$[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]\cdot 2Hen\cdot 3H_2O$. The First Dimeric Arsenic-Vanadium Cluster Linked by $Zn(en)_2$ Complex Bridge

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The hydrothermal reaction of $VOSO_4$, As_2O_3, $ZnCl_2$, en (ethylenediamine), HCl, and H_2O produces $[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]\cdot 2Hen\cdot 3H_2O$, which is the first dimeric As-V-O cluster linked by transition metal complex bridge. The structure of this compound was characterized by single crystal X-ray diffraction, elemental analysis, EPR, TGA, and IR spectrum.

The interest in polyoxometalates is rapidly expanding because of the enormous variety of structural topologies and unexpected properties in such diverse fields as catalysis, materials science and medicine.[1] Recently, hydrothermal method has been proven to be an effective technique for the preparation and crystal growth of metal-oxo clusters.[2] So far, a number of metal-oxo clusters, typically reduced Mo-O clusters, mixed-valence V-O clusters, and W-O clusters, are readily assembled to produce discrete clusters, one-, two-, and three-dimensional framework materials.[3–7] But the dimeric structure of metal-oxo clusters linked by bridge groups is rare. To our knowledge, only two dimeric structure of $(H_2NC_4H_8NH_2)_7[Mo^{VI}_{16}V^{IV}_{12}V^{V}_{2}O_{84}]\cdot nH_2O$[8] and $[\{(H_2O)Ni(enMe)_2Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}(V^{V}O_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$[9] were reported. The former contains two $\{Mo_8V_7O_{42}\}$ units linked together by two V–O–V bonds, while the latter contains two $[\{(H_2O)Ni(enMe)_2\}Mo_8V_9O_{44}]$ units joined together via one $Ni(enMe)_2$ complex bridge. Here, we report the hydrothermal synthesis and single crystal investigation of the first dimeric As-V-O cluster, $[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]\cdot 2Hen\cdot 3H_2O$ (**1**), containing two mixed As/V $[\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)]$ units connected together through zinc complex bridge.

Compound **1** was synthesized by hydrothermal method. A mixture of $VOSO_4$ (0.35 g), As_2O_3 (0.10 g), ZnO (0.17 g), en (0.40 mL), HCl (37 wt %, 0.2 mL) and H_2O (10 mL) in a molar ratio of 4:1:4:13:11:1111 was stirred for ca. 110 min in air, and then was transferred and sealed in a 30 mL Teflon-lined stainless bomb (pH = 7). After heating to 160 °C under autogenous pressure for 4 days, the bomb was cooled down to room temperature. Black block crystals of compound **1** were filtered off, washed with distilled water, and air-dried at room temperature (ca. 58% yield based on V). Anal. Calcd. for $C_{24}H_{108}As_{12}N_{24}O_{89}V_{30}Zn_5$: C, 5.87; H, 2.22; N, 6.84%. Found: C, 5.71; H, 2.09; N, 6.67%. IR (KBr) $\tilde{\nu}_{max}$: 979 and 1019 cm^{-1} (V=O); 629 and 749 cm^{-1} (M–O–M′) (M, M′ = As, V).

The X-ray analysis[10] reveals that the compound **1** consists of the novel $[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]^{2-}$ polyanion dimer, isolated singly protonated Hen^+ cations and lattice water molecules. The $[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]^{2-}$ dimeric anion (Figure 1) is constructed from two $[\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)]^{4-}$ units and one μ_2-$[Zn(en)_2]^{2+}$ group. The $[\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)]^{4-}$ unit is a mixed As/V cluster anion of $[As_6V_{15}O_{42}(H_2O)]^{6-}$ decorated by two $\{Zn(en)_2\}^{2+}$ complex groups. The $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion is essentially identical with the cluster anion in $K_6[As_6V_{15}O_{42}(H_2O)]\cdot nH_2O$.[11] But one remarkable difference between $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion in **1** and $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion in $K_6[As_6V_{15}O_{42}(H_2O)]\cdot nH_2O$ is that $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion in **1** acts as a ligand coordinated to Zn(1) and Zn(2), to give a new $[\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)]^{4-}$ anion, and then two $[\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)]^{4-}$ anions are further joined together through $Zn(3)(en)_2$ bridging group in the linkage of –V=O–Zn–O=V– to form a dimer cluster anion, while anion $[As_6V_{15}O_{42}(H_2O)]^{6-}$ in $K_6[As_6V_{15}O_{42}(H_2O)]\cdot nH_2O$ links directly K^+ cations via oxygen atoms from anion $[As_6V_{15}O_{42}(H_2O)]^{6-}$ to form a 3-D structure. The assignment of oxidation states for the vanadium and arsenic atoms of compound **1** is consistent with their coordination geometries and confirmed by bond valence sums (BVS),[12] that is, the average valence units (v.u.) for As and V are 3.05 and 3.90, respectively.

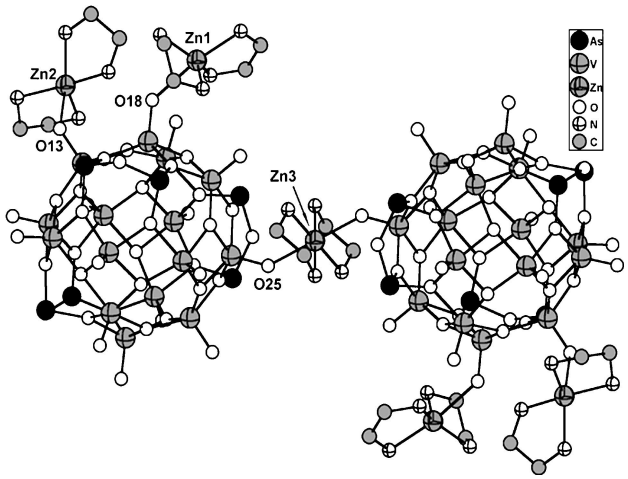

Figure 1. The view of the dimeric anion of $[\{\{Zn(en)_2\}_2As_6V_{15}O_{42}(H_2O)\}_2\{Zn(en)_2\}]^{2-}$.

Singly protonated Hen^+, acting as charge-compensating cations, and lattice water molecules occupy in the structure. To zinc atoms, there are two different coordination environments. The octahedral geometry around Zn(3) atom is completed by two en groups and two *trans*-oxo groups from two neigh-

boring clusters. The bridge of $Zn(3)(en)_2$ exhibits covalent attachments to the two adjacent clusters with Zn–O(25) distances of 2.260(8) Å. Because the shortest distances between Zn atoms (Zn(1), Zn(2)) and oxygen atoms from the adjacent dimeric clusters are 3.77 Å and 3.75 Å, respectively, each of the decorative $Zn(1)(en)_2$ and $Zn(2)(en)_2$ groups only connects one oxo atom from $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion and forms a distorted square-pyramidal environment of $Zn(1)N_4O(18)$ and $Zn(2)N_4O(13)$. The Zn–O bond distances in the square-pyramidal $Zn(1)N_4O(18)$ and $Zn(2)N_4O(13)$ are 2.415(9) Å and 2.281(8) Å respectively, and the N–Zn–N angles are in the range of 85.0(7)–140.2(7)° for Zn(1) and 83.9(5)–166.2(6)° for Zn(2).

In previous literature,[13,14] several Mo-O clusters and As-Mo-O clusters supported by transition metal complex have been reported. Compound **1** shows that the As-V-O clusters could also be decorated by transition metal complex under certain hydrothermal conditions. And the compound **1** is the first dimeric arsenic-vanadium cluster.

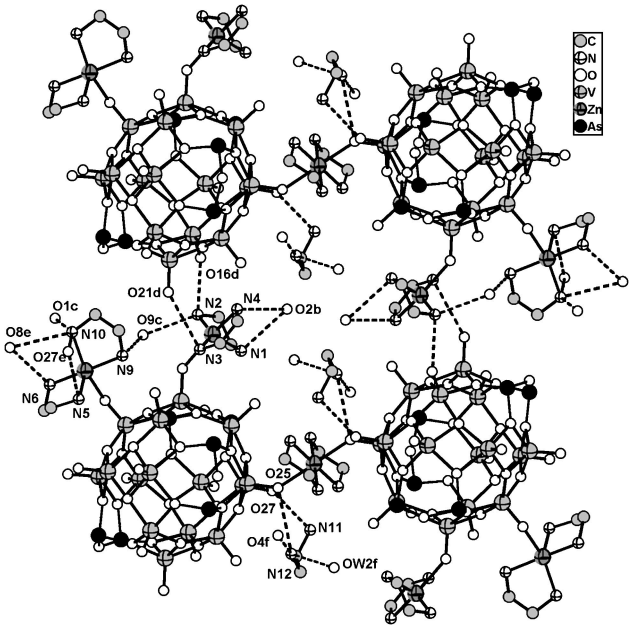

Figure 2. Hydrogen bonds of the cluster with Hen^+ and H_2O. The hydrogen atoms are omitted for clarity.

Compared with the known-structure of mixed Mo/V dimeric anion linked by coordination fragment, $[\{(H_2O)Ni(enMe)_2Mo^{V}{}_4Mo^{VI}{}_4V^{IV}{}_8(V^{V}O_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$,[9] the dimeric anions link together through very weak interactions betweeen the dimeric anions and charge-compensating cations $[Ni(enMe)_2]^{2+}$ to give 2-D layered structure; whereas, in compound **1**, each As-V-O dimeric anion joins adjacent dimeric anions through strong hydrogen bonds among the amine nitrogen atoms, water molecules and oxygen atoms of the dimeric anions, thus resulting in three-dimensional network. As shown in Figure 2, the supported $[Zn(en)_2]^{2+}$ cations interact with the dimer through hydrogen bonds: N1···O2b(b: $x-1$, y, z): 3.109(15) Å; N2···O9c(c: $x-1/2$, $-y+1/2$, $z-1/2$): 3.063(16) Å; N2···O16d(d: $x-1$, y, $z-1$): 2.848(15) Å; N3···O21d: 3.29(2) Å; N4···O2b: 3.307(19) Å; N5···O27e(e: x, y, $z-1$): 3.197(15) Å; N6···O8e: 3.023(15) Å; N9···O9c: 2.927(16) Å; N10···O1c: 2.931(16) Å; N10···O27e: 3.109(16) Å. The isolated Hen^+ cations interact with the dimer and lattice water molecules through hydrogen bonds of the type N12···O4f (f: $-x+2$, $-y$, $-z+2$): 2.87(2) Å; N12···O27: 3.054(19) and N12···OW2f: 2.92(2) Å. Such strong multipoint hydrogen bonding appears to be a structural determinant in the general class of inorganic–organic composite solids.[15]

The thermogravimetric analysis carried out in a flow of nitrogen for the compound **1** indicates that the weight loss of **1** can't be completely divided into distinct stages. The whole stage, which occurs from 238 to 735 °C, is attributed to the loss of H_2O, en and the sublimation of the As_2O_3. Assuming that the residue corresponds to VO_2 and ZnO, the obseved weight loss (41.21%) is in good agreement with the calculated value (41.05%). The EPR spectrum of **1** at liquid nitrogen temperature shows the g value is 1.9658 corresponding to the signal of V^{4+}. It is consistent with both black crystal and the result of valence sum calculations.

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References and Notes

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10 X-ray structure data for **1**. Monoclinic, space group $P2_1/n$, $a = 13.3644(2)$ Å, $b = 38.4698(7)$ Å, $c = 13.47740(10)$ Å, $\beta = 111.9390(10)°$, $V = 6427.29(16)$ Å^3, $Z = 2$, $D_{calcd} = 2.538$ g·cm^{-3}, μ(Mo Kα) = 6.149 mm^{-1}, Mo Kα radiation, $\lambda = 0.71073$ Å. A black block crystal with dimensions of $0.70 \times 0.38 \times 0.36$ mm was performed on a Bruker Smart CCD diffractometer at 298 K in the range of $2.12 < \theta < 24.99$ using ω and ϕ scan. A total of 18851 data were collected and were merged to give 10459 unique reflections of which 8167 were considered to be observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined using SHELXL 97 software. All the non-hydrogen atoms were refined anisotropically. Final R values ($R = 0.0762$, w$R = 0.1425$, and $S = 1.108$) were obtained for 8167 reflections with $I > 2\sigma(I)$ and a total 830 of parameters. Atomic coordinates, bond lengths and angles, and the terminal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 210804).
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