Self-assembly of a novel nanoscale giant cluster: $[Mo_{176}O_{496}(OH)_{32}(H_2O)_{80}]$†

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Reduction of an acidified solution of $Na_2MoO_4{\cdot}2H_2O$ by iron powder results in the formation of the title compound $[Mo_{176}O_{16}O_{480}(OH)_{32}(H_2O)_{80}]$; the compound is tyre shaped and consists of sixteen $\{Mo_8\}$ subunits being linked by forty-eight MoO_6 octahedra; remarkable features are the size and mass (which is of the order of a protein) and its nano-dimensional cavity of *ca.* 3 nm in diameter.

One of the challenges chemists are facing today is how to synthesize larger mesoscopic molecules from molecular fragments. The aim of such research is not only to improve the understanding of the extreme complexity of natural process, but also to synthesize molecular materials with novel properties, *e.g.* electric and magnetic, which may be anticipated for mesoscopic compounds. Indeed, considerable progress has been made in the field of polymetalate chemistry.[1,2] We have evolved the so-called 'reduction–reconstitution' self-assembly process and synthesized a class of large mixed-valent, nanoscale polyoxomolybdate anions[3–7]‡ constructed of $\{Mo_8\}$ or $\{Mo_{17}\}$ fragments:[2] $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$ **1**,[3] $[Mo_{57}V_6O_{180}(NO)_6(OH)_3(H_2O)_{18}]^{21-}$ **2**,[4] $[Mo_{57}Fe^{III}{}_6O_{174}(NO)_6(OH)_3(H_2O)_{24}]^{15-}$ **3**,[5] $[Mo_{57}Fe^{II}{}_6O_{177}(NO)_6(OH)_2(H_2O)_{22}(MoO)_2]^{18-}$ **4**[6] and $\{\{(H_2O)MoO_{2.5}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]O_{2.5}Mo(H_2O)\}^{12-}\}_n$ **5**[7] and some of them were also obtained later by Müller's group.[2] By slightly changing the reaction conditions in the same system, Müller *et al.* succeeded in isolating a giant cluster $[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]^{14-}$ **6**.[2,8] Now we have succeeded in synthesizing an even larger nanocompound $[Mo_{176}O_{496}(OH)_{32}(H_2O)_{80}]$ **7** which is also constructed of $\{Mo_8\}$ fragments.

Compound **7** was prepared following the general method leading to 'molybdenum blue'. A solution of $Na_2MoO_4{\cdot}2H_2O$ (5.0 g, 20.7 mmol) in H_2O (50 ml) was adjusted to a pH of *ca.* 1.0 with 36.5% hydrochloric acid. After addition of iron powder (50 mg, 0.9 mmol), the mixture was left to stand for one month to crystallize. The preparation yields blue–black, tetragonal-bipyramidal well defined crystals of **7** in *ca.* 30% yield. Reduction with elemental Al or Zn as well as $N_2H_4{\cdot}2HCl$ yields the same well defined crystals. The compound was characterized by IR and UV–VIS spectroscopy, cerium(IV) sulfate redox titration and elemental analysis,§ as well as by single-crystal X-ray diffraction.¶

The rather intricate single-crystal X-ray structure analysis reveals that the ring-shaped compound **7** consists of 160 MoO_6 octahedral and 16 pentagonal bipyramids of type MoO_7 (Figs. 1 and 2). The structure has approximate D_{8d} symmetry. Sixteen $\{Mo_8\}$ fragments are linked with sixteen Mo atoms in the equatorial plane and another sixteen $\{Mo_2\}$ groups.[2] Each of the sixteen subunits has a pentagonal-bipyramidal MoO_7 center about which seven other MoO_6 octahedral are grouped by corner- and edge-sharing to form an $\{Mo_8\}$ fragment. This $\{Mo_8\}$ fragment also occurs in **1**–**6**, which, however, possess a pentagonal bipyrimidal $Mo(NO)O_6$ centre.

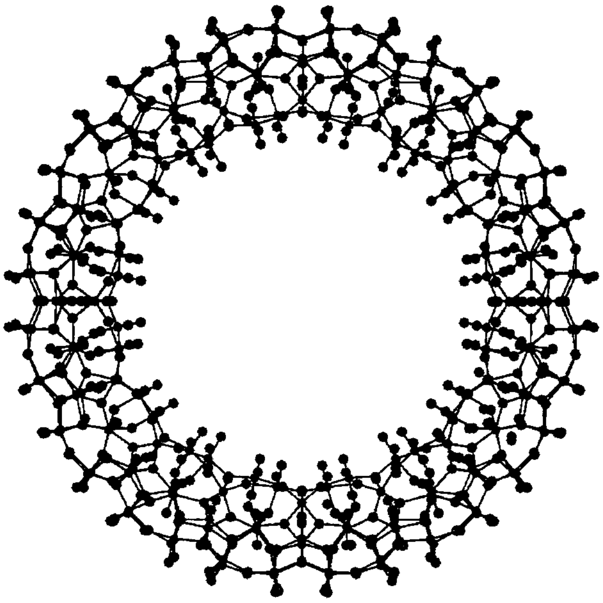

Fig. 1 Ball-and-stick model of the nanoscale cluster (view parallel to the C_8 axis)

The structure type of **1**–**5** is different from that of **6** and **7**. In **1**–**5** two $\{Mo_8\}$ fragments above and below the equatorial plane are linked through one equatorial Mo atom and are transformed into each other by reflection across the equatorial mirror plane. Thus anion **1** has approximate C_{2h} symmetry and anions **2** and **3** have D_{3h} symmetry. In other words, this kind of linking manner implies that there are $\{Mo_{17}\}$ fragments as building blocks in these anions. By contrast, the arrangement of $\{Mo_8\}$ fragments in **7** (D_{8d} symmetry), which is like that of **6** (D_{7d} symmetry), are twisted relative to each other. This shift means that in **6** and **7** two equatorial Mo atoms are required to link two $\{Mo_8\}$ fragments and so there are sixteen Mo atoms in the equatorial plane in **7** (fourteen in **6**). Two neighbouring $\{Mo_8\}$ fragments on the same side of the equatorial plane are linked

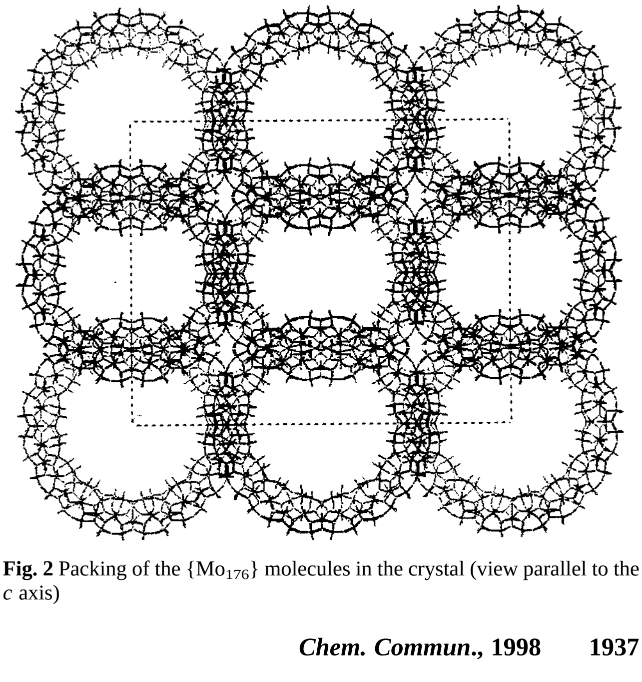

Fig. 2 Packing of the $\{Mo_{176}\}$ molecules in the crystal (view parallel to the *c* axis)

through two Mo atoms (or one $\{MoO_2(H_2O)(\mu_2\text{-}O)\text{-}MoO_2(H_2O)\}$ group) *i.e.* a $\{Mo_2\}$ unit, instead of only one V or Fe center as in **2** and **3**, respectively. However, the central $\{MoNO\}^{3+}$ group of the $\{Mo_8\}$ fragment of **6** is replaced by $\{MoO\}^{4+}$ group in **7**.

Whereas the basic structure of compound can be determined unambiguosly, it will probably never be possible to ascertain the exact number of crystallization waters by XRD owing to disorder of the lattice water molecules, the tendency to lose solvent and the weak diffraction of the crystal to X-rays. According to elemental analysis and TGA, the number of water is *ca*. 600 ± 50.

A remarkable feature of **7** is its nanoscale cavity and corresponding host properties. The cavity itself, which is like the inside of a tyre, measures about 3 nm in diameter. A further characteristic of **7** is that it dissolves extremely well in water, ethanol or acetone. This high solubility can be attributed to the large surface built up of a large number of H_2O molecules and OH groups. It is noteworthy that crystals of **7** are obtained from 'molybdenum blue'. 'Molybdenum blue' used to be regarded as amorphous, but recently Müller *et al.* have made some suggestions about its structure[9] and they also succeeded in isolating a compound $Na_{15}\{Mo_{144}O_{409}(OH)_{28}(H_2O)_{56}\}$, *ca.* 250 H_2O **8** from it[10] whose structure resembles **6** apart from some defects in **8**. Now it can be proposed that 'molybdenum blue' is a mixture of compounds which have a similar basic ring-shaped structure.

Polyoxoanions constitute a large class of inorganic compounds,[11] however, the number of different structural types is small. There are indications that **1–8** belong to the same kind structural type of compounds as they are all synthesized by a similar method and linked up *via* $\{Mo_8\}$ fragments in different ways. It can be presumed that under suitable reaction conditions, a variety of novel nanoscale clusters with high complexity and multifunctionality could be synthesized by the reduction–reconstruction self-assembly process developed in our laboratory.

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Notes and References

† Just before this manuscript was mailed, similar work by Müller *et al.* was published (*Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1220). However, they prepared their crystals by a different method and solved the structure in space group *Cmcm*.

‡ The charges given here are the values given by Müller *et al.* However, cluster anions with different charges are also obtained in our laboratory.

§ Elemental analysis. Calc. for $[Mo_{176}O_{16}O_{480}(OH)_{32}(H_2O)_{80}]\cdot(600 \pm 50)H_2O$: Mo, 44.9; Found: Mo, 44.0; Na, 0.2; Cl, 0.2%. Characterization of **7**: main IR bands (KBr disc): 1726s, 1618m, 974m, 914w, 668w, 558s cm^{-1}; UV–VIS (H_2O), 750, 220 nm. Cerium sulfate titration: 1 g of **7** reduces 0.830 mmol $Ce(SO_4)_2\cdot 2(NH_4)_2SO_4\cdot 4H_2O$ corresponding to 32 Mo^V atoms in each molecule.

¶ *Crystal data* for $[Mo_{176}O_{16}O_{480}(H_2O)_{80}(OH)_{32}]\cdot(600 \pm 50)\ H_2O$: M = 36 522.24, orthorhombic, space group *Amm*2 (no. 38), a = 66.628(13), b = 53.760(11), c = 31.775(6) Å, V = 113 816(39) Å^3, $F(000)$ = 71 024, Z = 4, D_c = 2.131 g cm^{-3}, Mo-Kα radiation, λ = 0710 69 Å, μ = 1.99 min^{-1}. Intensity data were collected on a Rigaku AFC6S diffractometer at 296 K and a total of 25 975 reflections were collected, of which 12 706 reflections were observed, the structure was solved with direct method and difference Fourier map using SHELXS97 and refined using SHELXL97. Owing to the poor ability of diffraction of the crystal and the limit of the number of reflections, only the Mo atoms are refined anisotropically with $R1$ = 0.1050 for observed reflections and $wR2$ = 0.2685 for all the data.

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