Two- and Three-Dimensional Frameworks Constructed From Bicapped Keggin Clusters

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The novel two- and three-dimensional solid materials $[Cu(en)_2(H_2O)]\{PMo^{VI}{}_8V^{IV}{}_6O_{42}[Cu(en)_2][Cu_{0.5}(en)]_3\}\cdot 5.5H_2O$ and $H_3\{V^VMo^{VI}{}_8V^{IV}{}_6O_{42}[Cu(en)_2]_4\}[MoO_4]_2\cdot 14H_2O$ (en = ethylenediamine) have been hydrothermally assembled and structurally characterized. Both networks are based on mixed Mo/V bicapped Keggin clusters interconnected through the transition metal complex moieties.

The design and synthesis of framework materials linked by well-defined building blocks is still a challenge for the solid-state inorganic and material chemist. Polyoxometalates (POMs) have received considerable attention due to their diverse structures and unusual properties, with potential applications in fields such as catalysis, magnetism, optics and medicine.[1] Some POMs of the bicapped Keggin structure have been synthesized, such as discrete clusters $[V_{15}O_{42}]^{9-}$, $[PMo_{12}V_2O_{42}]^{5-}$ and $[PMo_8V_6O_{42}]^{5-}$,[2] the dimer cluster anions $[Mo_{16}V_{14}O_{84}]^{14-}$ [3] and one-dimensional chains connected through V−O−V bonds.[4] Our group has recently reported the first transition metal coordination compound supported on a metal-oxygen cluster with a bicapped Keggin structure.[5] There has recently been increasing interest in the assembly of higher-dimensional networks comprised of POM clusters and various bridging groups, either inorganic or organometallic. Typical compounds connected by metal cations include $[(CH_3)_4]_4Na_2H[\alpha\text{-}PW_{11}O_{39}]\cdot 8H_2O$,[6a] $[Gd(H_2O)_3]_3[GdMo_{12}O_{42}]\cdot 3H_2O$[6b] and a series of mixed-metal framework materials based on spherical $[V_{18}O_{42}(XO_4)]$ cages linked through $[M(H_2O)_4]$ groups (X: V, S; M: Fe, Co, Mn, Zn).[6c,6d] By introducing organic groups, some two-dimensional solid materials consisting of POMs and transition metal complexes have been assembled, such as $[\{Cu_3(4,7\text{-phen})_3\}_2\{Mo_{14}O_{45}\}]$, $[\{Cu(en)_2\}_2Mo_8O_{26}]$, $[Co(2,2'\text{-bpy})Mo_3O_{10}]$ and $[Co(en)_2][Co(bpy)_2]_2[PMo_8V_8O_{44}]\cdot 4.5H_2O$,[7] however, only a few three-dimensional compounds like $[\{Cu_2(triazolate)_2(H_2O)_2\}Mo_4O_{13}]$, $[Cu_2Mo_2O_8(4,4'\text{-bpy})]_n\cdot 4H_2O$ and $[\{Cu(1,2\text{-pn})_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$[8] are known.

As a continuation of the hydrothermal synthesis of various polyoxometalates, we are trying to construct higher-dimensional frameworks from POM clusters through different bridging groups, especially transition metal complexes, and several compounds such as the two-dimensional $[\{Co(en)_2\}_2Sb_8V_{14}O_{42}(H_2O)]\cdot 6H_2O$ and $K\{V_{12}{}^{IV}V_6{}^{V}O_{42}Cl[Ni(en)_2]_3\}\cdot 8H_2O$ have been assembled.[9] Here, we report the hydrothermal synthesis and structural characterization of two- and three-dimensional framework materials $[Cu(en)_2(H_2O)]\{PMo^{VI}{}_8V^{IV}{}_6O_{42}[Cu(en)_2][Cu_{0.5}(en)]_3\}\cdot 5.5H_2O$ (**1**) and $H_3\{V^VMo^{VI}{}_8V^{IV}{}_6O_{42}[Cu(en)_2]_4\}[MoO_4]_2\cdot 14H_2O$ (**2**), both of which are based on the further condensation of the bicapped Keggin clusters $[XMo_8V_6O_{42}]^{7-}$ (X = P, V) through the linkage of $[Cu(en)_2]^{2+}$ bridging groups. To the best of our knowledge, no higher-dimensional networks constructed from bicapped Keggin clusters connected by transition metal coordination complexes have been reported until now.

The extended structure of compound **2** consists of $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ clusters, each of which is interconnected through eight $[Cu(en)_2]^{2+}$ bridging groups to eight other neighboring clusters via μ_2-O-Cu interactions, generating a three-dimensional network. The $MoO_4{}^{2-}$ anions and water molecules occupy the cavities of the network solid. The structure of the cluster anion $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ in compound **2** is shown in Figure 1. The polyoxomolybdovanadate $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ has a reduced bicapped Keggin structure, which can be described as one Keggin core of $[VMo_8V_4O_{40}]^{11-}$ capped by two additional $\{VO\}^{2+}$ units. The vanadium atoms in compound **2** display three different coordination environments, including a disordered VO_4 tetrahedron at the center, distorted VO_6 octahedra as the sphere shell com-

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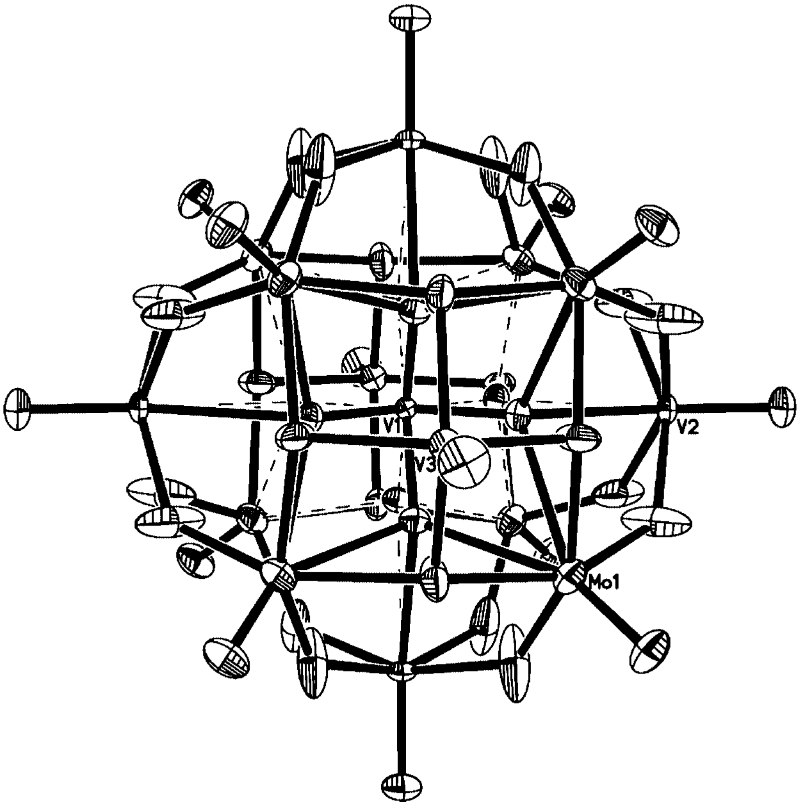

Figure 1. View of the $[V^{V}Mo^{VI}_{8}V_{6}^{IV}O_{42}]^{7-}$ cluster in compound **2**

position and VO_5 square pyramids at the capping positions. The central V(1) atom is located at the inversion center (0, 0, 0), which indicates that the central V(1) atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. All the central V(1)−O distances are 1.689(10) Å, while the O−V(1)−O angles vary from 109.1(3)° to 110.2(7)°. The V(2)−O bond lengths in each VO_6 distorted octahedron vary as follows: 1.607(8) Å for terminal oxygens, 1.942(8)−1.945(7) Å for double or triply bridging oxygens and 2.418(10) Å for the oxygens of the central VO_4 tetrahedron. The V(3)−O distances in the VO_5 square pyramid are 1.633(12) Å for the capping terminal oxygens and 1.938(6) Å for the bridging oxygens. The Mo(1) atoms in the cluster have a distorted octahedral environment with the following Mo(1)−O distances: Mo(1)−$O_{terminal}$ 1.676(6) Å; Mo(1)−O_{bridge} 1.797(7)−2.065(10) Å and Mo(1)−O_{center} 2.412(10)−2.465(10) Å. The MoO_4^{2-} ions contained in the cavities are slightly distorted tetrahedra with Mo(2)−O bond lengths 1.757(6) Å and O−Mo(2)−O angles of 107.3(4)° or 110.6(2)°.

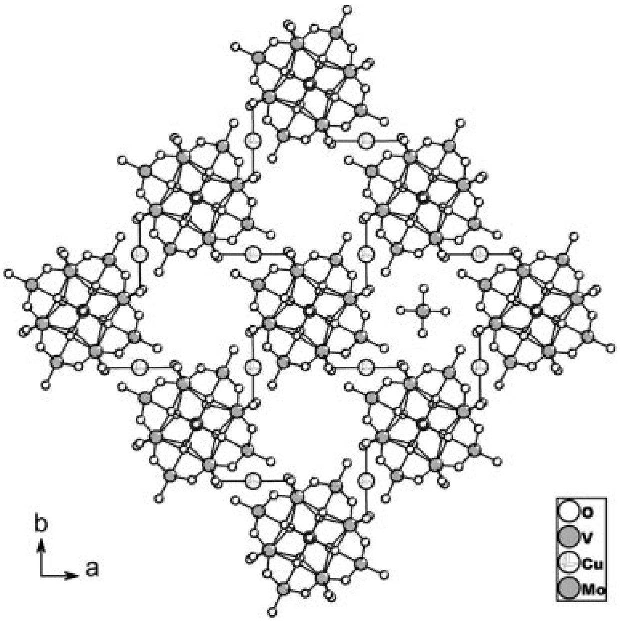

Figure 2. View of the three-dimensional framework structure of **2**, showing the clusters of $[V^{V}Mo^{VI}_{8}V_{6}^{IV}O_{42}]^{7-}$ interconnected through $[Cu(en)]^{2+}$ bridging groups; H_2O and en have been omitted for clarity

As shown in Figure 2, all eight terminal oxo groups of the distorted MoO_6 octahedra in every $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ cluster are connected to a copper center, which, in turn, is coordinated to four nitrogen donors from two ethylenediamine molecules. The CuN_4 moiety of each $[Cu(en)_2]^{2+}$ group is rectangular, with Cu−N bond lengths of 2.007 and 2.008 Å, and N−Cu−N angles of 94.7(3)° and 85.3 (3)°. We may therefore describe the CuN_4O_2 unit as a highly distorted octahedron, with two axial Cu−O bonds being obviously elongated. Thus, each $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ cluster is connected to all of the adjacent ones through $[Cu(en)_2]^{2+}$ bridging groups in different directions via weak μ_2-O-Cu interactions, forming a three-dimensional network. Usually, the lattice waters and/or some cations reside in the cavities, while in compound **2** the MoO_4^{2-} anions occupy the cavities of the three-dimensional network along with water molecules. Furthermore, this is the first example where MoO_4^{2-} ions are found together with bicapped Keggin $[(VO_4)Mo_8V_4O_{36}(VO)_2]^{7-}$ cluster anions.

The X-ray structure analysis of compound **1** reveals that the $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ cluster anion is similar to the polyoxoanion $[VMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ of compound **2**. In comparison with other bicapped Keggin polyoxoanions, the unusual feature[5] of **1** is that the $[Cu(en)_2]^{2+}$ units along the *b* axis supported on the bicapped Keggin structure unit $[PMo_8V_6O_{42}]^{7-}$ are not bridging groups. The two-dimensional network structure of **1** (Figure 3) consists of $\{PMo_8V_6O_{42}\ [Cu(en)_2]\}$ cages, each of which is connected to three other neighboring cluster units via $[Cu(en)_2]^{2+}$ bridging groups with Cu−O distances of 2.498−2.880 Å. This generates a two-dimensional network composed of $[\{PMo_8V_6O_{42}[Cu(en)_2]\}\{Cu(en)_2\}\{PMo_8V_6O_{42}[Cu(en)_2]\}]_n$, which is wave-like along the crystallographic *a* axis. To the best of our knowledge, this is the first example of such a compound possessing an extended structure constructed from bicapped Keggin structure clusters.

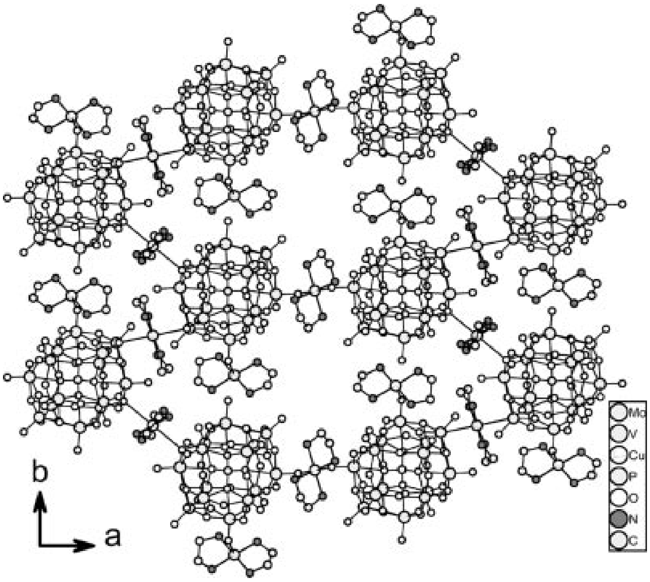

Figure 3. View of the two-dimensional network structure of **1**, showing the framework of $\{PMo_8V_6O_{42}[Cu(en)_2]\}$ clusters interconnected through $[Cu(en)_2]^{2+}$ bridging groups along the [001] direction

The assignments of oxidation states for the vanadium and molybdenum are consistent with their coordination geometries and are confirmed by valence sum calculations.[10] In compound **1**, the valence sums for the eight Mo atoms are 5.72, 5.74, 5.79, 5.85, 5.87, 5.83, 5.78 and 5.82, respectively, with an average value of 5.80; for the six V atoms the values are 3.96, 4.04, 4.12, 4.05, 4.12 and 4.07, respectively, with an average value of 4.06. The calculated values are 5.96 for Mo1, 6.04 for Mo2, 5.10 for the central V1 atom, 4.29 for V2 and 4.02 for the capping V3 atom in compound **2**. The room temperature ESR spectra of crystalline samples of compounds **1** and **2** display signals with $g = 1.976$ and $g = 2.055$, respectively, indicating the existence of V^{IV}. According to these ESR results, bond valence sum calculations, charge balance and elemental analyses, compounds **1** and **2** are formulated as $[Cu(en)_2(H_2O)]\{PMo^{VI}_8V^{IV}_6O_{42}[Cu(en)_2][Cu_{0.5}(en)]_3\}\cdot5.5H_2O$ and $H_3\{V^VMo^{VI}_8\ V^{IV}_6O_{42}[Cu(en)_2]_4\}[MoO_4]_2\cdot14H_2O$, respectively.

In summary, we have synthesized the first two- and three-dimensional solid materials constructed from bicapped Keggin structure clusters and $[Cu(en)_2]^{2+}$ bridging groups. The successful design and synthesis of compounds **1** and **2** confirms once more that the further condensation of various POM clusters into higher-dimensional extended networks through the linkage of the transition metal complexes is feasible by controlling the synthesis conditions of the hydrothermal system. The formation of a particular product is usually restricted by various factors, and the rational synthesis of many kinds of compounds, including POMs and their polymers, is still difficult even under hydrothermal conditions. However, certain conditions are important for the assembly of higher-dimensional networks, such as the pH value of the reaction system, the species and metal-to-organic ligand ratio. For example, both compounds **1** and **2** were prepared with an en:Cu^{2+} molar ratio of less than 2, with the pH value ranging from 7 to 8. We have found that the formation of the $[Cu(en)_2]^{2+}$ complex supported on the polyoxomolybdovanadate or its polymer is very difficult when the en:Cu^{2+} molar ratio is greater than 3. Under particular synthetic conditions, certain types of targeted POMs or their polymers are reproducible and their structural type are roughly predictable, although the mechanism of the assembly remains elusive. Further systematic research is currently under way.

Experimental Section

Synthesis of 1: Compound **1** was synthesized as black block-shaped crystals by a hydrothermal method. A mixture of $CuCl_2\cdot2H_2O$ (1.20 g), $Na_2MoO_4\cdot2H_2O$ (1.6 g), NH_4VO_3 (0.8 g), en (0.6 mL), H_3PO_4 (0.5 mL, 50%) and distilled water (12 mL) at pH 7.0 was placed in a Teflon-lined reactor and heated at 170 °C for three days. After cooling to room temperature crystals of the title compound were isolated. $C_{14}H_{69}Cu_{3.5}Mo_8N_{14}O_{48.5}PV_6$ (2536.3): calcd. C 6.63, H 2.74, N 7.73; found C 6.74, H 2.65, N 7.58. The IR spectrum of **1** exhibits an intense band at 725 cm^{-1} attributed to ν(Mo-O, V-O), other bands at 1596, 1455, 1397, 1283, 1125 cm^{-1} that are characteristic of en, and bands at 1106, 1049 cm^{-1} attributed to ν(P-O).

Synthesis of 2: This compound was also synthesized by a hydrothermal method. A mixture of $CuAc_2\cdot H_2O$ (0.8 g), $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (1.2 g), V_2O_5 (0.6 g), KOH (0.2 g), en (0.3 mL) and water (20 mL) was sealed in a 30 cm^3 Teflon-lined reactor and kept at 180 °C for four days at a pH of about 7.0. The autoclave was then cooled to room temperature. Black block-shaped crystals of **2** suitable for an X-ray diffraction analysis were isolated and washed with water, then dried at ambient temperature. Compound **2** is stable in air and insoluble in water and common organic solvents. $C_{16}H_{92}Cu_4Mo_{10}N_{16}O_{64}V_7$ (3103.1): calcd. C 6.16, H 3.08, N 7.22; found C 6.28, H 3.21, N 7.09. The infrared spectrum of **2** exhibits strong absorption peaks at 954, 929 and 853, 760 cm^{-1} attributed to the ν(M=O) or ν(M-O-M) (M = Mo or V) bands. A series of bands at 1591, 1457, 1281, 1197, 1113 and 1055 cm^{-1} is attributed to the en groups.

X-ray Crystallography: *Crystal data for **1**:* $C_{14}H_{69}Cu_{3.5}Mo_8N_{14}O_{48.5}PV_6$, dimensions 0.39 × 0.28 × 0.12 mm^3, orthorhombic, space group *Pccn*, $a = 47.8809$ (13), $b = 13.3322$ (4), $c = 20.2559$ (6) Å, $V = 12930.5(6)$ $Å^3$, $Z = 8$, $D_c = 2.606$ g/cm^3, μ(Mo-K_α) = 3.576 mm^{-1}. The data were collected at 293 K using a Rigaku R-AXIS RAPID diffractometer (graphite monochromated Mo-K_α radiation; $\lambda = 0.71073$ Å, $1.88 \leq \theta \leq 23.33°$). Unique reflections were used to solve the structure by direct methods (SHLXTL 97). The structure was refined on F^2 by full-matrix least-squares techniques, converging at $R = 0.0579$ [$I \geq 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.188 for 872 parameters and 58933 reflections, 9314 unique [R(int) = 0.0563]. The Cu(1), Cu(3) and Cu(4) atoms have an occupancy of 0.5 because of their special position. All non-hydrogen atoms were refined anisotropically.

*Crystal data for **2**:* $C_{16}H_{92}Cu_4Mo_{10}N_{16}O_{64}V_7$, dimensions 0.45 × 0.38 × 0.23 mm^3, tetragonal, space group *I*4/*m*, $a = 14.1958$ (5), $c = 20.1604$ (11) Å, $V = 4062.7(3)$ $Å^3$, $Z = 2$, $D_c = 2.537$ g/cm^3, μ(Mo-K_α) = 3.385 mm^{-1}**.** The data were collected at 293 K using a Rigaku R-AXIS RAPID diffractometer (graphite monochromated Mo-K_α radiation; $\lambda = 0.71073$ Å, $1.75 \leq \theta \leq 23.25°$). Unique reflections were used to solve the structure by direct methods (SHLXTL 97). The structure was refined on F^2 by full-matrix least-squares techniques, converging at $R = 0.0508$ [$I \geq 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.113 for 152 parameters and 9820 reflections, 1509 unique [R(int) = 0.0895]. The Mo(2), Cu(1), V(1), V(2), O(1), O(5) and O(6) have an occupancy of 0.25, 0.5, 0.125, 0.5, 0.5, 0.5 and 0.25, respectively, because of their special position. All non-hydrogen atoms were refined anisotropically.

CCDC-198448 (**1**) and -203045 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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