3D Supramolecular Array Assembled by Cross-like Arrangement of 1D Sandwich Mixed Molybdenum−Vanadium Polyoxometalate Bridged Coordination Polymer Chains: Hydrothermal Synthesis and Crystal Structure of $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2\cdot 4H_2O$

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ABSTRACT: A novel organic−inorganic hybrid material constructed from mixed molybdenum−vanadium polyoxoanion clusters and $[Ni(en)_2]^{2+}$ complex groups $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2\cdot 4H_2O$ (**1**) (en = ethylenediamine), has been prepared under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. Complex **1** exhibits an interesting three-dimensional supramolecular array through cross-like arrangement of a one-dimensional coordination polymer anion chain $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}^{4-}$, which is sandwiched by discrete cation complex fragments $[Ni(en)_2]^{2+}$. It is the first example of a three-dimensional organic/inorganic hybrid polyoxometalate formed by cross-like arrangement of a one-dimensional polyoxometalate bridged coordination polymer chain.

Introduction

The study of organic−inorganic hybrid polyoxometalates is a very active and expanding research area. The interest is stimulated by not only their rich structure chemistry but also their extensive potential applications in heterogeneous catalysis, host−guest chemistry, biochemistry, nanotechnology, and electrical, magnetic, photochemical materials.[1] Combining hydrothermal techniques with the structure-directing and coordination properties of organic amines has already provided an effective strategy for the syntheses of new polyoxometalate-based organic−inorganic hybrid solid materials. Recently, as an advance in this field, many polyoxometalates with covalently linked transition metal fragments have been prepared hydrothermally,[2−5] showing various structures of zero-dimensional (0D) discrete clusters,[2] one-dimensional (1D) chains,[3] two-dimensional (2D) networks,[3d,4] and three-dimensional (3D) frameworks.[3d,5] On the other hand, "dimensional expansion" through polymeric assemblies of lower dimensionality into an architecture of higher dimensionality is particularly interesting in the field of coordination polymer's crystal engineering.[6] For example, the 2D → 3D dimension expansion can be realized by means of either inclined[7] or parallel[8] interpenetration of 2D networks. Parallel and inclined interpenetration of 1D coordination polymers may generate 2D networks (1D → 2D)[9] and 3D frameworks (1D → 3D),[10] respectively. Recent research indicated the 1D → 3D dimension expansion will occur if 1D coordination polymer chains in the adjacent layers are arranged in a cross-like fashion.[7a,11] Nevertheless, to our knowledge, there has been little exploration of the dimension expansion of polyoxometalate coordination polymers. Herein we present the hydrothermal synthesis and crystal structure of a novel organic−inorganic hybrid material $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2\cdot 4H_2O$ (**1**) (en = ethylenediamine), in which the coordination polymer anion chains $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}^{4-}$ are arranged in a cross-like fashion to generate a 3D supramolecular array.

Experimental Procedures

Materials and Methods. $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ (reference fw: 1825.25) was obtained from Strem Chemicals, Inc. All other chemicals were of reagent grade and purchased from Beijing Shuanghuan Chemicals, Inc. Elemental analyses (C, H, and N) were performed on a Heraeus Chn-Rapid elemental analyzer. The infrared spectrum was recorded on a Pekin-Elmer 2000 spectrophotometer using pressed KBr pellets. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/max-2500 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.

Preparation of Complex 1. A mixture of NH_4VO_3 (3.0 mmol), $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ (0.5 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (1.0 mmol), ethylenediamine (3.0 mmol), and H_2O (16 mL) was stirred for 20 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 °C for 10 days. After the autoclave had cooled to room temperature over 6−7 h, black block-shaped crystals of **1** were isolated, washed with water and then dried at ambient temperature. Yield: 60% based on nickel. The phase purity of the as-synthesized sample was confirmed by its powder X-ray diffraction pattern, which is entirely consistent with the simulated pattern on the basis of the single-crystal structure. Complex **1** is stable in air and insoluble in water and common organic solvents. Anal. Calcd for $C_{12}H_{56}Mo_8N_{12}Ni_3O_{48}PV_8$ (**1**): C, 5.72; H, 2.24; N, 6.67. Found: C, 5.67; H, 2.30; N, 6.61. IR (KBr, cm^{-1}): 3422(s, br), 3325(s), 3276(s), 2946(w), 1584(m), 1458(w), 1324(w), 1215(w), 1103(w), 1029(w), 943(vs), 773(s),

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Table 1. Crystal Data for Complex 1

formula	$C_{12}H_{56}Mo_8N_{12}Ni_3O_{48}PV_8$
fw	2518.82
T (K)	293(2)
crystal system	monoclinic
space group	$C2/c$
a (Å)	26.186(5)
b (Å)	13.520(3)
c (Å)	19.559(4)
β (deg)	106.60(3)
V (Å^3)	6636(2)
Z	4
D_c (g cm^{-3})	2.513
μ(Mo Kα) (mm^{-1})	3.477
reflections collected	14112
independent reflections	7550 [R(int) = 0.0250]
observed data [$I > 2\sigma(I)$]	5115
final R1,^{a} wR2^b [$I > 2\sigma(I)$]	0.0371, 0.0948
goodness-of-fit on F^2	0.932

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $\Sigma\{[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$.

707(s). XPS: C 1s 284.80, O 1s 529.80, P 2p 132.40, Ni 2p$_3$ 855.30, V 2p$_3$ 516.20, Mo 3d 231.75 eV.

Crystallography. A single crystal of **1** with the approximate dimensions $0.38 \times 0.35 \times 0.18$ mm^3 was mounted on a Rigaku RAXIS RAPID IP imaging plate system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 14112 [7550 unique, R(int) = 0.0250] reflections were corrected in the range of $4.62 \leq 2\theta \leq 54.96°$ ($-33 \leq h \leq 33$, $-17 \leq k \leq 17$, $-25 \leq l \leq 25$), of which 5115 with $I > 2\sigma(I)$ were used in the refinement of the structure. The data were corrected for Lorentz-polarization effects, and absorption corrections were applied. The structure was solved by the Patterson method and refined by a full matrix least-squares technique based on F^2 using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms except those in hydrate molecules were allowed for as riding atoms. The crystal data and data collection and refinement parameters for complex **1** are given in Table 1; selected bond lengths and angles are listed in Table 2.

Results and Discussion

Synthesis. Hydrothermal synthesis has recently been proven to be a powerful technique in the preparation of organic−inorganic hybrid polyoxometalates. Several mixed molybdenum−vanadium polyoxometalates with covalently linked transitional metal complex fragments have been prepared successfully in our group[2g,2h,4f] and other groups[2i,2j,3e,4h] recently. When NH_4VO_3 and H_3-$[P(Mo_3O_{10})_4]\cdot xH_2O$ were used as starting materials, the resultant mixed molybdenum−vanadium polyoxoanion generally acted as a ligand to link complex fragments;[2g,4f] while when NH_4VO_3, Na_2MoO_4, and phosphorous acid were used as the corresponding precursors, the formed mixed molybdenum−vanadium polyoxoanion can act as either a counterion[2k] or a special ligand,[2i,2j,3e,4h] depending upon the reaction conditions, such as reactant stoichiometry, acidity, temperature, pressure, and time. The formation of complex **1** from the hydrothermal reaction of NH_4VO_3, $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$, $Ni(NO_3)_2\cdot$ $6H_2O$, ethylenediamine, and H_2O in the molar ratio of 3:0.5:1:3:889 at 170 °C for 10 days confirms that the approach to utilizing NH_4VO_3 and $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ as starting materials is suitable for construction of mixed molybdenum−vanadium heteropolyoxometalate decorated by transition metal complexes. It is noteworthy that the ethylenediamine molecule in this hydrothermal reaction acts as not only an organic ligand but also a reductive agent adjusting the pH value of the reaction system. Organic diamine ligands acting as

Table 2. Bond Lengths (Å) and Angles (deg) for Complex 1^a

Ni1−N2	2.083(5)	Ni1−N1	2.088(5)
Ni1−O13	2.156(4)	Ni2−N3	1.894(6)
Ni2−N4	1.921(6)	Ni2−N5	1.900(6)
Ni2−N6	1.909(6)	Mo1−O8	1.867(4)
Mo1−O10	1.669(4)	Mo1−O19	1.974(4)
Mo1−O22	1.992(4)	Mo1−O5$^{#1}$	1.869(4)
Mo2−O18	1.667(4)	Mo2−O5	1.863(5)
Mo2−O7	1.865(5)	Mo2−O16	1.978(4)
Mo2−O14	1.985(4)	Mo3−O9	1.664(4)
Mo3−O8$^{#1}$	1.866(4)	Mo3−O6	1.870(4)
Mo3−O23	1.982(4)	Mo3−O24$^{#1}$	1.996(4)
Mo4−O15	1.665(4)	Mo4−O6	1.861(4)
Mo4−O7	1.874(5)	Mo4−O20	1.967(4)
Mo4−O12	1.981(4)	V1−O13	1.626(4)
V1−O23$^{#1}$	1.933(4)	V1−O16	1.934(4)
V1−O14	1.935(4)	V1−O24	1.944(4)
V2−O17	1.599(4)	V2−O12	1.975(4)
V2−O16	1.979(4)	V2−O22	1.982(4)
V2−O24	1.991(4)	V3−O11	1.603(4)
V3−O20	1.939(4)	V3−O22	1.947(4)
V3−O12	1.950(4)	V3−O19	1.954(4)
V4−O21	1.592(4)	V4−O19	1.976(4)
V4−O20	1.981(4)	V4−O23	1.991(4)
V4−O14$^{#1}$	1.985(4)	O5−Mo$^{#1}$	1.869(4)
O23−V1$^{#1}$	1.933(4)	O24−Mo3$^{#1}$	1.996(4)
O8−Mo3$^{#1}$	1.866(4)	O14−V4$^{#1}$	1.985(4)
N2−Ni1−N1	82.4(2)	N2−Ni1−N2$^{#2}$	180.000(1)
N2$^{#2}$−Ni1−N1	97.6(2)	N2−Ni1−N1$^{#2}$	97.6(2)
N2$^{#2}$−Ni1−N1$^{#2}$	82.4(2)	N1−Ni1−N1$^{#2}$	180.000(1)
N2−Ni1−O13$^{#2}$	89.65(18)	N2$^{#2}$−Ni1−O13$^{#2}$	90.35(18)
N1−Ni1−O13$^{#2}$	89.20(18)	N1$^{#2}$−Ni1−O13$^{#2}$	90.80(18)
N2−Ni1−O13	90.35(18)	N2$^{#2}$−Ni1−O13	89.65(18)
N1−Ni1−O13	90.80(18)	N1$^{#2}$−Ni1−O13	89.20(18)
O13$^{#2}$−Ni1−O13	180.0(2)	N3−Ni2−N5	177.6(3)
N3−Ni2−N6	94.5(3)	N5−Ni2−N6	86.6(3)
N3−Ni2−N4	84.6(3)	N5−Ni2−N4	94.4(3)
N6−Ni2−N4	178.3(3)		

^{a} Symmetry code: (#1) $-x - 1/2$, $-y + 5/2$, $1 - z$; (#2) $-x$, $3 - y$, $1 - z$.

reductive agents under hydrothermal conditions have also been observed in the preparation of many other organic−inorganic hybrid materials.[2k,4f,12] Furthermore, the crystallization of **1** was found to be highly sensitive to the pH value of the reaction mixture, which was controlled at 6.0−6.5, and no crystalline product could be obtained beyond this pH range.

Crystal Structure. The structure of **1** consists of the 1D anion chains $\{[Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}^{4-}$ and the cation complex fragments $[Ni(en)_2]^{2+}$ as well as some solvent water molecules (Figure 1). The anion chain is a 1D nickel(II) coordination polymer containing mixed molybdenum−vanadium heteropolyoxometalate bridges $[Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}(PO_4)]^{6-}$. This heteropolyoxometalate is based on the Keggin structure of $[Mo_8V_4O_{36}(PO_4)]^{14-}$ with four capping five coordinated terminal VO^{2+} units, and it shows a tetracapping Keggin structure constructed from eight VO_5 square pyramids by sharing square edges to form a central belt and two Mo_4 rings bonded above and below this V_8 belt, and a disordered PO_4^{3-} anion in the center as a guest, which is very similar to that in $[Ni(tea)_2]_3[PMo^{VI}_5-Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ (tea = triethylenediamine),[2k] $\{Co-(tea)_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$,[2k] $[Co(en)_2][Co-(bpy)_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bpy = 2,2′-bipyridine),[4f] $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}-(PO_4)[Co(phen)_2(H_2O)]_2\}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$ (phen = 1,10-phenanthroline),[2g] and $\{Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}(PO_4)-[Co(phen)(en)(H_2O)]_2\}[Co(phen)_3]\cdot 1.5H_2O$ (en = ethylene-
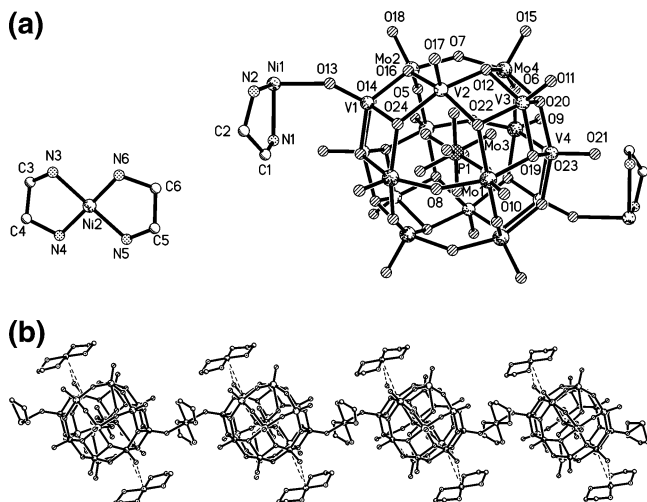
(a)

(b)

Figure 1. (a) ORTEP view of complex **1** with atom labels, showing 50% probability displacement ellipsoids. The H atoms and solvent water molecules are omitted for clarity. (b) Molecular structure of complex **1** showing a sandwich-like coordination polymer chain. All water molecules and H atoms are omitted for clarity.

diamine).[2g] The Mo$-$O and V$-$O bond lengths are as follows: Mo$-$O$_t$, 1.664(4)$-$1.669(4) Å; Mo$-$O$_b$, 1.861(4)$-$1.996(4) Å; V$-$O$_t$, 1.592(4)$-$1.626(4) Å; V$-$O$_b$, 1.934(4)$-$1.991(4) Å.

Each $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ cluster is covalently bonded to two complex fragments $[Ni(en)_2]^{2+}$ through the terminal oxygen atoms of two opposite capping V atoms. Therefore, the heteropolyoxometalate $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ acts as a special ligand toward Ni^{2+} ions, generating a 1D coordination polymer chain with the intrachain Ni$\cdots$Ni separation distance of 14.735 Å. These anion chains are arranged parallel to the direction [2 2 0] or [2 $-$2 0] to form layers along the *ab* plane, with the interchain distance of about 26.2 Å (in the same layer). The nickel atom (Ni1) in the anion chain exhibits a slightly distorted octahedral geometry, which is defined by two oxygen atoms from two different $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ clusters in the axial positions and four nitrogen atoms from two ethylenediamine ligands in the equatorial plane. The nickel atom (Ni2) in the discrete cation $[Ni(en)_2]^{2+}$ adopts a nearly planar square geometry with the average Ni$-$N distance of 1.906 Å, which is a little smaller than that in Ni1 (average 2.086 Å). Interestingly, there exist strong intermolecular contacts between the discrete cation $[Ni(en)_2]^{2+}$ and the $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ cluster in the anion chain with the shortest Ni$\cdots$O distance (Ni2$\cdots$O17 or their symmetry equivalents) of 2.774 Å. Each $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ cluster connects with two discrete cations $[Ni(en)_2]^{2+}$; consequently, a novel 1D sandwich-like coordination polymer chain containing polyoxometalate bridges is formed (Figure 1b).

The most unusual structural feature of complex **1** is that a 3D supramolecular network is formed. The adjacent chains in different layers are arranged in a cross-like fashion, resulting in a 3D supramolecular array (Figure 2). 1D rhombus channels should be formed, and supposedly, the bridges are linear rather than global,[7a,11] as shown in the topology represent of the Ni$-$Ni connections (Figure 3). In fact, the cage shape of the $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ bridge changes the
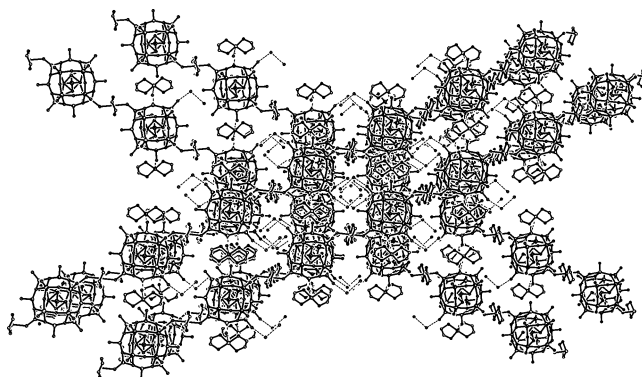

Figure 2. Illustration of the 3D supramolecular network constructed by the mixed molybdenum$-$vanadium heteropolyoxometalate bridged coordination polymer chains with short contacts and hydrogen bonds.
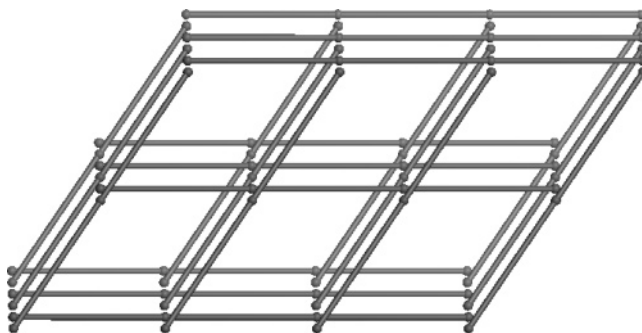

Figure 3. 3D supramolecular network based on the topology of Ni$-$Ni connections. The link represents the mixed molybdenum$-$vanadium heteropolyoxometalate bridge. The en ligands, the cation complex fragments, and the water molecules are omitted for clarity.

channel's feature and reduces its size. However, this 3D framework still creates hydrophobic channels along the *c*-axis, which are filled with those water molecules. Besides intermolecular short contacts between the discrete cation $[Ni(en)_2]^{2+}$ and the $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ cluster, the 1D $\rightarrow$ 3D dimension expansion in this structure is predominantly directed by extensive hydrogen bonds among water molecules with O1w$\cdots$O3w of 2.882 Å and O2w$\cdots$O2w's symmetry equivalent of 2.657 Å as well as between the water molecule (O3w) and the $[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)]^{6-}$ cluster with O11$\cdots$O3w of 2.751 Å. These weak interactions play important roles in stabilization of the molecule in the crystal structure of **1**.

The assignments of the oxidation states for the Mo atoms and the V atoms are in good agreement with the electric charge and are confirmed by bond valence sum calculations.[13] The valence sums for eight Mo atoms are Mo1 (2$\times$) 5.609, Mo2 (2$\times$) 5.658, Mo3 (2$\times$) 5.621, and Mo4 (2$\times$) 5.621, the average value of which is 5.643 (the expected average value for $Mo^{VI}_5Mo^V_3$ is 5.625); those for eight V atoms are V1 (2$\times$) 4.061, V2 (2$\times$) 3.919, V3 (2$\times$) 4.107, and V4 (2$\times$) 3.949 (average 4.009). The calculated results indicate that all V centers are in the +4 oxidation state, while three Mo centers are in the +5 oxidation state with three electrons delocalized within the two $\{Mo_4O_{18}\}$ rings. Similar mixed-valence Mo atoms have also been found in other mixed molybdenum$-$vanadium heteropolyoxometalates.[2g$-$k,3e,4f,4h]

Conclusion

Complex **1** provides a novel example of assembling a 3D supramolecular network by cross-like arrangement of the 1D mixed molybdenum−vanadium heteropoly-oxometalate bridged coordination polymer under hydrothermal conditions. This study demonstrates that the architecture of the higher dimensionality supramolecular network from the lower dimensionality coordination polymer using the "dimension expansion" method also can be realized in the field of organic−inorganic hybrid polyoxometalates.

Supporting Information Available: X-ray crystallographic information files (CIF) for complex **1**. This material is available free of charge via the Internet at http://pubs. acs.org.

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