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One- and Two-Dimensional Coordination Polymers Constructed from Bicapped Keggin Mixed Molybdenum−Vanadium Heteropolyoxoanions and Polynuclear Copper(I) Clusters Bridged by Asymmetrical Bipyridine (2,4′-bipy and 2,3′-bipy) Ligands

Cai-Ming Liu,* De-Qing Zhang, and Dao-Ben Zhu*

Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

ABSTRACT: Two novel trimetallic coordination polymers containing bridging bicapped Keggin mixed Mo/V polyoxoanions and asymmetrical aromatic amine bridging ligands 2,3′-bipyridine (2,3′-bipy) or 2,4′-bipyridine (2,4′-bipy), $[Cu^I_6(2,3′\text{-bipy})_6(2,3′\text{-bipy-}2′\text{-O})_2][V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]$ [2,3′-bipy-2′-OH = 3-(pyridin-2-yl)pyridin-2-ol] (**1**) and $[Cu^I_5(2,4′\text{-bipy})_6(OH)][PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]\cdot1.5H_2O$ (**2**), have been prepared under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. Gillard type hydration for the 2,3′-bipy ligand was observed during synthesis of **1**, which happens on the 2′-carbon atom rather than on the α-carbon atom of the coordinated nitrogen atom in the 2,3′-bipy ligand. Complex **1** is constructed from an alternatively arranged bivanadyl capped α-Keggin polymolybdate anion $[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]^{4-}$ and double 2,3′-bipy ligand bridged trinuclear copper(I) cluster $[Cu^I_3(2,3′\text{-bipy})_3(2,3′\text{-bipy-}2′\text{-O})]^{2+}$, forming a one-dimensional (1D) ribbon structure. The two-dimensional (2D) extended layer structure of **2** is composed of another type of bicapped Keggin mixed molybdenum−vanadium polyoxoanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ and copper(I) coordination polymer cation chain $[Cu^I_5(2,4′\text{-bipy})_6(OH)]^{4+}$; the latter consists of a 2,4′-bipy ligand bridged hexanuclear copper(I) cluster $[Cu^I_5(2,4′\text{-bipy})_6]^{5+}$ linked by double hydroxyl groups.

Introduction

In the past few decades, considerable efforts have been devoted to the design, crystallization, and characterization of organic−inorganic hybrid materials and/or transition metal coordination polymers due to their potential applications in fields such as magnetism, electric conductivity, nonlinear optics, molecular adsorption, and heterogeneous catalysis.[1] Because of their interesting magnetic, electrical, and optical properties, polyoxometalate anions are often utilized as the inorganic components,[2] while the organic components are generally composed of organic amines acting as structural directors. Recently, the study of polyoxometalates covalently linked by transition metal complex fragments has been an important advance in the realm of organic−inorganic hybrid materials.[3−5] One remarkable strategy for design of such polyoxometalates is using polyoxoanions' coordination ability; these polyoxoanions can coordinate the transition metal atoms as unusual ligands. While the organic amines do not work as charge-compensating constituents any more, they function as ligands, coordinating to the secondary metal centers directly to generate transition metal complex fragments.

Hydrothermal techniques are an effective approach for the preparation of hybrid materials, and many examples of polyoxoanions supported transition metal complexes including zero-dimensional (0D) clusters,[3] one-dimensional (1D) chains,[4] two-dimensional (2D) layer structures,[5] and three-dimensional (3D) frameworks[6] have been reported. The explored bridging polyoxoanions include not only simple homometal polyoxoanions but also mixed molybdenum−vanadium heteropolyoxoanions,[3i−3m,4c,4f,4g,5i] and both aliphatic amine and aromatic amine have been utilized. Some organic−inorganic hybrid materials are even constructed with the use of polyoxoanions and symmetrically bridging aromatic amines such as 4,4′-bipyridine (4,4′-bipy),[5g,5k] 4,7-phenanthroline (4,7-phen),[5a] 2,4,6-tripyridyltriazine (tptz),[5d] and quinoxaline.[4d] However, to our knowledge, no organic−inorganic hybrid polyoxometalate containing asymmetrically aromatic amine bridging ligands have been reported yet, although the asymmetrically aromatic amine ligand 2,4′-bipyridine (2,4′-bipy) has been utilized as a bridge to construct several silver(I) coordination polymers.[7] As a continuing goal in searching for new organic−inorganic hybrid polyoxometalates, with the strategy of employing the asymmetrically aromatic amine bridging ligands as organic components, we have successfully prepared two coordination polymers constructed from bicapped Keggin mixed molybdenum−vanadium polyoxoanions and 2,3′-bipy or 2,4′-bipy bridged polynuclear copper(I) clusters: $[Cu^I_6(2,3′\text{-bipy})_6(2,3′\text{-bipy-}2′\text{-O})_2][V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]$ [2,3′-bipy-2′-OH = 3-(pyridin-2-yl)pyridin-2-ol] (**1**) and $[Cu^I_5(2,4′\text{-bipy})_6(OH)][PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]\cdot1.5H_2O$ (**2**). It is noteworthy that the bridging ability of the 2,3′-bipy ligand was observed for the first time, and the hydration of 2,3′-bipy to produce 2,3′-bipy-2′-OH was also observed during formation of **1**, which is consistent with the Gillard type of covalent hydration[8] and further provides structural evidence for the Gillard mechanism.[9]

Experimental Procedures

Materials and Methods. $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ 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 spectra were recorded on a Pekin-Elmer 2000 spectrophotometer using pressed KBr pellets. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG-Scientific using 300W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

Preparation of Complex 1. A mixture of NH_4VO_3 (3.0 mmol), $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ (reference FW: 1825.25) (0.5 mmol), $Cu(C_2O_2)_2\cdot0.5H_2O$ (1.0 mmol), 2,3′-bipyridine (2.0 mmol), and H_2O (14mL) was

* To whom correspondence should be addressed. (C.-M.L.) Fax: +86-1062559373. E-mail: cmliu@iccas.ac.cn. (D.-B.Z.) E-mail: zhudb@iccas.ac.cn.

Table 1. Crystal Data for Complexes 1 and 2

	1	2
formula	$C_{80}H_{62}Cu_6Mo_{12}N_{16}O_{44}PV_2$	$C_{60}H_{52}Cu_5Mo_8N_{12}O_{44.5}PV_6$
fw	3616.83	3074.96
T (K)	293(2)	293(2)
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.289(3)	12.945(3)
b (Å)	14.121(3)	13.050(3)
c (Å)	14.326(3)	15.374(3)
α (°)	71.29(3)	103.30(3)
β (°)	88.96(3)	103.91(3)
γ (°)	77.91(3)	112.39(3)
V (Å^3)	2486.3(9)	2176.1(8)
Z	1	1
D_c (g cm^{-3})	2.416	2.343
μ (Mo−Kα) (mm^{-1})	3.000	3.029
reflections collected	11209	12869
independent reflections	11209	9042 [R(int) = 0.0485]
observed data [$I > 2\sigma(I)$]	5637	5036
final $R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0642, 0.1881	0.0555, 0.1438
goodness-of-fit on F^2	0.969	0.924

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[wF_o{}^2]^2\}^{1/2}$.

stirred for 20 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25mL) and kept at 160 °C for 13 days. After the autoclave had cooled to room temperature over 6−7 h, black block-shaped crystals of **1** were isolated from blue mother liquid, washed with water, and then dried at ambient temperature. Yield was 50% based on copper. Complex **1** is stable in air and insoluble in water and common organic solvents. Anal. Calc. for $C_{80}H_{62}Cu_6Mo_{12}N_{16}O_{44}PV_2$ **1**: C, 26.57; H, 1.73; N, 6.20%; found: C, 26.64; H, 1.79; N, 6.15%. IR (KBr, cm^{-1}): 3099(w), 1622(m), 1602(m), 1561(w), 1541(w), 1479(w), 1463(m), 1449(w), 1434(w), 1410(w), 13359w), 1282(w), 1236(w), 1200(w), 1166(w), 1050(w), 941(vs), 711(s), 696(w), 654(m), 616(w), 536(w), 452(w), 427(w). XPS: C1s 284.55, O1s 530.30, P2p 132.85, Cu2p3 932.70, V2p3 515.95, Mo3d 231.95 eV.

Preparation of Complex 2. A mixture of NH_4VO_3 (3.0 mmol), $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ (0.5 mmol), $Cu(CH_3CO_2)_2\cdot H_2O$ (1.0 mmol), 2,4′-bipyridine (2.0 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 160 °C for 10 days. After the autoclave had cooled to room temperature overnight, black block-shaped crystals of **2** were isolated from blue mother liquid, washed with water, and then dried at ambient temperature. Yield 65% based on copper. Complex **2** is stable in air and insoluble in water and common organic solvents. Anal. Calc. for $C_{60}H_{52}Cu_5Mo_8N_{12}O_{44.5}PV_6$ **2**: C, 23.44; H, 1.70; N, 5.47%; Found: C, 23.37; H, 1.74; N, 5.39%. IR (KBr, cm^{-1}): 3455(s, br), 3094(w), 1612(m), 1593(w), 1562(w), 1537(w), 1470(m), 1437(w), 1414(m), 1328(w), 1288(w), 1218(w), 1160(w), 1051(w), 944(s), 838(m), 777(s), 650(m), 578(w), 565(w), 534(w), 495(w), 455(w). XPS: C1s 284.50, O1s 530.45, P2p 132.80, Cu2p3 932.72, V2p3 516.40, Mo3d 232.20 eV.

X-ray Crystal Structure Determination. Suitable single crystals of **1** (with the approximate dimensions $0.36 \times 0.24 \times 0.15$ mm^3) and **2** (with the approximate dimensions $0.38 \times 0.21 \times 0.13$ mm^3) were 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 11 209 reflections were collected in the range $2.11° < \theta < 27.48°$ ($0 \le h \le 17$, $-17 \le k \le 18$, $-18 \le l \le 18$), of which 11 209 are unique ($R_{\text{int}} = 0.0000$) and 5637 with $I > 2\sigma(I)$ were used in the refinement of the structure of **1**. A total of 12 869 reflections were collected in the range $1.46° < \theta < 27.48°$ ($-14 \le h \le 16$, $-16 \le k \le 16$, $-19 \le l \le 19$), of which 9042 are unique ($R_{\text{int}} = 0.0485$) and 5036 with $I > 2\sigma(I)$ were used in the refinement of the structure of **2**. Empirical absorption corrections from Ψ scan were applied. The two structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms except those in solvent water molecules and hydroxyl groups of **2** were allowed for as riding atoms. Selected crystallographic data and structure determination parameters for complexes **1** and **2** are given in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2 and Table 3, respectively.

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

V(1)−O(16)	1.614(3)	V(1)−O(23)	1.925(3)
V(1)−O(9)	1.925(3)	V(1)−O(10)	1.929(3)
V(1)−O(15)	1.933(3)	Mo(1)−O(17)	1.662(3)
Mo(1)−O(5)	1.791(4)	Mo(1)−O(7)	1.795(3)
Mo(1)−O(10)	2.030(3)	Mo(1)−O(9)	2.030(3)
Mo(2)−O(12)	1.687(3)	Mo(2)−O(20)	1.791(3)
Mo(2)−O(14)	1.824(3)	Mo(2)−O(10)	2.039(3)
Mo(2)−O(15)	2.046(3)	Mo(3)−O(19)	1.668(3)
Mo(3)−O(21)	1.791(3)	Mo(3)−O(13)	1.801(3)
Mo(3)−O(15)	2.035(3)	Mo(3)−O(23)	2.044(3)
Mo(4)−O(22)	1.663(3)	Mo(4)−O(6)	1.770(3)
Mo(4)−O(8)	1.788(3)	Mo(4)−O(9)	2.057(3)
Mo(4)−O(23)	2.083(3)	Mo(5)−O(11)	1.617(3)
Mo(5)−O(7)$^{#1}$	1.912(3)	Mo(5)−O(8)	1.921(4)
Mo(5)−O(13)	1.927(3)	Mo(5)−O(14)$^{#1}$	1.932(3)
Mo(6)−O(18)	1.628(4)	Mo(6)−O(5)$^{#1}$	1.910(3)
Mo(6)−O(20)	1.914(3)	Mo(6)−O(21)	1.931(3)
Mo(6)−O(6)$^{#1}$	1.940(3)	Cu(1)−N(4)	1.947(4)
Cu(1)−N(1)	1.964(4)	Cu(1)−O(16)	2.104(3)
Cu(1)−O(24)	2.201(4)	Cu(2)−N(3)	1.903(4)
Cu(2)−N(6)	1.893(4)	Cu(3)−N(8)	1.919(4)
Cu(3)−N(5)$^{#2}$	1.919(4)		
N(4)−Cu(1)−N(1)	146.27(16)	N(4)−Cu(1)−O(16)	98.01(13)
N(1)−Cu(1)−O(16)	110.48(13)	N(4)−Cu(1)−O(24)	104.64(16)
N(1)−Cu(1)−O(24)	88.80(15)	O(16)−Cu(1)−O(24)	98.96(12)
N(6)−Cu(2)−N(3)	164.57(17)	N(5)$^{#2}$−Cu(3)−N(8)	174.4(2)
N(5)$^{#2}$−Cu(3)−O(18)	89.10(15)	N(8)−Cu(3)−O(18)	96.29(16)

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

Results and Discussion

Syntheses. To isolate complexes **1** and **2**, hydrothermal techniques were employed. Because hydrothermal conditions can cause a reaction to shift from the kinetic to the thermodynamic domain and overcome the difficulties due to differential solubilities of organic and inorganic starting materials,[10] many organic−inorganic hybrid polyoxometalates with diverse structural architectures have been synthesized using these versatile methods.[3−6] For a mixed molybdenum−vanadium heteropolyoxometalate system, the starting materials play a great role in the outcome of the reaction besides other factors such as stoichiometry, temperature, pressure, acidity, and time of reaction.[3k,4g] Complex **1** was separated from the hydrothermal reaction of NH_4VO_3, $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$, $Cu(C_2O_2)_2\cdot 0.5H_2O$, 2,3′-bipy, and H_2O at 160 °C for 13 days, while complex **2** was synthesized by hydrothermal reaction of NH_4VO_3, $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$, $Cu(CH_3CO_2)_2\cdot H_2O$, 2,4′-bipy,

Table 3. Bond Lengths (Å) and Angles (°) for Complex 2[a]

V(1)−O(18)	1.628(6)	V(1)−O(19)	1.912(6)
V(1)−O(21)	1.924(6)	V(1)−O(16)	1.919(6)
V(1)−O(23)	1.938(6)	V(2)−O(10)	1.600(6)
V(2)−O(9)	1.892(8)	V(2)−O(13)	1.895(7)
V(2)−O(8)#1	1.918(7)	V(2)−O(12)#1	1.918(8)
V(3)−O(11)	1.604(7)	V(3)−O(14)	1.901(7)
V(3)−O(7)#1	1.918(7)	V(3)−O(22)	1.923(7)
V(3)−O(6)#1	1.933(7)	Mo(1)−O(20)	1.675(6)
Mo(1)−O(8)	1.796(7)	Mo(1)−O(6)	1.795(7)
Mo(1)−O(19)	2.040(6)	Mo(1)−O(21)	2.060(7)
Mo(2)−O(15)	1.668(6)	Mo(2)−O(12)	1.782(7)
Mo(2)−O(22)	1.785(7)	Mo(2)−O(23)	2.041(6)
Mo(2)−O(21)	2.050(6)	Mo(3)−O(5)	1.668(6)
Mo(3)−O(9)	1.792(7)	Mo(3)−O(14)	1.819(7)
Mo(3)−O(16)	2.050(6)	Mo(3)−O(23)	2.061(6)
Mo(4)−O(17)	1.668(6)	Mo(4)−O(13)	1.793(7)
Mo(4)−O(7)	1.805(7)	Mo(4)−O(16)	2.052(7)
Mo(4)−O(19)	2.058(6)	Cu(1)−N(5)	1.921(8)
Cu(1)−N(2)	1.942(7)	Cu(1)−O(18)	2.176(6)
Cu(2)−N(3)	1.918(8)	Cu(2)−N(1)	1.919(8)
Cu(3)−O(24)	1.885(18)	Cu(3)−N(4)	2.015(10)
Cu(3)−N(6)#3	2.099(10)		

N(5)−Cu(1)−N(2)	161.2(3)	N(5)−Cu(1)−O(18)	98.6(3)
N(2)−Cu(1)−O(18)	100.2(3)	N(3)−Cu(2)−N(1)	167.2(4)
N(3)−Cu(2)−O(10)#2	93.5(3)	N(1)−Cu(2)−O(10)#2	98.6(3)
N(4)−Cu(3)−N(6)#3	125.0(4)		

[a] Symmetry code: (#1) −x + 1, −y + 1, −z − 1; (#2) −x + 1, −y, −z − 2; (#3) −x, −y, −z − 3.

and H_2O in similar conditions. Both two complexes contain bicapped Keggin mixed molybdenum−vanadium heteropoly-oxoanions; however, our previous research indicated when the Ni^{2+} or Co^{2+} salts rather than the Cu^{2+} salts were utilized as starting transition metal cation sources, the tetracapped Keggin mixed molybdenum−vanadium heteropolyoxoanions were formed in the products.[3i,3m,4g,5i] The oxidation states of the copper atoms in **1** and **2** are assigned as +1 on the basis of charge neutrality, coordination environments, and valence sum calculations,[11] although the corresponding starting reagents are the copper(II) salts. The main reason is that the organonitrogen species generally act not only as ligands but also as reducing agents under hydrothermal conditions. Similar trends were also observed in other polyoxometalates bridged by organonitrogen ligands coordinating to the copper atom.[4a,4d,5a,5c,5d,6a]

Interestingly, part of the 2,3′-bipy ligand was hydrated to produce 2,3′-bipy-2′-OH during formation of **1**, which is agreement with the covalent hydration of the Gillard mechanism.[9] The primary steps proposed for generating 2,3′-bipy-2′-OH are shown in Scheme 1: First, 2,3′-bipy ligands are coordinated to the copper(II) ion to form the [Cu^{II}(2,3′-bipy)$_2$-(o-POM)] species; the 2′-carbon atom of the pyridine in one 2,3′-bipy ligand is activated by the coordination role, benefiting the following nucleophilic attack by hydroxide ion, which generates a covalent hydrate. The nucleophilic attack is the key step of the Gillard mechanism. Then, the deprotonation of the covalent hydrate produces the pseudobase species. Finally, intramolecular electron transfer and dehydrogenation of the pseudobase species induces the copper(I) species. It is noteworthy that the hydration of 1,10-phenanthroline and 2,2′-bipyridine in previously reported complexes[10] occurs on the α-carbon position of the coordinated nitrogen atom, while the hydration of the 2,3′-bipy ligand in **1** happens on the 2′-carbon atom of 2,3′-bipy ligand (the α-carbon position of the neighboring pyridine ring).

Crystal Structure of 1. The structure of **1** consists of a 1D ribbon of [Cu^I_6(2,3′-bipy)$_6$(2,3′-bipy-2′-O)$_2$][$V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}$(PO$_4$)] (Figures 1 and 2), which is a 1D copper(I) coordination polymer containing the reduced bivanadyl capped α-Keggin

Scheme 1. Gillard Mechanism for the Hydration of 2,3′-bipy in 1.
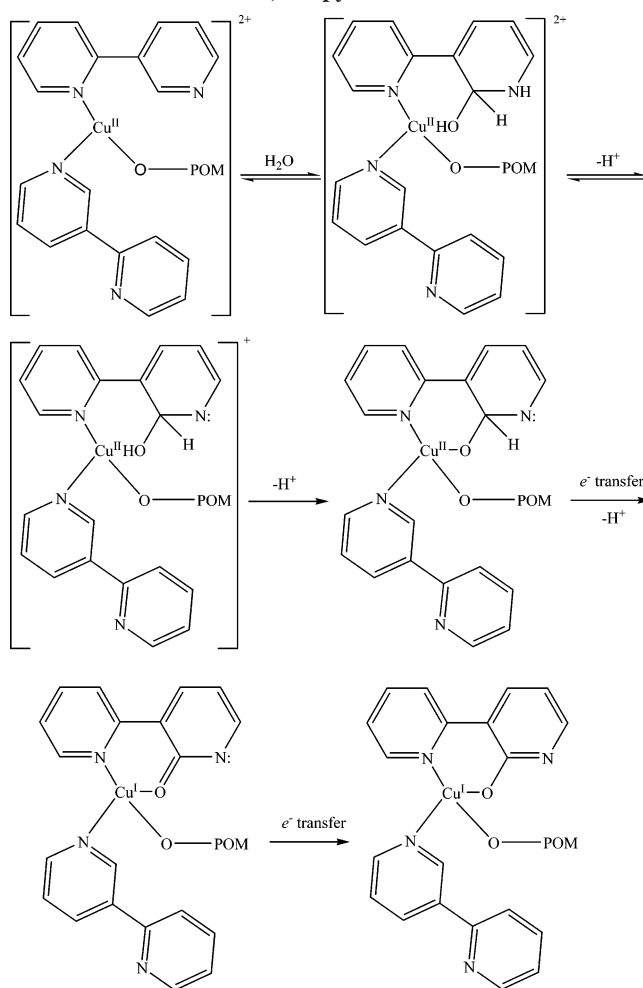
polymolybdate anion [$V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}$(PO$_4$)]$^{4−}$. This mixed molybdenum−vanadium heteropolyoxoanion is based on the α-Keggin structure of [$Mo_{12}O_{36}$(PO$_4$)]$^{8−}$ with two capping five coordinated terminal [VO]$^{2+}$ units, which shows a bicapped α-Keggin core constructed from four internally edge-shared triads (Mo_3O_{13}) that are corner-shared to each other.[12] The ligation of oxygen atoms on the two opposite {Mo_4O_4} faces or pits to each {VO} unit to form two caps, generating two square pyramidal vanadium coordination environments, while a disordered PO$_4^{3−}$ anion is located in the center of the polyoxoanion as a guest. This bicapped α-Keggin structure is very similar to that in (Et$_3$NH)$_5$[PMo$^V_6$Mo$^{VI}_6$O$_{40}$(V^{IV}O)$_2$] (NEt$_3$ = triethylamine),[12] but the latter is just an isolated polyoxoanion and does not coordinate to other transition metal atoms as a special ligand. The Mo−O and V−O bond lengths of **1** are Mo−O$_t$, 1.617(3)−1.687(4) Å; Mo−O$_b$, 1.770(3)−2.083(3) Å; V−O$_t$, 1.614(3) Å and V−O$_b$, 1.925(3)−1.933(3) Å.

Each [$V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}$(PO$_4$)]$^{4−}$ polyoxoanion is covalently bonded to four complex fragments [Cu^I_3(2,3′-bipy)$_3$(2,3′-bipy-2′-O)]$^{2+}$ through two terminal oxygen atoms from two opposite capping V atoms and two terminal oxygen atoms from the Mo6 atom and its symmetry equivalent. There are three crystallographically independent copper(I) atoms in the complex fragment [Cu^I_3(2,3′-bipy)$_3$(2,3′-bipy-2′-O)]$^{2+}$; they are bridged by two 2,3′-bipy ligands to form a special trinuclear copper(I) cluster, which connects with the [$V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}$(PO$_4$)]$^{4−}$ polyoxoanion as another type of bridge. The Cu1 atom is coordinated by one deprotonated 2,3′-bipy-2′-OH ligand, one
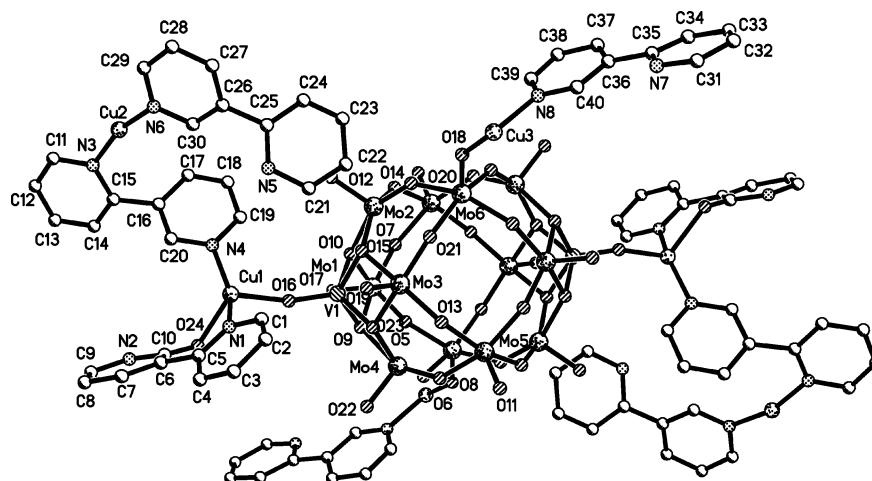
Figure 1. Molecular drawing of **1** with atom labels; all hydrogen atoms and the disordered PO_4^{3-} anion are omitted for clarity.
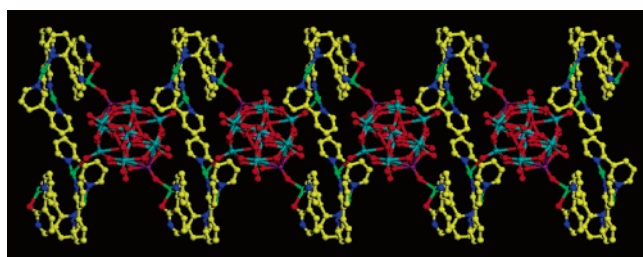

Figure 2. 1D ribbon of **1**; all hydrogen atoms are omitted for clarity.

2,3′-bipy bridging ligand, and one terminal oxygen atom (O16) from the capping V atom of the polyoxoanion $[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]^{4-}$, forming a slightly distorted tetrahedral coordination environment; the Cu2 atom is two-coordinate with two nitrogen atoms from two 2,3′-bipy bridging ligands to generate a slightly distorted linear coordination configuration, while the Cu3 atom possesses a slightly distorted T-type coordination environment, which is coordinated by one 2,3′-bipy bridging ligand, one 2,3′-bipy terminal ligand, and one terminal oxygen atom (O18) from the Mo atom of the polyoxoanion $[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]^{4-}$. To our knowledge, no complex with 2,3′-bipy acting as bridging ligand has been reported before and the coexistence of three types of copper(I) coordination configurations in the same complex is rare.

The polyoxoanion $[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]^{4-}$ and the double trinuclear copper(I) clusters $[Cu^I_3(2,3′-bipy)_3(2,3′-bipy-2′-O)]^{2+}$ link to each other to generate the 1D coordination polymer ribbon (Figure 2). These ribbons are arranged in parallel along the *b*-axis, forming the layer in the plane defined by the *b*-axis and the diagonal of the *ac*-plane (Figure 3). This arrangement is favored by strong π⋯π stacking interactions, as indicated by short contacts of pyridine rings in 2,3′-bipy terminal ligands (separated by 3.2−3.6 Å) from neighboring ribbons, which extend the structure into a 2D-layered supramolecular array.

The valence sum calculations for the Cu atoms[11] give Cu1(2×) 1.23, Cu2(2×) 0.917, and Cu3(2×) 0.868 (average value 1.005), which indicate that all six Cu atoms are in the +1 oxidation state. The assignments of the oxidation states for the Mo atoms and the V atoms are in agreement with the electric charge and confirmed by bond valence sum calculations.[13] The valence sums for six Mo atoms are Mo1(2×) 5.625, Mo2(2×) 5.506, Mo3(2×) 5.743, Mo4(2×) 5.825, Mo5(2×) 5.765, Mo6(2×) 5.669, the average value of which is 5.689 (the expected average value for $Mo^V_5Mo^{VI}_7$ is 5.58); the values for
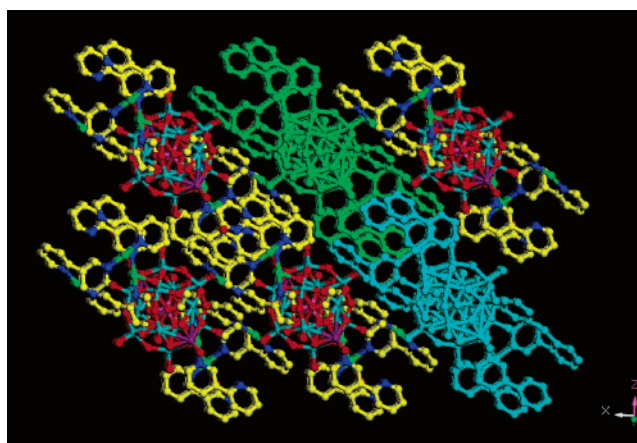

Figure 3. The packing arrangement of complex **1** viewed down the *b*-axis, showing two neighboring 1D molecular ribbons (in green and light blue) possessing π⋯π stacking interactions.

two V atoms are V1 (2×) 4.179 (average 4.179). The calculated results indicate that all V centers are in the +4 oxidation state, while five Mo centers are in the +5 oxidation state with five delocalized electrons. Similar mixed-valence Mo atoms have also been found in other mixed molybdenum−vanadium heteropolyoxometalates.[3i−3m,4c,4f,4g,5i]

Crystal Structure of 2. The structure of **2** is constructed from the linking of a heteropolyoxanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ and a 1D copper(I) coordination polymer cation chain $[Cu^I_5(2,4′-bipy)_6(OH)]^{4+}$ (Figures 4 and 5). The mixed molybdenum−vanadium polyoxoanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ is based on the α-Keggin structure of $[PMo^{VI}_8V^V_3V^{IV}O_{40}]^{8-}$, which contains eight MoO_5 and four VO_5 square pyramids and one disordered PO_4^{3-} in the center as a guest, with two additional five-coordinated terminal $[VO]^{2+}$ units. This bicapped α-Keggin structure is very similar to those in $Na_{0.5}K_{6.5}[Mo^{VI}_8V^{IV}_4O_{36}(V^VO_4)(V^{IV}O)_2]\cdot12.5H_2O$,[14a] $[H_2N(C_2H_4)_2NH_2](H_3O)[PMo^V_2Mo^{VI}_6V^{IV}_4O_{40}(V^{IV}O)_2]\cdot H_2O$[14b], and $[Cu(en)_2(H_2O)]_4[Cu(en)_2]_{3.5}[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2Cu(en)(1,10-phen)]_3\cdot14H_2O$ (1,10-phen = 1,10-phenanthroline).[3l] However, the bicapped α-Keggin heteropolyoxanions in $Na_{0.5}K_{6.5}[Mo^{VI}_8V^{IV}_4O_{36}(V^VO_4)(V^{IV}O)_2]\cdot12.5H_2O$,[14a] and $[H_2N(C_2H_4)_2NH_2](H_3O)[PMo^V_2Mo^{VI}_6V^{IV}_4O_{40}(V^{IV}O)_2]\cdot H_2O$[14b] do not take part in coordination role as special ligands, while the complex $[Cu(en)_2(H_2O)]_4[Cu(en)_2]_{3.5}[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2Cu(en)(1,10-phen)]_3\cdot14H_2O$ (1,10-phen = 1,10-phenanthroline)[3l] is a 0D heteropolyoxanion supported
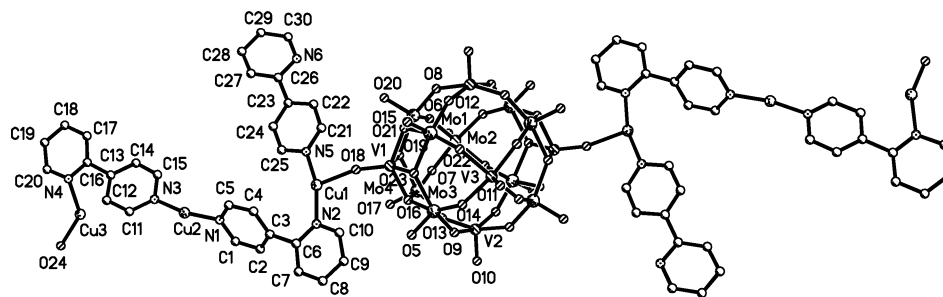
Figure 4. Molecular drawing of **2** showing the labeling of atoms; all hydrogen atoms, solvent water molecules, and the disordered PO_4^{3-} anion are omitted for clarity.
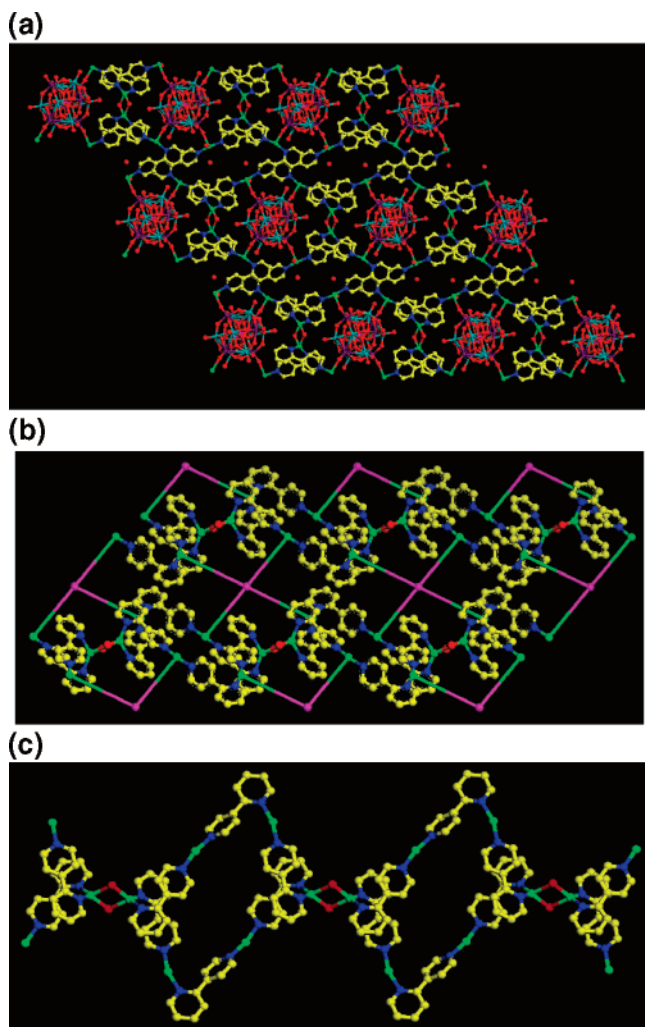

Figure 5. (a) 2D layer network of **2**. (b) A view of the linking of 1D copper(I) coordination polymer cation chains $[Cu^I_5(2,4'-bipy)_6(OH)]^{4+}$ by the heteropolyoxoanions $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ (denoted as purple dots for clarity). (c) A view of the 1D copper(I) coordination polymer cation chain constructed from hexanuclear copper(I) clusters bridged by double μ^2-hydroxyl groups; all hydrogen atoms are omitted for clarity.

complex rather than a coordination polymer. The Mo–O and V–O bond lengths of **2** are Mo–O_t, 1.668(6)–1.675(6) Å; Mo–O_b, 1.782(7)–2.061(6) Å; V–O_t, 1.600(6)–1.628(6) Å and V–O_b, 1.892(8)–1.938(6) Å.

The 1D copper(I) coordination polymer cation chain $[Cu^I_5(2,4'-bipy)_6(OH)]^{4+}$ contains a unique hexanuclear copper(I) cluster $[Cu^I_5(2,4'-bipy)_6]^{5+}$, where one copper atom is situated in two positions with 50% disordered occupied, while four copper atoms fill the other four positions. These copper atoms are

bridged by six 2,4'-bipy ligands in end-to-end mode, generating a distorted quadrangle hexanuclear copper(I) cluster; its cavity clathrates some solvent hydrate molecules. These hexanuclear copper(I) cluster rings $[Cu^I_5(2,4'-bipy)_6]^{5+}$ are further bridged by the double μ^2-hydroxyl groups to generate a novel 1D copper(I) coordination polymer along the [011] direction. Both the Cu1 atom and the Cu2 atom have a slightly distorted T-type coordination configuration, which is coordinated by two nitrogen atoms from two 2,4'-bipy bridging ligands and one terminal oxygen atom from the heteropolyoxoanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$. The Cu3 atom is coordinated in slightly distorted tetrahedral geometry, with two nitrogen atoms from two 2,4'-bipy bridging ligands and two oxygen atoms from two hydroxyl groups.

Each heteropolyoxoanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ is covalently bonded to four hexanuclear copper(I) clusters from two neighboring 1D copper(I) coordination polymer cation chains $[Cu^I_5(2,4'-bipy)_6(OH)]^{4+}$ through four terminal oxygen atoms from two pairs of opposite V atoms, generating a 2D layered network in the plane defined by the diagonal of *bc*-plane and the diagonal of *ab*-plane. Another previously reported 2D coordination polymer $[Cu_3(4,7-phen)_3]_2(Mo_8O_{26})(Mo_6O_{19})\cdot0.5H_2O$ (4,7-phen = 4,7-phenanthroline) is also constructed from polyoxoanions and polynuclear copper(I) clusters;[5a] however, in $[Cu_3(4,7-phen)_3]_2(Mo_8O_{26})(Mo_6O_{19})\cdot0.5H_2O$, the trinuclear copper(I) clusters $[Cu_3(4,7-phen)_3]^{3+}$ formed by three symmetrically bridging aromatic amine ligands 4,7-phenanthroline connecting three copper(I) atoms are bridged by the polyoxoanion β-$(Mo_8O_{26})^{4-}$ rather than the double μ^2-hydroxyl groups to form 1D ribbons, which are then linked through another type of polyoxoanion $(Mo_6O_{19})^{2-}$ to generate a 2D sheet structure.

The valence sum calculations for the Cu atoms[11] give Cu1(2×) 1.046; Cu2(2×) 0.869; and Cu3 1.057 (average value 0.977), suggesting that all five Cu atoms are in the +1 oxidation state. The assignments of the oxidation states for the V atoms and the Mo atoms are also in correspondence with the electric charge and confirmed by bond valence sum calculations.[13] The valence sums for six V atoms are V1 (2×) 4.297, V2 (2×) 4.598, V2 (2×) 4.465, the average value of which is 4.453 (the expected average value for $V^V_3V^{IV}_3$ is 4.5); the values for eight Mo atoms are Mo1(2×) 5.861, Mo2(2×) 6.039, Mo3(2×) 5.811, Mo4(2×) 5.865, the average value of which is 5.894. The calculated results suggest that all Mo centers are in the +6 oxidation state, while three V centers are in the +4 oxidation state with three delocalized electrons.

Conclusion

Hydrothermal reactions of NH_4VO_3, $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ and suitable Cu^{2+} salts in the presence of asymmetrical aromatic amine ligands 2,3'-bipy or 2,4'-bipy at 160 °C yielded two novel

trimetallic coordination polymers containing bridging bicapped Keggin Mo/V polyoxoanions: $[Cu^I_6(2,3'\text{-bipy})_6(2,3'\text{-bipy-}2'\text{-O})_2]$-$[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]$ (**1**) and $[Cu^I_5(2,4'\text{-bipy})_6(OH)]$-$[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]\cdot1.5H_2O$ (**2**). The 2,3'-bipy ligand was hydrated partially to form 2,3'-bipy-2'-OH following the Gillard mechanism during hydrothermal synthesis of **1**. Complex **1** is constructed from the bivanadyl capped α-Keggin polymolybdate anion $[V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]^{4-}$ and the copper(I) trinuclear cation cluster $[Cu^I_3(2,3'\text{-bipy})_3(2,3'\text{-bipy-}2'\text{-O})]^{2+}$; they connect to each other with a stoichiometry of 1:2, forming the 1D ribbon. The 2D extended layer structure of **2** is generated through bonding of the terminal oxo-groups in the bicapped α-Keggin polyoxoanion $[PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ to the copper(I) sites of the hexanuclear cluster in the cation chain $[Cu^I_5(2,4'\text{-bipy})_6(OH)]^{4+}$. This study demonstrates that asymmetrical aromatic amine ligands 2,3'-bipy or 2,4'-bipy can connect copper(I) atoms as bridges to form special polynuclear clusters, which are further linked by heteropolyoxanions to generate extended coordination polymers under hydrothermal conditions; when the Cu^{2+} salts were utilized as starting transition metal cation sources, the bicapped rather than the tetracapped Keggin mixed molybdenum−vanadium polyoxoanions were inclined to be obtained. Furthermore, the variations in the structures arise owing to the differences in not only the asymmetrical aromatic amine ligands bridged polynuclear clusters but also the bicapped α-Keggin heteropolyoxanions.

Supporting Information Available: X-ray crystallographic information files (CIF) for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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