$[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$: The First Dimer of Polyoxometalates Linked through Coordination Fragment

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The hydrothermal reaction of V_2O_5, MoO_3, $NiCl_2\cdot 6H_2O$, enMe (1,2-diaminopropane) and H_2O produces $[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$, which is the first compound containing polyanion dimer linked by transition metal coordination fragment. The structure of this compound was determined by single crystal X-ray diffraction, EPR and IR analysis.

The chemistry of polyoxometalates continues to attract interest as a result of their realized and potential applications in fields as catalysis, material science and medicine.[1,2] Recently an important advance in the metal oxo cluster chemistry is that some interesting compounds with open framework structures have been prepared by hydrothermal synthesis.[3–6] These structures are constructed from some bridge groups and polyanions, such as $[H_2en]_2[\{Cu(en)(OH)_2\}Mo_5P_2O_{23}]\cdot 4H_2O$,[3] $[H_2en]_2[\{Cu(en)_2\}Mo_5P_2O_{22}(OH)_2]\cdot 2H_2O$,[3] $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]\cdot 3H_2O$,[3] $[Ni(en)_2]_2[Ni(en)_2Mo_6V_{10}O_{40}(VO_4)]\cdot 4H_2O$,[4] $[en]_{0.5}[Cu(en)_2]_2[Cu(en)_2Mo_8V_8O_{40}(MoO_4)]\cdot 0.5H_2O$,[4] $[Co(en)_3][\{Co(en)_2\}_2As_6V_{15}O_{42}]\cdot 4H_2O$[5] and $Na_{0.5}K_{6.5}[Mo_8V_4O_{36}(VO_4)(VO)_2]\cdot 12.5H_2O$.[6] To the best of our knowledge, the dimeric structure of polyoxoanions linked by bridge groups is very limit.[7] Here we reported the first heteropolyanion dimer compound, $[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$ (**1**),[8] containing two mixed Mo/V heptadecaoxometalate clusters linked by transition metal coordination fragment.

Compound **1** was synthesized by hydrothermal method. A mixture of V_2O_5 (0.20 g), MoO_3 (0.32 g), $NiCl_2\cdot 6H_2O$ (0.26 g), enMe (0.16 g), and H_2O (20 ml) in a molar ratio of 1 : 2 : 1 : 2 : 1000 was stirred for ca. 10 min in air, and then was transferred and sealed in a 30 ml Teflon-lined stainless bomb. After heated to 160 °C under autogenously pressure for 48 h, the bomb was cooled down to room temperature. Black block crystals of compound **1** were filtered off, washed with water, and air-dried at room temperature (ca. 20% yield based on V). Anal. Calcd. for $C_{42}H_{160}Mo_{16}N_{28}Ni_7O_{98}V_{18}$: C, 9.19; H, 2.94; N, 7.15; Ni, 7.48; V, 16.71; Mo, 27.97%. Found: C, 8.37; H, 2.45; N, 7.07; Ni, 7.29; V, 16.08; Mo, 27.54%. IR spectrum: 972 and 955 cm^{-1} ($\nu_{M=O}$); 840 and 675 cm^{-1} (ν_{M-O-M}) (M=V or Mo).

The X-ray analysis reveals that the compound **1** consists of the novel $[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}]^{8-}$ (**2**) polyanion dimer, $[Ni(enMe)_2]^{2+}$ cations and lattice water molecules. The anion **2** (Figure 1) contains two $[(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}]^{5-}$ (**3**) units and one bridged $[Ni(enMe)_2]^{2+}$ group. Each unit **3** is a reduced $[Mo^{VI}_4Mo^V_4V^{IV}_8O_{40}(VO_4)]^{7-}$ (**4**) polyanion supported by transition metal complex $[Ni(enMe)_2(H_2O)]^{2+}$. The anion **4** is

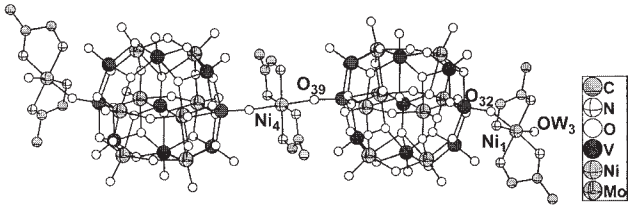

Figure 1. The view of the polyoxometalates dimer $[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}]^{8-}$.

based on the α-Keggin structure of $[XM_{12}O_{40}]^{n-}$ with four *trans* five-coordinated capping VO^{2+} units. Compared to the first tetra-capped Keggin structure $[Mo_8V_8O_{40}(PO_4)]^{5-}$,[9] each anion **4** contains a central V^{5+} in an almost regular VO_4 tetrahedron with V–O distances in the range 1.687(9)–1.703(9) Å, bond angles of 108.7(4)–110.5(4)°. All atoms in anion **4** are order, while some Mo, V and O atoms in $[Mo_8V_8O_{40}(PO_4)]^{5-}$ are disorder. All the Mo atoms in **4** have a distorted octahedral environment, while V atoms, except the central VO_4, display two different coordination environments: square pyramidal and distorted octahedral. The Mo–O and V–O bond lengths are in the range of 1.674(9)–2.443(9) and 1.581(11)–2.444(10) Å, respectively, comparable to those found in capping-Keggin structures. The cage of anion **4** consists of a central V_8 ring constructed from four VO_5 pyramids and four VO_6 octahedra, and two Mo_4 rings bonded above and below this V_8 ring (Figure 2). There are two reduced Mo atoms in

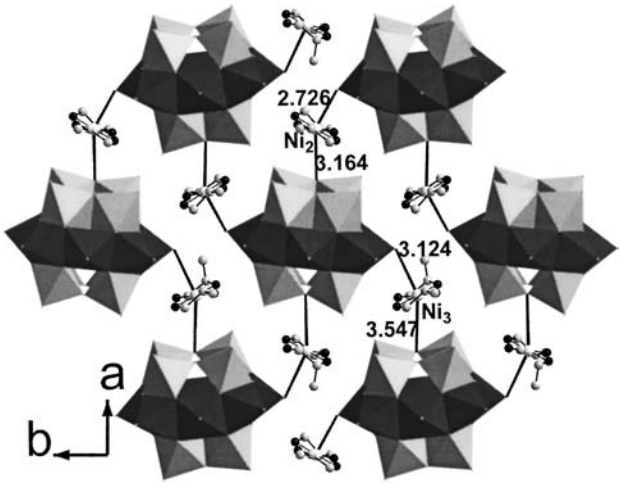

Figure 2. The polyhedral and ball-and-stick representation of the 2-D layered structure of the compound **1** along *c* axis. The deep grey polyhedrons represent the VO_5 pyramids and VO_6 distorted octahedra, and the light grey polyhedrons represent the MoO_6 octahedra.

each Mo_4 ring of **4**, while only one reduced Mo atom in Mo_4 ring of $[Mo_8V_8O_{40}(PO_4)]^{5-}$. One remarkable difference between anion **4** and $[Mo_8V_8O_{40}(PO_4)]^{5-}$ is that anion **4** acts as a ligand toward Ni(1), to give a novel polyanion **3**. Two identical anions **3** are further linked together via $Ni(4)(enMe)_2$ bridging group in the linkage of –V=O–Ni–O=V– to form dimer **2**. In anion **3**, the bond lengths for Ni(1)–O(32), Ni(1)–Ow(3) and Ni(1)–N are 2.120(9), 2.120(14) and 2.071(18)–2.124(17) Å, respectively. The Ni(4)–O(39) distance is 2.105(9) Å and the Ni(4)–N length ranging from 2.041(19)–2.118(18) Å in dimer **2**.

As shown in Figure 2, the dimeric anion **2** as building blocks links together through *trans*-$O_2Ni(2)(enMe)_2$ and *trans*-$O_2Ni(3)(enMe)_2$ groups to give 2-D layered structure. The thickness of the layer is just the length of the dimer. It is worth noting that each Ni atom of the $Ni(2)(enMe)_2$ and $Ni(3)(enMe)_2$ groups is coordinated to two different oxygen atoms from two adjacent **2**, respectively; one oxygen atom is a terminal oxygen of V=O group, another is a sharing bridged oxygen from two MoO_6 octahedra. The distances for (μ_3-O)–Ni (3.164(8), 3.547(8) Å) and (μ_2-O)–Ni (2.726(10), 3.124(10) Å) represent very weak interactions between anion **2** and *trans*-$Ni(enMe)_2$ groups. To our knowledge, the linking mode between anion **2** and *trans*-$Ni(enMe)_2$ groups has not been reported before.

The assignment of the oxidation state for the metal atoms is consistent with the electric charge and confirmed by bond valence sum calculations. The BVS[10] values of the V(1)–V(9) are 4.15, 4.28, 4.17, 4.18, 4.13, 4.03, 4.01, 3.99 and 5.30 respectively, clearly indicating that the oxidation state of V(1)–V(8) is +4, while V(9) is +5. The BVS[10] values of the Mo(1)–Mo(8) are 5.46, 5.47, 5.29, 5.54, 5.46, 5.56, 5.33 and 5.28, respectively, which indicates that the Mo atoms of compound **1** is mixed valence. The average value for calculated oxidation state of Mo is 5.42, consistent with the formula of **1**.

The EPR spectra of **1** at room temperature and liquid nitrogen temperature show no signals for Mo^{5+} and V^{4+}. The lack of signals for Mo^{5+} and V^{4+} indicates that the 12 electrons of the polyanion unit $[Mo^{V}{}_4Mo^{VI}{}_4V^{IV}{}_8(V^{V}O_4)O_{40}]^{7-}$ are in spin-spin coupling.

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8 X-ray structure data for **1**. Monoclinic, space group $P2_1/n$, $a = 19.68200(10)$ Å, $b = 13.5806(2)$ Å, $c = 27.7928(3)$ Å, $\beta = 90.5960(10)^\circ$, $V = 7428.43(14)$ Å^3, $Z = 4$, $D_{calcd} = 4.908\,g\,cm^{-3}$, μ(Mo Kα) $= 6.672\,mm^{-1}$, Mo Kα radiation, $\lambda = 0.71073$ Å. A black block crystal with dimensions of $0.28 \times 0.20 \times 0.16$ mm was mounted on a glass fiber. Data collection was performed on a Bruker Smart CCD diffractometer at 298 K in the range of $1.67 < \theta < 25.05$ using ω and ϕ scan. A total of 26009 data were collected and were merged to give 12422 unique reflections of which 7777 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 except C(21) were refined anisotropically. Final R values ($R = 0.0780$, $wR = 0.1303$, and $S = 1.083$) were obtained for 7777 reflections with $I > 2\sigma(I)$ and a total 937 of parameters. Atomic coordinates, bond lengths and angles, and the terminal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 189963).
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