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A Novel Sodium Germanomolybdate Constructed from $[H_2Ge_2Mo_6O_{26}]^{6-}$ Polyoxoanions and $[Na_6(H_2O)_{12}]^{6+}$ Clusters

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A novel sodium germanomolybdate compound $[Na_6(H_2O)_{12}][H_2Ge_2Mo_6O_{26}]$ (**1**) has been successfully synthesized by conventional solution method. The structure was determined by single-crystal X-ray diffraction analysis and further characterized by IR and UV spectroscopy and X-ray powder diffraction (XRPD). X-ray structural analysis reveals that **1** crystallizes in triclinic space group $P\bar{1}$, with lattice constants $a = 8.466(4)$ Å, $b = 10.290(4)$ Å, $c = 11.159(5)$ Å, $\alpha = 72.305(6)°$, $\beta = 71.115(6)°$, $\gamma = 76.969(5)°$, $V = 867.5(6)$ Å, and $Z = 1$, which consists of a novel polyoxoanion $[H_2Ge_2Mo_6O_{26}]^{6-}$ and a $[Na_6(H_2O)_{12}]^{6+}$ cluster. Furthermore, the dimeric polyoxoanion units link alternate $[Na_6(H_2O)_{12}]^{6+}$ clusters to generate a 3D framework.

The investigation of polyoxometalates (POMs) continues to attract interest, and numerous effort have been devoted not only for their enormous structural diversities and topological beauty but also for their potential applications in the fields of catalysis, sorption, electrochemistry, optics, medicine, magnetism, and functional materials.[1,2] Heteropolymolybdates (HPMs) are an important part of this field[3,4] because of the redox-active nature of molybdenum. Meanwhile HPMs could be molecularly fine-tuned and provide potential new types of catalyst systems, as well as interesting functionalized materials with other properties. As we all know, HPMs contain Keggin,[5] Dawson,[6] Anderson,[7] Waugh,[8] Silverton,[9] Strandberg,[10] and Weakely[11] types and their lacunary species.[12] To date, the existence of Ge^{IV}-containing HPMs has been known for several decades, and most of the published work has been based on chiefly the Keggin-type germanomolybdates. In 1982, Strandberg and Hedman reported a plenary Keggin-type germanomolybdate $[C(NH_2)_3]_4[GeMo_{12}O_{40}]$.[13] In 2003, Wang et al. isolated three novel lanthanide-containing germanomolybdates $[Ln(NMP)_4(H_2O)_4][H_xGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ ($Ln = Ce^{IV}$, Pr^{IV}, $x = 0$; $Ln = Nd^{III}$, $x = 1$; NMP = *N*-methyl-2-pyrrolidone).[14] Since the first monolacunry germanomolybdate $[Nd(GeMo_{11}O_{39})_2]^{13-}$ was reported in 1990,[15] lacunary germanomolybdate derivatives have been discovered successively. In 2009, five novel transition-metal-substituted sandwich-type germanomolybdates $Na_{12}(H_2O)_{36}[Cu_2(\beta\text{-Y-GeMo}_9O_{33})_2]_3\cdot 3H_2O$, $[N(CH_3)_4]_4[Na_6(H_2O)_{24}][Cr_2(\beta\text{-Y-GeMo}_9O_{33})_2]_3\cdot 7H_2O$, and $[Na_{11}(H_2O)_{25}]H[M_4(H_2O)_2(\alpha\text{-B-GeMo}_9O_{34})_2]_3\cdot 6H_2O$ ($M = Ni^{II}/Mn^{II}/Co^{II}$) were separated by our group.[16] In 2010, Xu's group reported a 1D chain compound $(Him)_8Na_7H_7[Cu(im)_4(CuGeMo_9O_{33})_2][(CuGeMo_9O_{33})_2]\cdot 41H_2O$ (im: imidazole).[17] As shown above, the reports on lacunary germanomolybdates are very rare. The reason for this phenomenon is probably that lacunary HPM polyoxoanions are labile and easy to rearrange into a saturated Keggin polyoxoanion; therefore the successful isolation of lacunary HPM polyoxoanions still remains a great challenge. In this context, we have spent much time and attention on this field with the aim of finding rational reaction conditions to obtain novel compounds based on lacunary HPM polyoxoanion building units. Finally, we obtained a novel 3D network POM, $[Na_6(H_2O)_{12}][H_2Ge_2Mo_6O_{26}]$ (**1**).[18] To the best of our knowledge, compound **1** represents the first HPM based on $[H_2Ge_2Mo_6O_{26}]^{6-}$ clusters. Moreover, it is the first 3D network structure based on germanomolybdate clusters $[H_2Ge_2Mo_6O_{26}]^{6-}$.

Compound **1** was synthesized successfully by the reaction of simple starting materials containing $Na_2MoO_4\cdot 2H_2O$, GeO_2, $In(NO_3)_3\cdot 5H_2O$, and 2,6-bipy-dica (2,6-bipy-dica: 2,6-bipyridinedicarboxylic acid) in stoichiometric amounts. Unfortunately, the $In(NO_3)_3\cdot 5H_2O$ and 2,6-bipy-dica did not occur in the final compound. In contrast, without addition of $In(NO_3)_3\cdot 5H_2O$ and 2,6-bipy-dica, compound **1** was not formed. Hence, we presume that $In(NO_3)_3\cdot 5H_2O$ and 2,6-bipy-dica in the preparation of **1** play a catalytic role.

X-ray diffraction analysis[19] reveals that the molecular structural unit of **1** consists of a sodium cluster $[Na_6(H_2O)_{12}]^{6+}$ and a polyoxoanion $[H_2Ge_2Mo_6O_{26}]^{6-}$. The polyoxoanion $[H_2Ge_2Mo_6O_{26}]^{6-}$ is an A-type isomer (Figure 1a); that is, two $[GeO_4]$ tetrahedra were capped with the opposing faces of a Mo_6O_6 ring. The Mo_6O_6 ring is constructed from six $[MoO_6]$ octahedra linked to each other in the edge-sharing mode. Each capped $[GeO_4]$ tetrahedron is linked to $[MoO_6]$ octahedra via corner-sharing. This structural feature is similar to the reported $[H_2As_2Mo_6O_{26}]^{6-}$ cluster.[20] Three kinds of oxygen atoms exist in the $[H_2Ge_2Mo_6O_{26}]^{6-}$ cluster: the terminal oxygen O_t, double-bridging oxygen $O(\mu_2)$, and three-bridging oxygen $O(\mu_3)$. Thus the Mo–O bond lengths can be grouped into three sets: $Mo\text{–}O_t = 1.720(4)\text{–}1.725(4)$ Å, $Mo\text{–}O(\mu_2) = 1.917(4)\text{–}1.950(4)$ Å, and $Mo\text{–}O(\mu_3) = 2.237(4)\text{–}2.295(4)$ Å. The Ge–O bond lengths fall into two classes: $Ge\text{–}O_t = 1.784(4)$ Å and $Ge\text{–}O(\mu_3) = 1.766(4)\text{–}1.780(4)$ Å. Bond valence sum calculations confirm that all the Mo atoms are in +6 oxidation state, both Ge atoms are in +4 oxidation state, and all the oxygen atoms in the polyoxoanion are −2 oxidation state. The calculation results indicate the two terminal oxygen atoms (O13 and O13A) attached to the two Ge atoms are protonated. In addition, six Na^+ cations in the $[Na_6(H_2O)_{12}]^{6+}$ cluster display different coordination modes. The $Na(1)^+$ and $Na(2)^+$ ions inhibit six-coordinate octahedral geometry, but the $Na(3)^+$ ion adopts a trigonal bipyramid environment, and all the coordination oxygen atoms come from water molecules and polyoxoanions. The six Na^+ ions join together through corner-sharing forming a

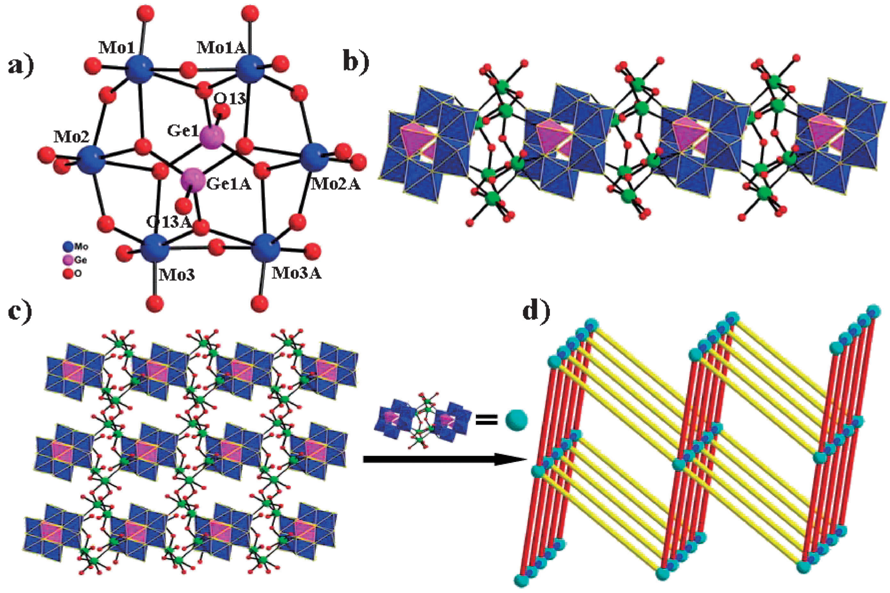

Figure 1. (a) The polyhedral view of the structural unit of **1**. The sodium and hydrogen atoms were omitted for clarity, A: $1 - x$, $1 - y$, $1 - z$; (b) the polyhedral/ball-and-stick representation of 1 D chain of **1**. The hydrogen atoms were omitted for clarity; (c) the polyhedral/ball-and-stick representation of 2 D sheet structure of **1**. The lattice water molecules have been omitted for clarity; (d) schematic illustrating the 3-D topological network of **1**.

hexatomic ring, and all the Na–O$_{\mu1/\mu2}$ bond lengths are in the range of 2.313(8)–2.973(5) Å. Moreover, the $[H_2Ge_2Mo_6O_{26}]^{6-}$ polyoxoanions are alternately linked by the hexatomic rings. Based on such linking fashion, the 1D chain-like assembly is generated (Figure 1b). In addition, adjacent 1D chains are connected by multiple Na(1)–O(3W)–Na(1) bonds forming a 2D sheet structure (Figure 1c). Furthermore, the adjacent 2D planes are joined together by Na–O bonds generating a 3D network structure. To the best of our knowledge, compound **1** represents the first example of 3D net structure based on germanomolybdate cluster $[H_2Ge_2Mo_6O_{26}]^{6-}$. From a topological viewpoint, when the dimeric polyoxoanion units with a sodium oxygen hexaatomic ring is viewed as a six-connected node and the adjacent sodium oxygen hexaatomic rings acts as the bridges, the structure of **1** can be described as a six-connected framework with the Schönflies symbol of $(4^{12}\cdot6^{3})$ (Figure 1d).

In the IR spectrum of compound **1** (Figure S1[23]), the characteristic peaks at 927, 892, 740, and 629 cm^{-1} correspond to ν(Mo–O$_t$), ν(Ge–O$_{\mu3}$), ν(Mo–O$_{\mu2}$), and ν(Mo–O$_{\mu3}$) stretches, respectively.[21] In addition, the resonances at 1000–1650 cm^{-1} are possibly due to an impurity such as 2,6-bipy-dica.

The compound **1** displays a strong absorption at 205 nm that can be assigned to the charge-transfer transition of the Mo–O band.[22] To investigate the influences of the pH value on the stability of the compound in aqueous solution, in situ UV spectroscopic measurements of **1** were performed in aqueous solution. The pH values in the acidic direction were adjusted using dilute HCl solution while the pH values in the alkaline direction were adjusted using dilute NaOH solution. The pH value of **1** dissolved in water (5×10^{-5} mol L^{-1}) was 4.25. As shown in Figure S2,[23] the UV spectrum of **1** in aqueous solution displays absorption bands at pH 4.25; when the pH value gradually decreased under 3.58, the absorption band at 205 nm was gradually red-shifted. A conclusion can be drawn that the skeleton of **1** has been destroyed when the pH value is lower than 3.58. In contrast, when the pH value of **1** increased, the absorption band at 205 nm was weaker until it vanished suggesting the decomposition of skeleton of **1**. The above analyses show that the pH stable ranges of **1** in aqueous solution are about 3.58–9.72.

The experimental XRPD pattern of the bulk products of **1** is in good agreement with the simulated XRPD pattern based on the results from single-crystal X-ray diffraction, indicating the phase purity of the sample (Figure S3[23]). The intensity difference between the experimental and simulated XRPD pattern is due to the variation in preferred orientation of the powder sample during collection of the experimental XRPD.

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18 Synthesis of **1**: $Na_2MoO_4 \cdot 2H_2O$ (2.08 g, 8.59 mmol) and GeO_2 (0.1 g, 1 mmol) were successively dissolved in 40 mL of HAc–NaAc buffer solution (pH 5.0, 0.5 mol L^{-1}), and then $In(NO_3)_3 \cdot 5H_2O$ (0.19 g, 0.49 mmol) and 2,6-bipy-dica (0.1 g, 0.60 mmol) were added. The resulting mixture was heated in a water bath (80 °C) for 1 h and filtered after cooling. Slow evaporation at room temperature led to colorless crystals suitable for X-ray diffraction within 2–3 weeks, which were collected by filtration and dried in air (Yield: ca. 30% based on GeO_2). Elemental analyses calcd for $H_{26}Ge_2Mo_6Na_6O_{38}$: H, 1.85; Na, 9.33; Ge, 9.62; Mo, 38.61%. Found: H, 1.76; Na, 9.24; Ge, 9.73; Mo, 38.56%. IR (KBr) pellets, (ν/cm^{-1}): ν(Mo–O_t), ν(Ge–O_a), ν(Mo–O_b), and ν(Mo–O_c) appear at 927, 892, 740, and 629 cm^{-1}.

19 Crystallographic data: For **1**: $H_{26}Ge_2Mo_6Na_6O_{38}$, $M_r = 1493.04$, Triclinic, $P\bar{1}$, $a = 8.466(4)$ Å, $b = 10.290(4)$ Å, $c = 11.159(5)$ Å, $\alpha = 72.305(6)$, $\beta = 71.115(6)$, $\gamma = 76.969(5)°$, $V = 867.5(6)$ Å^3, $T = 296(2)$ K, $Z = 1$, $\mu = 4.001$ mm^{-1}, 4341 reflections measured, 3005 independent ($R_{int} = 0.0157$), $R_1 = 0.0350$ ($I > 2\sigma(I)$), $wR_2 = 0.0916$ (all data). CSD number: 424088.

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