge transfer transitions (IVCT). The second ε value corresponds because of a linearity relation to the abundance of altogether 28 Mo^V centers. Using an excitation within the contour of the 1070 nm band gives rise to a *Resonance Raman Spectrum*. It shows five bands at 802 (s),
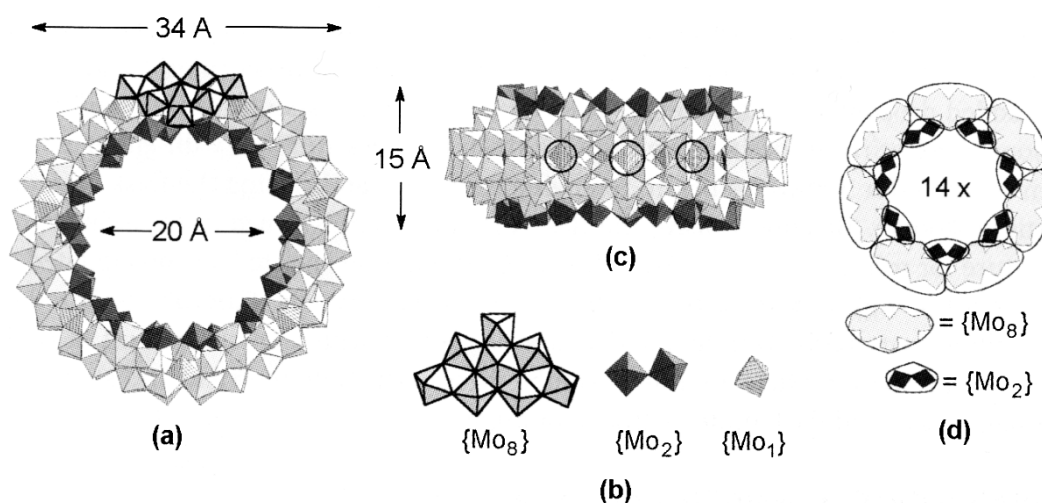
Fig. 4.27-3 Top and side views of the giant-ring shaped anion with the metal coordination sphere drawn as polyhedra (a), while the {Mo$_8$}, {Mo$_2$} and {Mo$_1$} building blocks are shown separately for clarity (b). The positions of the {Mo$_1$} building blocks in the equator of the ring are highlighted with circles in the side view (c). A cartoon representation of the top half of the ring showing how the {Mo$_8$} and {Mo$_2$} building blocks are connected (d).

535 (m), 462 (s), 326 (s) and 215 (s) cm^{-1} and is also characteristic for all *molybdenum blue* species.

Analytical exercises

Although a reasonable formula for the anion may be determined using the crystallographic data, the number of sodium ions and the number of Mo(VI)/Mo(V) centers cannot.

(1) Determine, if possible, the number of water solvent molecules present in the sample using thermogravimetric analysis to confirm or adjust the number of water solvent molecules deduced using crystallography. Keep a part of the sample open on your desk for two hours and a second part for four hours. Repeat the thermogravimetry on these samples. From the results try to extrapolate approximately the loss of water due to weathering to t = 0.

(2) Determine the number of sodium ions per cluster by performing a sodium analysis using a suitable method (e.g. by flame photometry or potentiometrically with a sodium selective electrode).

(3) Determine the number of Mo(V) ions per ring by conducting several redox titrations. This can be achieved by dissolving between 50 and 100 mg of the material in ca. 50 ml of water (flushed with nitrogen or argon for some minutes). Then by monitoring the solution with a redox electrode, titrate the blue solution with a 0.01 M solution of Ce(IV)(SO$_4$)$_2$ in 0.5 M of H$_2$SO$_4$. By carefully recording the voltage (this should be of the order of 400 mV) as a function of volume of Ce(IV) solution added it should be possible to determine the total number of Mo(V) centres present. The end-point of the titration is characterised by a potential jump (e.g. from around 400 mV to 1100 mV) at the point when all the Mo(V) centres

present have been oxidised (the solution will also no longer be blue!). Record the volume of Ce(IV) added at this point and continue adding past this point whilst still recording the voltage to ensure that all the Mo(V) is oxidised (if the potential jump continues adjust the end point accordingly). Analyse these data graphically to confirm the end point position and determine the volume of the Ce(IV) solution added at the end point.

Using the above results, including the crystallographically deduced formula as a basis, to calculate the number of Mo(V) centres per formula unit and the charge of the ring-cluster anion. Discuss the significance of any possible errors or discrepancies in the results you have obtained and possible approaches to overcoming them.

b) Preparation of the "Giant Ball" Type Compound

0.8 g (6.1 mmol) hydrazinium sulfate is added to a solution of 5.6 g (4.5 mmol) ammonium heptamolybdate tetrahydrate and 12.5 g (162 mmol) ammonium acetate in 250 ml water under stirring, and finally after stirring for 10 min 83 ml of 50% (v/v) acetic acid (use a 500 ml Erlenmeyer flask). The deep green reaction mixture is then kept at room temperature without further stirring for four days (colour change to dark brown) and then filtered through a glass frit (pore size G2). The reddish-brown crystalline residue is washed with 90% ethanol, then with a 1:1 mixture of ethanol/diethylether and finally dried in air. The yield is about 3 g.

Analysis of the Giant Ball compound

The formula determined for this product is $(NH_4)_{42}[\{Mo^{VI}(Mo^{VI}_5O_{21})(H_2O)_6\}_{12}$ $\{(Mo^V_2O_4)(CH_3COO)\}_{30}] \cdot$ ca. 300 $H_2O \cdot$ ca. 10 CH_3COONH_4 (The anion has the general formula $[\{pentagon\}_{12}\{linker\}_{30}]^{42-}$). It forms octahedral and truncated octahedral crystals which crystallize cubic (space group Fm-3) with a = 46.0576(14) Å. The IR spectrum (nujol suspension) shows peaks (in cm^{-1}) at 1626 (m) ($\delta(H_2O)$), 1546 (m) ($\nu_{as}(COO)$), 1440 (sh), 1407 (m) ($\delta(CH_3)$, $\nu_s(COO)$, $\delta_{as}(NH_4^+)$), 969 (m), 936 (w-m) ($\nu(Mo=O)$), 853 (m), 792 (s), 723 (s)and 567 (s). Due to the very high symmetry of the cluster anion only very few Raman bands are observed (may be assigned to symmetric vibrations): 953 (m), 935 (m), 875 (s) ($\nu(Mo=O)$, ca. 845 (sh), 374 (m-s), 314 (m) and 212 (w) cm^{-1}. The electronic absorption spectrum (H_2O/CH_3COOH, pH=4) shows only one intense band at 450 nm.

Analytical exercises

(1) Determine the number of ammonium cations per formula unit (you may either use a classical Kjeldahl setup without employing Devarda's alloy (why not?) or a ammonium sensitive electrode).

(2) Determine the number of reduced Mo centers per formula unit using the cerimetric procedure as explained above.

(3) If possible, obtain a X-ray powder pattern from the finely grinded sample (which is not easy because this may lead to loss of crystal water and crystallinity). Try to index the pattern on the basis of the unit cell dimensions given above. What is

the effect of *large* and *symmetric* cells on the appearance of such patterns. – The lattice is made up from almost perfect spherical entities. What kinds of packing would be possible? (hint: compare with close packing of metals). Could you relate the crystal symmetry to its morphology?

(4) If possible, measure the magnetic susceptibility of the finely grinded sample at room temperature (either with a magnetometer or even with a simple magnetic balance of the Evans type). Can you give an explanation for your findings?

References

M. T. POPE, A. MÜLLER, Angew. Chem. Int. Ed. Engl. **1991**, *30*, 34–48.

A. MÜLLER, C. SERAIN, Acc. Chem. Res. **2000**, *33*, 2–10.

A. MÜLLER, P. KÖGERLER, C. KUHLMANN, Chem. Commun. **1999**, 1347–1358.

A. MÜLLER, S. K. DAS, V. P. FEDIN, E. KRICKEMEYER, C. BEUGHOLT, H. BÖGGE, M. SCHMIDTMANN, B. HAUPTFLEISCH, Z. anorg. allg. Chem. **1999**, *625*, 1187–1191.

A. MÜLLER, E. KRICKEMEYER, H. BÖGGE, M. SCHMIDTMANN, F. PETERS, Angew. Chem. Int. Ed. Engl. **1998**, *37*, 3360–3363.