Inorg. Chem. **2000,** *39,* 2706−2707

$(NH_4)_{15}[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(VO)_6]\cdot{\sim}60H_2O$: New Nanocompound Obtained by Chemical Embellishment of $\{M_{57}V_6\}$

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Received October 25, 1999

Because of the rich variety of their components, structures, and properties, significant attention continues to be focused on the polyoxometalatic anions in many research fields such as catalysis, biology, medicine, and materials science.[1] A handful of mixed-valence nanoscale polyoxomolybdate anions,[2] constructed of $\{Mo_8\}$ or $\{Mo_{17}\}$ units, have been reported. However, it remains a great challenge to synthesize rationally new nanoscale materials possessing novel structures and desirable properties.[2g] Although these nanostructural anions were synthesized generally via “reduction−oxidation−reconstitution” self-assembly processes,[2g,3] the so-called “chemical embellishment” has been recently desirable for the syntheses of more polyoxometalates (POMs) with unique properties, by the introduction of metal−oxygen fragments, organimetallic groups, or small cluster molecules into known POMs. Prof. Müller et. al. have pointed out that the three cavities located on the outer sphere of $\{Mo_{57}M_6\}$ (M = Fe, V) can be further blockaded step by step by some suitable metal−oxygen fragments such as $\{MoO\}^{4+}$.[3] We have been trying to introduce some special units into the cavities of $\{Mo_{57}M_6\}$ (M = V, Fe) and have been successful in introducing six $\{VO\}^{3+}$ units to give rise to a new nanocompound formulated as $(NH_4)_{15}[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(VO)_6]\cdot{\sim}60H_2O$ (**1**). In this communication, we report the synthesis, crystal structure, and properties of the title compound containing one nanoanion formulated as $[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(VO)_6]^{15-}$ (**1a**).

The nanocompound **1** was simply synthesized from the acidified aqueous solution of Na_2MoO_4 and $(NH_4)_2MoS_4$ [4] and characterized by single-crystal X-ray diffraction,[5] as well as by IR, vis−NIR, solid-state ^{51}V NMR, and ESR spectra.[6] Conventional methods including elemental analyses,[7] bond valence sum calculations,[8] and thermogravimetric (TG) measurements[9] were also applied to analyze the compound.

The X-ray single-crystal structure analysis reveals that the interesting toruslike nanoanion **1a** with $\bar{6}m2$ symmetry, exhibiting an enormous variety of polyhedra (Figures 1 and 2), consists of three large $\{Mo^{VI}_{15}(MoNO)_2O_{58}(H_2O)_2\}^{20-}$ ($\{Mo_{17}\}$) moieties that are built up by two $\{Mo_8\}$ units and one $\{Mo_1\}$ unit. This can be seen nicely in the polyhedral plots. Viewed along the 3-fold rotation axis, one $\{Mo_8\}$ building block of the $\{Mo_{17}\}$ subunits and the connecting $\{Mo_1\}$ unit are hidden. Each of the basic $\{Mo_8\}$ units possesses a seven-coordinated $\{Mo(NO)O_6\}$ pentagonal bipyramid, which is symmetrically connected to five $\{MoO_6\}$ octahedra via edge-sharings. Four of the $\{MoO_6\}$ octahedra are further linked to the other two $\{MoO_6\}$ octahedra by sharing corners to form the $\{Mo_8\}$ unit. Three $\{Mo^V(\mu_3\text{-}O)_2(\mu\text{-}OH)Mo^V\}^{5+}$ cationic centers link the three $\{Mo_{17}\}$ moieties, leading to a six-cavity anionic $[Mo_{57}(NO)_6O_{180}(OH)_3(H_2O)_6]^{45-}$ frame. Three of the six cavities, which are positioned at the inner

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(4) A solution of $Na_2MoO_4\cdot 2H_2O$ (1.94 g, 8 mmol) and $(NH_4)_2MoS_4$ (0.52 g, 2 mmol) in H_2O (50 mL) was acidified with hydrochloric acid (1.0 mL, 3.5%). After addition of NH_4VO_3 (0.23 g, 2 mmol) and $NH_2OH\cdot HCl$ (3.47 g, 50 mmol), the mixture was allowed to stand for 12 h at 75 °C (with no stirring, the color changed from red to greenish-brown to blue to deep-violet). The precipitate was filtered off, and the filtrate was allowed to stand at ambient temperature. A large number of deep-violet crystals were obtained within 2−3 days (0.62 g, yield, 32.8%). Similar reactions without adding $(NH_4)_2MoS_4$ had been carried out, but $\{Mo_{57}V_6\}$ was the main product. Moreover, we found that the final product and yield are of great concern to the mole ratio of Na_2MoO_4 to $(NH_4)_2MoS_4$. Obviously, $(NH_4)_2MoS_4$ plays an important role in the formation of **1**, although the details of the role is yet unclear.

(5) Crystal data: $H_{207}Mo_{57}N_{21}O_{273}V_{12}$, M = 10950.7 g mol^{-1}, hexagonal, space group $P6_3/mmc$, $a = 23.613(3)$ Å, $b = 23.612(3)$ Å, $c = 26.859(5)$ Å, $V = 12968(4)$ Å^3, $Z = 2$, $F(000) = 10416$, $D_c = 2.804$ g cm^{-1}, $\mu = 3.189$ mm^{-1}, crystal size = 0.65 × 0.55 × 0.55 mm^3. The diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) using the $\omega-2\theta$ scan technique at 293 K. A total of 9173 reflections ($1.25 < \theta < 26.03°$) were collected, of which 4691 independent reflections ($R_{int} = 0.0442$) were used. The structure was solved by direct methods and succeeding difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence with $R_1 = 0.0546$, $wR_2 = 0.1699$ ($I > 2\sigma(I)$).

(6) Characterization of the title compound. (a) Main characteristic bands in IR (KBr pellet, ν[cm^{-1}]): 1608 (m, $\delta(H_2O)$, $\nu(NO)$), 1410 (vs, $\delta(NH_4^+)$), 974 (m, $\nu(V{=}O)$), 945 (s) 889 (vs, $\nu(Mo{=}O)$. (b) Characteristic Raman bands (1064 nm, KBr powder diluted, ν[cm^{-1}]): 950 (w), 879 (vs), 844 (s) (all $\nu(Mo{=}O)$). (c) UV−vis λ_{max}/nm (H_2O): 755 (IVCT). (d) The solid-state ^{51}V NMR spectrum (referenced to neat NH_4VO_3, chemical shift −573.0 ppm) exhibits a strong and broad peak at −570.5 ppm, which is assigned to V^V (the ^{51}V NMR peak of V^V was broadened owing to the paramagnetic effect of V^{IV}). (e) The recorded ESR spectrum (at 77 K) of the title compound only exhibits one pattern for paramagnetic vanadium with a value of $g_{\|} = 1.9175$, $A_{\|} = 199.62$ G; and $g_{\perp} = 1.9641$, $A_{\perp} = 74.40$ G. The observed **g** tensor values are expected for vanadium (IV) centres.[13] Owing to the coupling of the unpaired electron with the nuclear spin, eight hyperfine lines were observed in the spectrum.

(7) Elemental analysis for $(NH_4)_{15}[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(VO)_6]\cdot{\sim}60H_2O$. Anal. Calcd: N, 2.69%; Mo, 49.94%; V, 5.58%. Found: N, 2.61%; Mo, 50.51%; V, 5.32%.

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(9) According to the charge requirement of the cluster, the valance sum calculations, elemental analyses, and thermogravimetric analyses (TGA), the number of NH_4^+ ions and the number of crystallized water are ~15 and ~60, respectively. The title compound lost some crystallized water when exposed to air.

10.1021/ic991249o CCC: $19.00

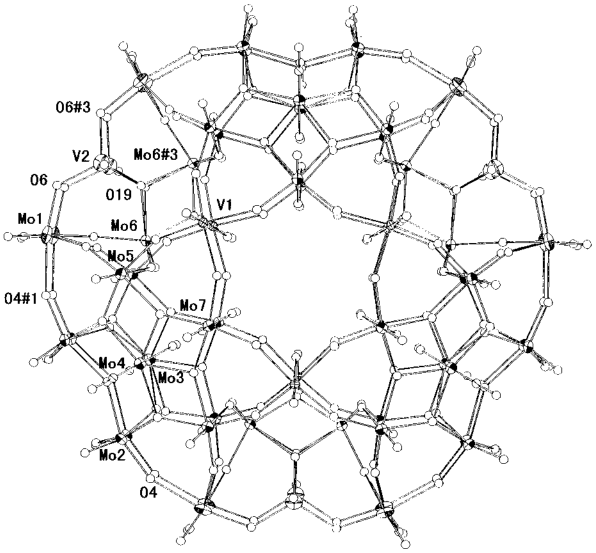

Figure 1. Perspective drawing of **1a** (viewed along the 3-fold rotation axis) (bond lengths in Å, bond angles in deg): V(2)−O(25), 1.79(2); V(2)−O(19), 1.80(2); V(2)−O(6)#3, 1.871(9); V(2)−O(6), 1.871(9); O(25)−V(2)−O(19), 111.1(9); O(25)−V(2)−O(6)#3, 110.4(4); O(19)−V(2)−O(6)#3, 108.4(4); O(25)−V(2)−O(6), 110.4(4); O(19)−V(2)−O(6), 08.4(4); O(6)#3−V(2)−O(6), 108.0(5). Symmetry transformations used to generate equivalent atoms are the following: (#1) $-y + 1, -x + 1, z$; (#2) $x, y, -z + {}^1/_2$; (#3) $-x + y + 1, y, z$; (#4) $-x + y + 1, -x + 1, z$; (#5) $-y + 1, x - y, z$; (#6) $-y, -x, z$. Other bond lengths and bond angles are within normal ranges; please see Supporting Information.

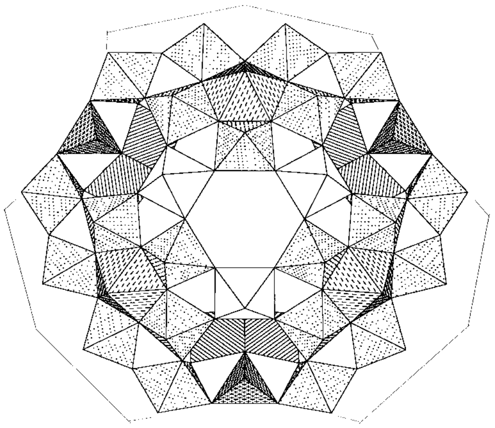

Figure 2. Polyhedral representation of **1a** (viewed along the 3-fold rotation axis) showing the $\{Mo_{17}\}$ subunits, built up by two $\{Mo_8\}$ units and one $\{Mo_1\}$ unit (from this view, another $\{Mo_8\}$ and the connecting $\{Mo_1\}$ unit are hidden). The $\{Mo^V(\mu_3\text{-}O)_2(\mu\text{-}OH)Mo^V\}$ moieties consisting of face-sharing octahedra are marked with parallel lines, the VO_4 tetrahedra are marked with crosses, and the $(O{=})V^VO_4(H_2O)$ octahedra are blank. The pentagonal Mo(NO) bipyramids have a pattern of dashed lines, and the other MoO_6 octahedra are regularly dotted.

part of the anionic frame, are blockaded by six six-coordinated $\{V^{IV}O(H_2O)\}^{2+}$ units (V1 and symmetrical positions), whereas the three outer cavities are further blockaded by six highly electrophilic, four-coordinated $\{VO\}^{3+}$ units (V2). According to the building-block principle, the giant cluster anion **1a** can be described as $[\{V^{IV}(H_2O)O\}_6\{Mo^V(\mu_3\text{-}O)_2(\mu_2\text{-}OH)Mo^V\}_3\{Mo^{VI}_{15}(MoNO)_2O_{58}(H_2O)_2\}_3\{V^VO\}_6]^{15-}$.

The IR and Raman spectra show that **1a** and $[Mo_{57}V_6(NO)_6O_{183}(OH)_3(H_2O)_{18}]^{21-}$ ($\{Mo_{57}V_6\}$) (**2**) belong to the same "family". In fact, it can be regarded that six $\{VO\}^{3+}$ groups are embedded in the three outer cavities of **2**, giving rise to the giant anion **1a** with some interesting results, such as shrinkage of the outer ring and violet shift of the IR spectrum. However, the reaction mechanism still needs to be studied further. The O19 atom is drawn toward out, while the O6 atom is drawn to the contrary (compared with that of **2**), resulting in a slight shrinkage of the angles O(6)−Mo1−O(4)#1 and Mo6−O19−Mo(6)#3 from 170.1° [2a] to 169° and 90° to 87.5°, respectively. In addition, these six embedded vanadium centers have tetrahedral coordination environments, which have seldom been found in other polyoxomolybdates except the keggin anions $\{(VO_4)M_{12}O_{36}\}^{n-}$ (M = Mo, W).

The determination of the electronic structure and of the relatively accurate formula for very large clusters is a general problem.[2,10] However, by taking into account its crystallographic data as well as elemental analyses and the thermogravimetric measurements of **1**, the formula $(NH_4)_{15}[\{V^{IV}(H_2O)O\}_6\{Mo^V(\mu_3\text{-}O)_2(\mu_2\text{-}OH)Mo^V\}_3\{Mo^{VI}_{15}(MoNO)_2O_{58}(H_2O)_2\}_3\{V^VO\}_6]^{15-}\cdot{\sim}60H_2O$ for **1** was first proposed, then verified via application of different physical methods. In anion **1a**, surely six symmetry-related V2 centers are V^V ions (they are in a tetrahedral environment, and to our knowledge, no example of V^{IV} atoms in such an environment[11] is reported), which are confirmed by solid ^{51}V NMR spectrum at room temperature.[6d] The summation of the exponentially weighed V−O bond lengths[12] shows that the octahedral vanadium centers are V^{IV}, which has been verified via ESR spectrum.[6e] The results of the ^{51}V NMR and ESR spectra are consistent with its structure in which six tetrahedral vanadium centers located on the outer sphere are V^V, while the other six octahedral vanadium atoms located on the inner side are V^{IV}.

The synthesis and characterization of **1** might provide useful information for the design synthesis of transition metal oxide based materials. It is very likely that the embedded $\{VO\}^{3+}$ units in **1a** may be replaced by other metal−oxygen fragments to give new materials with desirable properties. We are currently trying to introduce some highly electrophilic groups containing rare earth metals into the cavities of $\{Mo_{57}M_6\}$ (M = V, Fe). It is also possible to synthesize the interesting linear layer or even network compounds in connection with these relatively large cavities by suitable functional groups.

Summary

(1) The synthesis and characterization of **1** provide useful information for the design synthesis of POMs with desirable properties. (2) Chemical embellishment leads to new nanostructural anion **1a** with some interesting results. (3) Furthermore, tetrahedral-coordinated vanadium (V) is first found in nanostructural polyoxomolybdenum.

Acknowledgment. The authors thank the Chinese Academy of Sciences and the State Education Ministry for financial support.

Supporting Information Available: Ball and stick model showing the side view of **1a**, ESR and NMR plots of **1a**, a DT-TGA plot of **1**, and two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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