Communication

$[H_2N(C_2H_4)_2NH_2]_4(H_3O)[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]\cdot H_2O$: A New Highly Reduced, Bicapped Pseudo-Keggin Vanadylpolymolybdophosphate

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A new vanadylpolymolybdophosphate, $[H_2N(C_2H_4)_2NH_2]_4(H_3O)[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]\cdot H_2O$, was hydrothermally synthesized and structurally characterized by elemental analyses, IR, UV-vis, XPS, ESR spectra, and single crystal X-ray diffraction analysis. The compound contains an unusual highly reduced pseudo-Keggin type polyoxoanion with nine negative charges and exhibits an interesting phosphorus-centered alternate layer arrangement of molybdenum and vanadium oxides.

Keywords vanadylpolymolybdophosphate, highly reduced, hydrothermal synthesis, crystal structure, pseudo-Keggin

Polyoxometalates (POMs) containing Keggin moieties have been receiving extensive attention in recent years owing to their great fundamental and practical interest.[1] Especially the unusual electronic property (high negative charges), one of the most important properties of POMs, has potential applications in catalysis, medicine, electron conductivity, magnetism and photochemistry.[2-6] It is therefore vital to design and synthesize highly reduced POMs with more negative charges in order to explore their applications. In this aspect, vanadium-containing polymolybdophosphate anions with Keggin structure $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ (n = 1—3) have recently been intensively studied.[7-9] Generally, these Keggin anions have low V/Mo ratios. When V/Mo ratios are high, the negative charges of polyoxoanions increase and the anions are unstable. Introduction of electrophilic $\{VO\}^{3+}$ or $\{VO\}^{2+}$ capping groups is a rational way to stabilize the anions with higher negative charges.[10] However, the charge of the polyoxoanion will lower if more $\{VO\}^{3+}$ or $\{VO\}^{2+}$ capping groups are introduced.[11,12] Until now, no Keggin-type vanadylpolymolybdophosphates with more than seven negative charges have been structurally characterized. More recently, the introduction of hydrothermal technique and use of various organic templates have provided an effective route to synthesize various metastable compounds.[13] In this paper, we report the hydrothermal synthesis and crystal structure of an unusual highly reduced vanadylpolymolybdophosphate, $[H_2N(C_2H_4)_2NH_2]_4(H_3O)[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]\cdot H_2O$ (**1**), which contains a bicapped pseudo-Keggin polyoxoanion with nine negative charges and exhibits a novel phosphorus-centered alternate layer arrangement of molybdenum and vanadium oxides.

The compound **1** was prepared hydrothermally from a mixture of NH_4VO_3, $Na_2MoO_4\cdot 2H_2O$, H_3PO_4, $MnCl_2\cdot 4H_2O$, piperazine and H_2O in the molar ratio 1:1:2:1:2:444 heated to 150 ℃ for 6 d. After cooling to room temperature, black block crystals of **1** were isolated (yield: 65% based on V). No product is obtained without $MnCl_2\cdot 4H_2O$ in the reaction system, although Mn is not incorporated into the structure of **1**. Thus, it is supposed that

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Received February 4, 2002; revised May 10, 2002; accepted July 1, 2002.

Project supported by the National Natural Science Foundation of China (No. 20171010).

the introduction of $MnCl_2 \cdot 4H_2O$ into the reaction system is necessary for the preparation of compound **1**. Such a phenomenon is often observed in the hydrothermal preparation of oxovanadate clusters.[20]

Single crystal X-ray analysis[14] reveals that **1** consists of an unusual bicapped pseudo-Keggin polyoxoanion $[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]^{9-}$, four piperazinium dications, one protonated water and a lattice water molecule. In the polyoxoanion of **1** (Fig. 1), all molybdenum centers exhibit a distorted $\{MoO_6\}$ octahedral environment. The Mo—O distances can be grouped into three sets: Mo—O_t (terminal oxygen) 0.1661(9)—0.1685(9) nm, Mo—O_a (oxygen of the central tetrahedron) 0.243(3)—0.250(2) nm, and Mo—O_b (bridged oxygen) 0.1785(10)—0.2070(10) nm, which are similar to the previous reports.[4,5b,15] The bond angles at Mo atoms vary from 63.5(5)° to 160.2(5)°. All vanadium centers have a distorted $\{VO_5\}$ square pyramidal environment with V—O distances in the range of 0.1575(9)—0.1954(9) nm. The bond angles at V atoms range from 80.0° to 157.5°. The central P atom is surrounded by a cube of eight oxygen atoms with each site of them half-occupied. The P—O distances are in the range of 0.148(2)—0.157(2) nm, and O-P-O angels 108.0(8)°—110.3(8)°. Four $\{MoO_6\}$ octahedra form a $\{Mo_4O_{18}\}$ ring via the corner- and/or edge-sharing mode. Two $\{Mo_4O_{18}\}$ rings are connected with four $\{VO_5\}$ pyramids via the corner-sharing mode and capped with two $\{VO_5\}$ pyramids through the edge-sharing mode. Thus, a closed spherical structure with two half-occupied $\{PO_4\}$ tetrahedral encapsulated is formed.

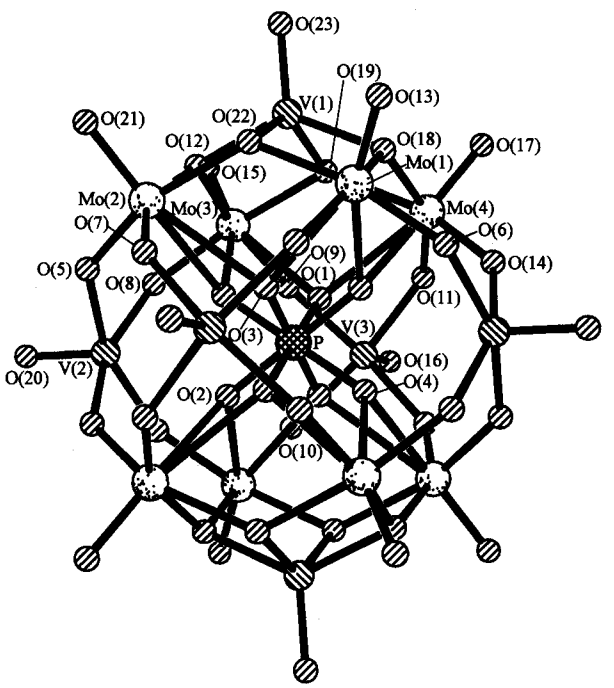

Fig. 1 Structure and numbering scheme for $[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]^{9-}$.

It is noteworthy that the polyoxoanion of **1** exhibits an unusual structural feature in contrast to the similar bicapped α-Keggin polyoxoanion $[PMo_{12}O_{40}(VO)_2]^{5-}$.[15] That is, four $\{VO_5\}$ square pyramids, while not $\{VO_6\}$ octahedra, substitute four $\{MoO_6\}$ octahedra in the equatorial sites of the $[PMo_{12}O_{40}(VO)_2]^{5-}$ to form a novel bicapped pseudo-Keggin polyoxoanion. Thus, the polyoxoanion exhibits a phosphorus-centered regular arrangement of vanadium and molybdenum oxide layers in the sequence of $\{VO_4\}/\{Mo_4O_{18}\}/4\{VO_4\}/\{Mo_4O_{18}\}/\{VO_4\}$ (Fig. 2). To the best of our knowledge, there is no precedent for such an alternate arrangement in discrete Keggin-type polyoxoanions.

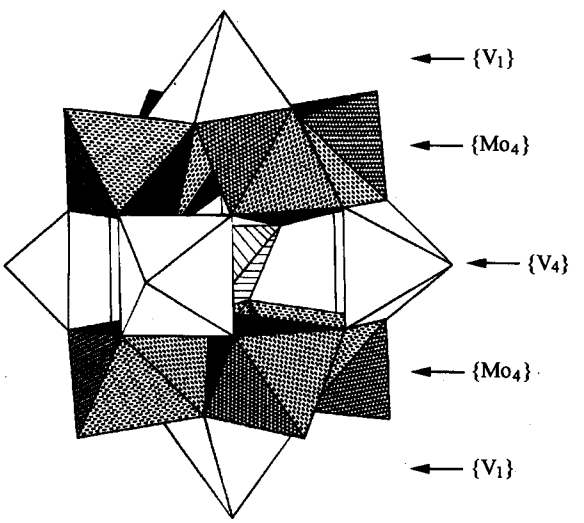

Fig. 2 Polyhedral representation of $[PMo_2^{V}Mo_6^{VI}V_4^{IV}O_{40}(V^{IV}O)_2]^{9-}$.

Another unusual feature of compound **1** is that the polyoxoanion exhibits a peculiarly high negative charge (−9), which is observed in the capped Keggin vanadylpolymolybdophosphate. Due to the introduction of a strong reductive templating reagent piperazine,[19] the polyoxoanion is highly reduced. The valence sum calculations[16] show that all oxygen atoms on the polyoxoanion have the values higher than 1.5, indicating that there ex-

ist no hydroxyl groups in the polyoxoanion.[21] The valence sum calculations give the average values of 4.10 and 5.76 for calculated oxidation states of V and Mo, respectively. The calculations show that all vanadium centers are in the +4 oxidation state, while two molybdenum atoms are in the +5 oxidation state, which confirms the molecular formula of **1**. It is also indicated that the $\{Mo_4O_{18}\}$ rings both contain one Mo^{5+} center and three Mo^{6+} centers. Furthermore, six out of eight electrons are primarily localized on six vanadium centers, while the remaining two electrons are mainly delocalized on the upper and lower $\{Mo_4O_{18}\}$ rings, respectively. Such results are also consistent with the charge requirement of the cluster and the coordination geometries of the metal atoms.

ESR spectrum at room temperature only shows a V^{4+} signal with $g = 2.07$, in accordance with the valence sum calculations. The lack of the Mo^{5+} signal suggests that the two electrons of Mo^{5+} centers are delocalized.[11,12,15] This is also proved by X-ray photoelectron spectrum (XPS) measurements of compound **1** in the energy regions of V_{2p}, $Mo_{3d}{}^{3/2}$ and $Mo_{3d}{}^{5/2}$. The XPS spectra (Fig. 3)

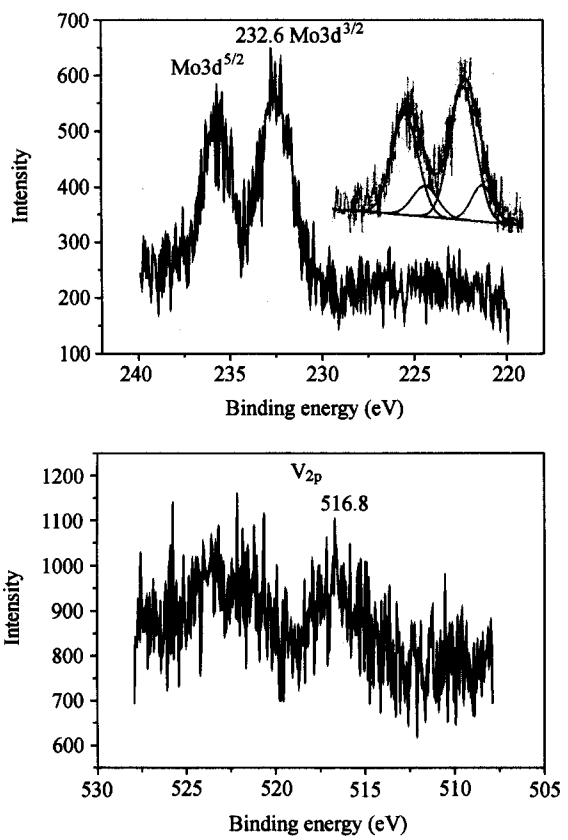

Fig. 3 XPS spectra of compound **1**.

give one peak at 516.8 eV attributable to V^{4+},[17] and two overlapped peaks at 232.7 and 231.6 eV attributable to Mo^{6+} and Mo^{5+}, respectively.[18] These results further confirm the valences of V and Mo atoms.

In the IR spectrum of **1**, the strong bands at 926, 768, 655 and 604 cm^{-1} are due to the $\nu(M=O)$ or $\nu(M\text{-}O\text{-}M)$ (M = Mo or V) vibrations. The strong peak at 1036 cm^{-1} is attributed to the vibrations of P—O bands. Two peaks at 1720 and 1609 cm^{-1} are characteristic of protonated H_3O^+ groups.[22,23] Bands in the range of 1454—1195 cm^{-1} are characteristic of N—H and C—N bonds of the organic groups.

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14 UV-vis ($BaSO_4$) λ_{max}: 196, 326, 578 nm; IR (KBr) ν: 1720, 1701, 1609, 1533, 1454, 1195, 1036, 926, 768, 655 cm^{-1}. Anal. calcd for $C_{16}H_{53}N_8O_{44}PMo_8V_6$: C 8.87, H 2.47, N 5.17, P 1.43, Mo 35.44, V 14.11; found C 8.93,

H 2.51, N 5.23, P 1.54, Mo 35.49, V 14.21. Crystal data of **1**: $C_{16}H_{53}Mo_8N_8O_{44}P_6V_6$, $M_r = 2165.80$, orthorhombic, space group *Pbca*, $a = 1.5227(5)$ nm, $b = 1.9491(4)$ nm, $c = 1.8737(3)$ nm, $V = 5.123(2)$ nm^3, $Z = 4$, $D_c = 2.807$ Mg/m^3, $T = 293(2)$ K, $F(000) = 4180$, $\mu = 3.007$ mm^{-1}. Goodness-of-fit on F^2 was 1.192. $R_1 = 0.0726$ [for $I > 2\sigma(I)$] and $wR_2 = 0.1416$ for 4513 independent reflections. A black block single crystal was mounted inside a glass fiber capillary. Data were collected on a Simens P4 four-circle diffractometer with Mo Kα ($\lambda = 0.071073$ nm) in the range of $2.07° < \theta < 25.01°$ using the ω-scan technique. Empirical absorption correction (ψ scan) was applied. The structure was solved by the direct method and refined by the Full-matrixleast-squares on F^2 using the SHELXL-93 software. All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps.

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(E0202049 LI, L. T.; DONG, L. J.)