Polyoxometalate Anions

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A Large, Bowl-Shaped $\{Mo_{51}V_9\}$ Polyoxometalate**

Sheng Wang, Xiang Lin, Ying Wan, Wenbin Yang, Shengmin Zhang, Canzhong Lu, and Honghui Zhuang*

Polyoxometalates (POMs) have been extensively studied for several decades because of their potential applications in the fields of materials science[1,2] and medicine.[3] Different POMs usually show specific physicochemical properties associated with their nano-sized cavities or highly active surface sites.[4,5] Many of the POMs synthesized to date are large or extremely large, have quite different structures, and are mainly composed of $\{Mo_8\}$ or $\{Mo_{17}\}$ moieties (two $\{Mo_8\}$ units linked by one $\{Mo_1\}$ bridge). Most POMs and related species are anionic clusters that are generally formed by redox self-assembly processes in the presence of reductants, such as $SnCl_2$, hydroxylamine, and so on. New aggregates are commonly built by one of two main linking methods using the same or similar building blocks ($\{Mo_8\}$ or $\{Mo_{17}\}$). The first method involves connecting different units directly one by one, and the other indirectly linking several units together through some appropriate coordination centers. Both methods have been used to synthesize compounds containing moieties such as $\{Mo_{36}\}$,[6] $\{Mo_{57}\}$,[6b,7] $\{Mo_{154}\}$,[8] and $\{Mo_{176}\}$[9] and derivatives, and some examples of ball-shaped clusters[10] and $\{Mo_{368}\}$.[11] We have recently synthesized a new bowl-shaped POM, namely $((NH_4)_{21}[Mo_{51}V_9(NO)_{12}O_{165}(OH)_3(H_2O)_3(NHMe_2)_3]\cdot x\,H_2O$ ($x \approx 60$, abbreviated as $\{Mo_{51}V_9\}$), by a hydrothermal method. This new POM contains an anion-type cluster ($\{Mo_{51}V_9\} = [\{Mo_8\}_3\{Mo_6V_2\}_3\{Mo\}_9V_3]$) with a structure that is quite different from that of any other reported POMs. Herein we report the synthesis and structural analysis of this POM.

Many POMs contain $\{Mo_8\}$ units linked together either directly or indirectly. The $\{Mo_{36}\}$ series, for instance, usually consists of two pairs of $\{Mo_8\}$ units (with one $\{Mo_8\}$ unit containing seven $\{MoO_6\}$ octahedra and one $\{MoO_6(X)\}$ bipyramid (X = O or NO)), which are linked by two $\{Mo_1\}$ bridges to form two $\{Mo_{17}\}$ units that are symmetrical to a C_2 axis, whereas the $\{Mo_{57}\}$ series normally contains three pairs of $\{Mo_8\}$ units that are symmetrical to an S_3 axis. If these symmetries are examined in detail, it can be seen that the two $\{Mo_8\}$ units overlap completely along the symmetry axis. For $\{Mo_{154}\}$ and its defect-containing analogues, however, one $\{Mo_8\}$ unit from one side of the equatorial plane is linked to another two $\{Mo_8\}$ units on the other side. This arrangement is also found for the $\{Mo_{176}\}$ series. The linkages between $\{Mo_8\}$ units, which are composed of four Mo atoms from one $\{Mo_8\}$ unit located on one side of the equatorial plane and four Mo atoms from two $\{Mo_8\}$ units on the other side of the equatorial plane, for the $\{Mo_{154}\}$ or $\{Mo_{176}\}$ series are almost the same except that the two most closely linked $\{Mo_8\}$ units are twisted by an angle of 360/14 in $\{Mo_{154}\}$[8] and 360/16 in $\{Mo_{176}\}$.[9] The ball-shaped and $\{Mo_{368}\}$ clusters are all made up of a series of $\{Mo(Mo_5)\}$ units linked by $\{Mo_2\}$ and $\{Mo_1\}$ bridges.[10,11]

Figure 1 shows a ball-and-stick model of our newly synthesized compound. It can clearly be seen that the building blocks of this compound are different from those reported for similar compounds. The model shown in Figure 1 has been divided into two parts, namely the bowl opening and the bottom of the bowl, in order to visualize the structure in more detail; these parts are depicted in Figure 2a and b, respectively. It should be noted that the two parts are not symmetrical against an equatorial plane. Only one of the "bat-like" $\{Mo_8\}$ units has its Mo atoms labeled in Figure 2a.

Several characteristics can be noted from Figure 2. Firstly, the $\{Mo_8\}$ units of the bowl opening part have two additional $\{MoO_6(NO)\}$ moieties (e.g., Mo28–N2–O95 and Mo2f–N2a–O95a; some terminal O atoms of the NO groups are disordered with an occupancy of less than one) that are located at the apexes of the "wings". Such an arrangement has not been reported previously. All the Mo atoms of $\{Mo_8\}$ units are usually located almost in the same plane. However, in this case it is clear that there is a deviation in the $\{Mo_8\}$ units of the bowl opening between the head atom and the other Mo atoms. The head atom, for example Mo14, deviates from the plane of the others by an angle of around 36.4°. The plane of each $\{Mo_8\}$ unit in the bowl opening folds down to connect the $\{Mo_8\}$ units in the bottom of the bowl. The two apexes of the "wings" of these latter $\{Mo_8\}$ units are occupied by a $\{VO_6\}$ moiety rather than $\{MoO_6\}$ (they are sometimes linked by $\{VO\}^{3+}$ in the reported $\{Mo_{57}\}$ series).[7] In addition, there are two pentacoordinate Mo atoms in each $\{Mo_8\}$ unit in the bottom of the bowl (labeled Mo8 and Mo8a in Figure 2b). To our knowledge, this situation is different from all other similar reported $\{Mo_8\}$ units. On the basis of the above observations, it is clear that the $\{VO_6\}$ groups from different $\{Mo_8\}$ units in

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[*] Dr. S. Wang, Prof. Y. Wan, Prof. S. Zhang
Advanced Biomaterials and Tissue Engineering Center
Huazhong University of Science and Technology
Wuhan, 430074 (P. R. China)
Fax: (+86) 278-779-2205
E-mail: wtscrystal@sina.com

Dr. X. Lin, Dr. W. Yang, Prof. C. Lu, Prof. H. Zhuang
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, 350002 (P. R. China)

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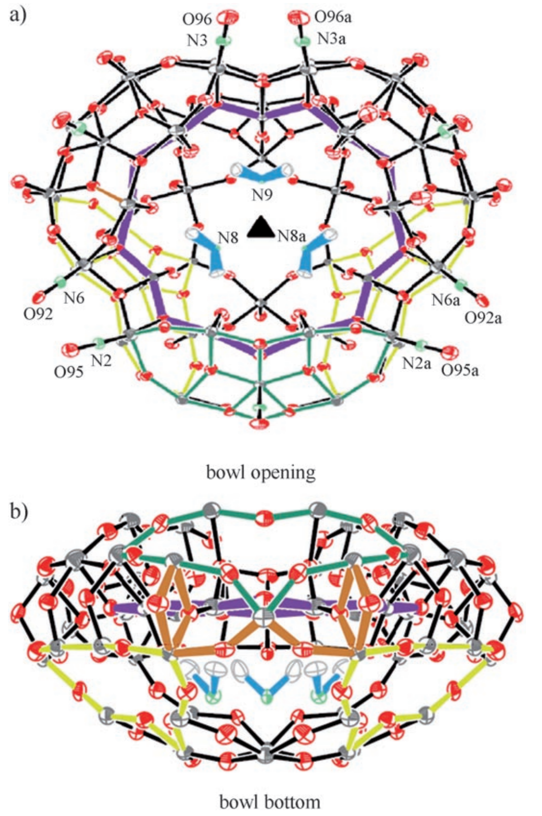

Figure 1. Ball-and-stick representation of $\{\mathrm{Mo}_{51}\mathrm{V}_9\}$ with certain moieties highlighted and a few atoms removed for clarity. a) View (from upper side to bottom) of the anionic cluster with the threefold axis indicated by a black triangle. Three $\{\mathrm{NHMe}_2\}$ groups are located at the bottom of the bowl in this view. The outer diameter is 1.93 nm (1.97 nm for $\{\mathrm{Mo}_{57}\}$), the upper internal diameter is 0.8 nm, and the lower internal diameter is 0.4 nm (0.5 nm for $\{\mathrm{Mo}_{57}\}$); b) side view of the anionic cluster showing the bowl-shaped profile. The yellow bonds are those between the $\{\mathrm{Mo}_8\}$ moieties of the bowl opening and the bottom of the bowl (see text for meaning of other colored bonds). Red O, green N, gray Mo/V.

the bottom of the bowl are linked to the head atoms of the $\{\mathrm{Mo}_8\}$ units in the bowl opening, which results in the lower part being forced upwards.

The present bowl-shaped $\{\mathrm{Mo}_{51}\mathrm{V}_9\}$ moiety has another unique characteristic, namely that there are three $\{\mathrm{NH(CH_3)_2}\}$ groups located at the bottom of the bowl close to the pentacoordinate head atoms of the $\{\mathrm{Mo}_8\}$ units in the bottom of the bowl, with a distance of 2.432 Å between the N and Mo atoms (light blue C–N bonds in Figures 1 and 2b).[12] The C-N-C angles are smaller than the expected bond angle of about 88.5° as a result of steric factors. Another feature of the present compound is that it contains an almost equator-like ring of nine Mo atoms (broad purple bonds in Figure 1) which connects the bowl opening and the bottom of the bowl to form the whole structure. Such a ring has not been reported previously.[8,9] Three of the oxygen atoms, namely O54, O82, and O82a, are protonated and are connected to three Mo atoms from the ring of nine Mo atoms.

The most interesting feature of this structure is that the $\{\mathrm{Mo}_8\}$ linkages are totally different from those found in other

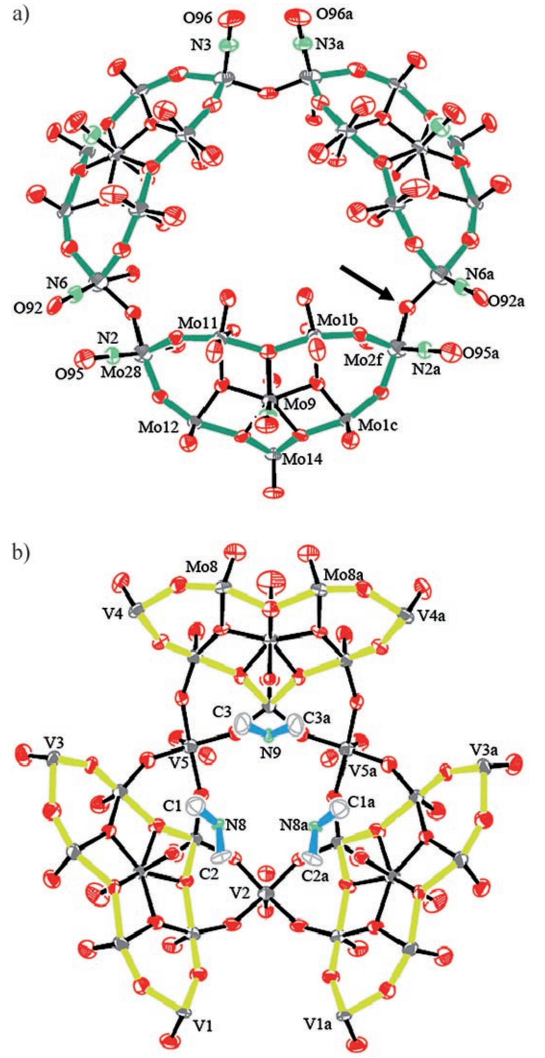

Figure 2. The bowl opening (a) and bottom of the bowl (b) of the title compound in the same orientation. The labeled "bat-like" $\{\mathrm{Mo}_8\}$ units in (a) bear different moieties at the wingtips ($\{\mathrm{Mo(NO)}\}$) than other reported $\{\mathrm{Mo}_8\}$ moieties. The head of the $\{\mathrm{Mo}_8\}$ moiety in the bowl opening, namely Mo14, is bound to the lower V1 and V1a atoms from two $\{\mathrm{Mo}_8\}$ units in (b) through two bridging oxygen atoms (O15 and O15A). The $\{\mathrm{Mo(NO)}\}$ apexes of the bowl opening are linked by a bridging oxygen (indicated by the arrow). See text for meaning of colored bonds.

POMs. To our knowledge, all reported $\{\mathrm{Mo}_8\}$ units tend to align along the same direction (in the $\{\mathrm{Mo}_{36}\}$ series)[6] or point inwards towards the center (e.g. in $\{\mathrm{Mo}_{57}\}$[7] and $\{\mathrm{Mo}_{154}\}$[8]). At first glance our compound looks similar to the $\{\mathrm{Mo}_{57}\}$ series observed from above, however, a detailed examination of its structure makes it clear that there are important differences (Figure 1a). The bat-like $\{\mathrm{Mo}_8\}$ units of the bowl opening point outwards without any $\{\mathrm{Mo_2O_5(H_2O)_2}\}$ ($\{\mathrm{Mo}_2\}$) or $\{\mathrm{VO}_6\}$ linkages (blue-green bonds in Figure 2a), whereas those in the bowl bottom point inwards (yellow bonds in Figure 2b). In addition, the head atoms ($\{\mathrm{MoO}_5\}$, pentacoordinate) in the bowl opening are connected to two V atoms from the wing apexes of the bat-like units in the bottom of the bowl (orange Mo–O–V bonds in Figure 1b). The two apexes of the $\{\mathrm{Mo}_8\}$ units in the bowl opening are linked together by one O bridge

(Figure 3), which means that there are no cavities on the outside surface of the present compound (cavities are always found in the defect-containing $\{Mo_{57}\}$ series).

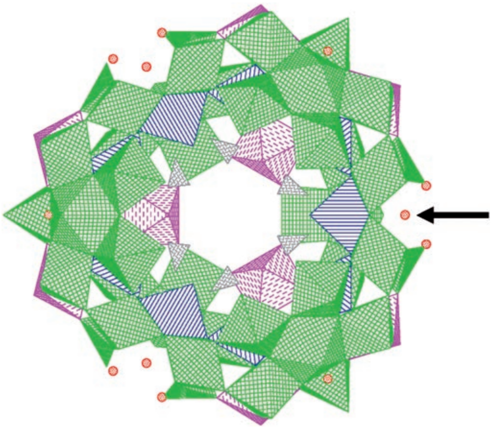

Figure 3. Polyhedral representation of the bowl-shaped anion-type cluster (perspective view) that has no external cavities. One of the bridging oxygen atoms is marked by the arrow (red circles for O atoms; polyhedrons with purple dashes indicate $\{VO_n\}$; polyhedrons with blue parallel lines indicate nine-atom ring containing $\{MoO_n\}$ units; gray hatching indicates methyl groups. Green-hatched polyhedrons indicate all of the other $\{MoO_n\}$ units, $n = 5$–7).

The precursors of building units are generally formed first and are then linked directly through O bridges or cations to form larger species. It is generally accepted that highly soluble precursors help to prevent uncontrolled linking or precipitation. It has been noted that the overall generation of complexity in those reactions that occur in living biosystems frequently occurs under dissipative conditions (far from equilibrium) and with an increase of entropy.[13,14] Since the reaction system is sealed in an autoclave in our case, the reduction effect is greater than that of other reactions that occur in open systems. This situation leads to the production of some clusters with a high proportion of $\{MoNO\}^{3+}$, which is more negatively charged and therefore more nucleophilic, instead of $\{MoO\}^{4+}$. As stated previously, our compound contains more $\{MoNO\}^{3+}$ groups in the bowl-opening portion and thus this part is likely to be formed first in the presence of abundant reductant. The more negative bowl-opening parts are stabilized by more positive bowl bottoms for charge balance, and the $\{Mo_8\}$ head groups in the bowl opening deviate sharply from the main plane in order to link to the bottom of the bowl to finally form a stable system. The strain in the whole structure, which could lead to an unusual reactivity and interesting properties, is greater than for other POMs.

The title $\{Mo_{51}V_9\}$ compound has been synthesized by a hydrothermal method. This bowl-shaped cluster is significantly different to similar reported compounds. The three $\{NHMe_2\}$ groups located at the bottom of the bowl are formed during the hydrothermal process. Surprisingly, we found that when a small amount of $NHMe_2$ was added directly before sealing the autoclave, the reaction produced an amorphous precipitate, and no crystals of $\{Mo_{51}V_9\}$ were isolated. It can therefore be concluded that formation of the three $\{NHMe_2\}$ groups is closely related to the catalysis of the polyoxometalate fragments under these reaction conditions.[12] Owing to the fact that the $\{Mo_8\}$ units in the present compound have unique orientations and linkages when compared to previously reported $\{Mo_2\}$ moieties, the whole bowl contracts inwards slightly to finally form a bowl-shaped cluster which may act as a highly selective host–guest reaction catalyst. Since many catalysts are harmful to the environment, POMs and other green catalysts are receiving an increasing amount of interest in the fields of chemistry and biology.

Experimental Section

$Na_2MoO_4 \cdot 2H_2O$ (1.0 g, 4.13 mmol), $NH_2OH \cdot HCl$ (1.3 g, 18.71 mmol), NH_4VO_3 (0.2 g, 1.71 mmol), CH_3COONH_4 (0.3 g, 3.89 mmol), H_2O (10 mL), and HCl solution (3.5% in H_2O, 1.25 mL, pH 4.0) were mixed with stirring. The mixture was heated in an autoclave at 160 °C for 24 h. After cooling, the mixture was filtered and the filtrate was placed in a conical flask at room temperature for crystallization. After two weeks dark-red crystals were isolated in low yield. The crystal structure (space group *Pnma*) was determined by X-ray analysis;[15] the product was also characterized by elemental analysis, thermogravimetric analysis, and various spectroscopic methods.[16]

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[12] The {NHMe$_2$} groups might form from CH_3COONH_4 during the self-assembly process, although the detailed mechanism is still unclear.

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[15] Crystal data for $\{Mo_{51}V_9\}$: $M_r = 9493.3$, orthorhombic, space group *Pnma*, $a = 28.0330$, $b = 23.3094$, $c = 37.8240$ Å, $V = 24\,715.43$ Å^3, $Z = 4$, $F(000) = 17\,805.8$, $\mu(Mo_{K\alpha}) = 2.92$ mm^{-1}, $R_{int} = 0.0745$, $R_\sigma = 0.1000$. The data were collected at room temperature. The structure converged for unique reflections and parameters to give $R_1 = 0.0726$ and $wR_2 = 0.244$ ($w = 1/[\sigma^2(F_o^2) + (0.0915\,P)^2 + 684.00\,P]$, where $P = (\mathrm{Max}(F_o^2,\ 0) + 2\,F_c^2)/3$). The results of BVS calculations show that the valence of all Mo atoms is +6 and that there are also six V^{5+} and three V^{4+} centers (the BVS is defined by $S = (R/R_1)^{-N}$, in which R is the i^{th} bond length, while N and R_1 have empirical values, for V–O, $N = 5.1$, $R_1 = 1.791$ and for Mo–O, $N = 6.0$, $R_1 = 1.882$). The whole anion therefore has a negative charge of −21, with three protons on atoms O54, O82, and O82a. It proved difficult to determine the exact positions of some NH^{4+} ions in the crystal lattice because of disorder of the NH^{4+} ions and the water of crystallization.

[16] Element analysis (%) calcd: C 0.76, Mo 51.5, N 5.3, V 8.27; found: C 0.71, Mo 50.81, N 5.41, V 8.32. Thermogravimetric analysis(TGA): weight loss of 11% between 35 °C and 200 °C corresponding to 60 crystallized waters; the weight loss between 200 °C and 450 °C most likely corresponds to the loss of NH_4^+. IR (KBr pellet): $\tilde{\nu} = 3480$ (br v as, σ(H_2O)), 3150 (s, σ(NH_4^+)), 2850 (m sh, σ(C–H), 1616 (m, δ(H_2O), ν(NO)), 1402 (s, δ(N-H)), 958 (m, ν(V=O)), 903 (m, ν(M=O)), 694 (m), 606 cm^{-1} (m) (ν(M-O-M, M = Mo or V)). ^{1}H NMR (500 MHz, D_2O): $\delta = -2.00$ (m, 18 H, N-CH_3), −4.82 ppm (s, H_2O ligands). EI-MS: m/z (%): 44 $[CH_3NCH_3]^+$, 30 $[CH_3N{-}H]^+$, 15 $[CH_3]^+$.