

Are the cations templates or encapsulated? – The synthesis and characterization of a new polyoxomolybdate

Guang Liu, Qi Li, Shi-Wei Zhang *

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

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Abstract

A new girdle-like polyoxomolybdate was synthesized and characterized by single crystal X-ray diffraction. Study on its hollow central hole indicates that it is some kind of “inorganic crown ether” and can act as the host of some cations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since Berzelius [1] synthesized the first heteropolyacid in 1826, metal–oxo cluster chemistry has been actively studied owing to interest in the chemistry itself and its various applications in fields such as catalysis, electric conductivity, magnetism, nonlinear optical properties and medicine [2]. There has been a great deal of research activity aimed at the so-called ‘reduced polyoxometalates’ [3–5], as opposed to those polyoxo anions that have nd^0 electronic configuration at the metal center. Among the reduced polyoxometalates studied to date, polyoxo anions of molybdenum, especially mixed-valence ones, have received great attention. It can be concluded that in the reduced polyoxomolybdates, if the Mo(V):Mo(VI) ratio is high, structures of those polyoxomolybdates are preferred with Mo(V)–Mo(V) pairs and red color, while if it is smaller, highly delocalized system with the characteristic dark-blue color (due to intervalence charge-transfer transitions) are favored [6]. Self-assembly assumptions such as ‘reduction–oxidation–reconstitution’ [7] and ‘polymerization–reduction–polymerization’ [8] have been presented following that some large polyoxomolybdates have been synthesized. A useful strategy is to generate in solution relatively large,

directly linkable intermediates (such as heptamolybdate, Keggin ions, etc.) by a self-assembly process and to use these as educts, e.g., together with cationic metal centers as linkers [6]. For example, when the heptamolybdate anions in solution are reduced, they are broken into pieces. Some small pieces have Mo centers and water ligands, so they appear positive charges and can act as linkers. Some large pieces that have $\{MoO_x\}_n$ structures appear negative charges and can be linked by linkers to form larger polyoxomolybdates. After adding glycine ligands into such a reactive mixture, we have obtained several novel girdle-like polyoxomolybdates with a general formula of $[A@Mo_{10}^{VI}Mo_8^VO_{56}]$ ($A = Ca^{2+}$ or Na^+) [9–11]. Müller et al. [12] reported a similar one with the glycine being replaced by acetic group. In the central holes of these girdle-like structures, Ca^{2+} or Na^+ were found to bond to the oxygen atoms of the backbone. What roles are these cations? In our previous paper [9], an assumption was presented that they might be templates during the formation of the polyoxomolybdates. In order to investigate the self-assembly process of polyoxomolybdates formation, we did a lot of work in trying to get an isostructural complex without the central cation. Here we report the successful preparation of a new girdle-like polyoxomolybdate with a hollow center.

* Corresponding author. Fax: +86-10-62751725.
E-mail address: zsw@chem.pku.edu.cn (S.-W. Zhang).



2. Experimental

2.1. Synthesis

Complex **1** was synthesized from the reaction of 1.36 g (1.08 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 3.00 g (39.0 mmol) $\text{CH}_3\text{COONH}_4$ and 0.20 g (1.5 mmol) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ in 60 ml (3.3 mol) water. The mixture was stirred for 10 min at room temperature while a color change occurred from colorless to blue. Three ml concentrated hydrochloric acid was added and the mixture color turned to green. Then it was left to stand without disturbance for one day. Green precipitation was filtered off and dark blue solution was left to stand. Red block crystals of **1** were obtained after 10 days with the co-existence of a kind of blue crystal. The crystals of **1** were carefully selected out and washed with water.

2.2. Elemental analysis

Calc. for complex **1** $\text{C}_4\text{H}_{96}\text{Mo}_{18}\text{N}_{10}\text{O}_{83}$: C, 1.44%; H, 2.90%; Mo, 51.7%; N, 4.19%; found: C, 1.50%; H, 2.69%; Mo, 51.5%; N, 4.15%.

2.3. X-ray crystallography

A red block single crystal with dimensions 0.25 mm \times 0.20 mm \times 0.10 mm was mounted on a Rigaku RAXIS-RAPID X-ray diffractometer. The data were measured using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). An absorption correction was applied by correction of symmetry-equivalent reflections using the ABCOR program [13]. The structure was solved by direct methods and successive difference maps (SHELXS 97) [14] and refined by full-matrix least squares on F^2 using all unique data (SHELXL 97) [15]. The non-hydrogen atoms were refined anisotropically.

$(\text{NH}_4)_{10}[\text{Mo}_{10}^{\text{VI}}\text{Mo}_8^{\text{V}}\text{O}_{52}(\text{OH})_4(\text{CH}_3\text{COO})_2] \cdot 23\text{H}_2\text{O}$, $M = 3339.83$, triclinic, space group P-1 (No. 2), $a = 9.481(2)$, $b = 14.087(3)$, $c = 15.402(3) \text{ \AA}$, $\alpha = 99.00(3)$, $\beta = 102.29(3)$, $\gamma = 103.01(3)^\circ$, $V = 1912.7(7) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 2.900 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.980 \text{ mm}^{-1}$, $T = 173 \text{ K}$, 16099 reflections collected, 8426 unique, 7342 observed for $F_0 > 4\sigma(F_0)$ ($R_{\text{int}} = 0.0288$). $R_1 = 0.0329$ (observed data) and $wR_2 = 0.0869$ (all data) for 586 parameters.

3. Results and discussion

Single crystal structural analysis shows that complex **1** is composed of girde-like polyoxomolybdates that each is built up by 18 distorted Mo–O octahedra (Fig. 1). The backbone structure details are similar to those of the complexes reported in [9–12]. These complexes can

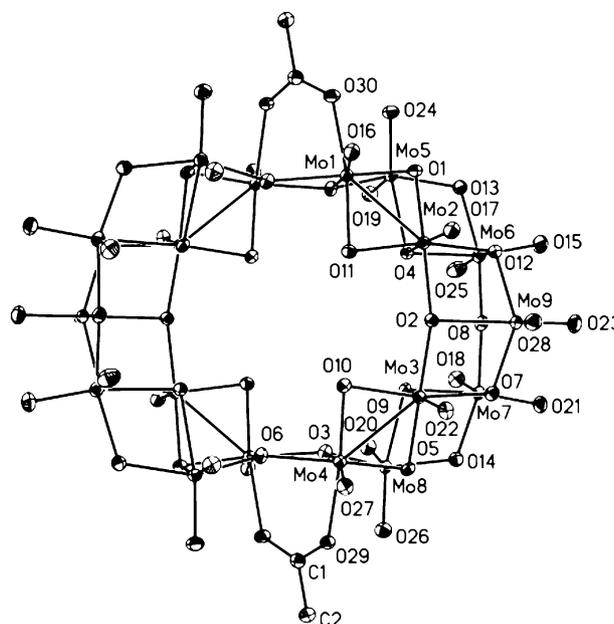


Fig. 1. The crystal structure of complex **1**.

be concluded in a structural type with a general formula of $[\text{Mo}_{18}\text{O}_{56}]$. Two acetic groups coordinate to the polyacids in μ_2 mode. The polyoxomolybdate is of -10 charge. Ten ammonium cations fill in the interspace in crystal to balance the charge. Twenty-three crystal water molecules are also found in the interspace and construct a hydrogen bond network in help of the ammonium cations. As in circumstances of some other compounds [16], crystal water and ammonium cation cannot be distinguished in different Fourier map. So all the positions of N and O were refined as O. We determined the ammonium amount according to elemental analysis.

The main difference between complex **1** and other complexes reported in previous papers [9–12] is that there is no cation in the central hole. In our previous paper [9], we have assumed that the central cations might be templates during the formation of polyoxomolybdates. But the obtaining of isostructural complex without such central cations indicates that this assumption is very probably incorrect. The central cations are not the propelling force and original kernel that decides the size and structure of produced polyoxomolybdates. It should be the polyoxomolybdates that forms first. The oxygen atoms on the inner side of the girde engender a negative charge hole that can attract positive cations in the solution. Only the size-fitting cations can enter the hole and bond to the oxygen atoms. Ca^{2+} and Na^+ cations have the appropriate ion radii ($r(\text{Ca}^{2+}) = 0.99 \text{ \AA}$ and $r(\text{Na}^+) = 0.95 \text{ \AA}$) [17], so polyoxomolybdates containing them could be obtained in the previous experiments. In the reactive mixture of current experiment, no metal cation exists except molybdenum, but the radius of $\{\text{MoO}_x\}$ is obviously too large. The radii

of hydronium and ammonium are also much larger than those of Ca^{2+} and Na^+ . So in current experiment, no cation can enter the hole.

The study on this type of complexes of $[\text{Mo}_{18}\text{O}_{56}]$ indicates that these complexes behave like crown ethers. These two kinds of compounds both have relatively steady backbone structures that form active centers. The active centers can selectively coordinate to ions of suitable radii and charges, or other parameters. This selectivity is a significance of crown ethers and some other bioactive systems. It is known that some inorganic systems, like zeolite, also have such properties. But zeolite like systems are not molecular complexes and do not have constant molecular weight and composition. Thus, $[\text{Mo}_{18}\text{O}_{56}]$ complexes are more similar to crown ethers and can be called “inorganic crown ether”. They can act as the hosts of some cations.

In conclusion, the obtaining of complex **1** is a success that proves that the central cations are not templates during the formation of this type of polyoxomolybdates. The polyoxomolybdates should construct first and form holes to encapsulate suitable cations. This type of polyoxomolybdates behaves like crown ether and can be called inorganic crown ether.

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