Inorg. Chem. **2003**, *42*, 3670–3676

Inorganic Chemistry

Article

Modified Polyoxometalates: Hydrothermal Syntheses and Crystal Structures of Three Novel Reduced and Capped Keggin Derivatives Decorated by Transition Metal Complexes

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Received December 23, 2002

Three novel polyoxometalate derivatives decorated by transition metal complexes have been hydrothermally synthesized. Compound **1** consists of $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co\ (2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$ polyoxocations and $[PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]^{3-}$ polyoxoanions, which are both built on mixed-metal tetracapped $[PMo_8V_8O_{44}]$ subunits covalently bonded to four or two $\{Co(2,2'\text{-bpy})_2(H_2O)\}^{2+}$ clusters via terminal oxo groups of the capping V atoms. Compound **2** is built on $[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^{I}(phen)\}_2]^{5-}$ clusters constructed from mixed-metal bicapped $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ subunits covalently bonded to two $\{Cu(phen)\}^{+}$ fragments in the similar way to **1**. The structure of **3** is composed of $[PMo^{VI}_9Mo^{V}_3O_{40}]^{6-}$ units capped by two divalent Ni atoms via four bridging oxo groups. The crystal data for these are the following: $C_{120}H_{126}Co_6Mo_{16}N_{24}O_{103}P_2V_{16}$ (**1**), triclinic $P\bar{1}$, $a = 15.6727(2)$ Å, $b = 17.3155(3)$ Å, $c = 19.5445(2)$ Å, $\alpha = 86.1520(1)°$, $\beta = 81.2010(1)°$, $\gamma = 63.5970(1)°$, $Z = 1$; $C_{120}H_{85}Cu_6Mo_8N_{20}O_{44}PV_6$ (**2**), triclinic $P\bar{1}$, $a = 14.565(4)$ Å, $b = 15.899(3)$ Å, $c = 16.246(4)$ Å, $\alpha = 116.289(2)°$, $\beta = 103.084(2)°$, $\gamma = 94.796(2)°$, $Z = 1$; $C_{60}H_{40}Mo_{12}N_{10}Ni_3O_{40}P$ (**3**), monoclinic $P2_1/c$, $a = 14.804(3)$ Å, $b = 22.137(4)$ Å, $c = 25.162(5)$ Å, $\alpha = 90°$, $\beta = 98.59(3)°$, $\gamma = 90°$, $Z = 4$.

Introduction

Over the past decades, polyoxometalates (POMs)[1] have been attracting extensive interest in solid state materials chemistry, owing to the wide range of their topological properties and great potential applications in catalysis, photochemistry, electrochromism, and magnetism.[2,3] Several successful strategies have been developed to design materials built on POMs. Müller's group has reported giant mixed-valence polyoxomolybdates from the "big wheel" Mo_{154} anion[4] to capped cyclic Mo_{248}[5] and "basket" Mo_{116}[6] architectures; Pope's group has reported a new simple way to yield infinite one-dimensional POMs with lanthanide (Ln) or actinide cations as assembling groups,[7,8] and Zubieta and co-workers have reported a number of organic−inorganic hybrid materials built on oxometalates with 1D and 2D frameworks.[9] Furthermore, a new higher-dimensional polyoxoanion-based architecture, $[Gd(H_2O)_3]_3[GdMo_{12}O_{42}]\cdot 3H_2O$,[10] which is constructed from Silverton-type anions linked by gadoli-

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(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.

(2) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.

(3) Special issue on polyoxometalates: Hill, C., Guest Ed. *Chem. Rev.* **1998**, *98*, 1 and references therein.

(4) Müller, A.; Krickemeyer, E.; Meyer, J.; Bögge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122.

(5) Müller, A.; Shah, S. Q. N.; Bögge, H.; Schmidtmann, M. *Nature* **1999**, *397*, 48.

(6) Müller, A.; Polarz, S.; Das, S. K.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Hauptfleisch, B. *Angew. Chem. Int. Ed.* **1999**, *38*, 3241.

(7) Kin, K. C.; Pope, M. T. *J. Am. Chem. Soc.* **1999**, *121*, 8512.

(8) Sadakane, M.; Dickman, M. H.; Pope, M. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 2914.

(9) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(10) Wu, C. D.; Lu, C. Z.; Zhuang, H. H.; Huang, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 3836.

10.1021/ic026296m CCC: $25.00

nium(III) cations into a three-dimensional framework, has been recently reported. In contrast, the direct modification to the surface of POM molecular clusters remains a great challenge.

In the field of modified POMs, capped polyoxoanions with discrete cluster structures have been regarded as an important family. A number of capped structures have been reported,[11−22] such as bicapped $[PMo^{V}_{6}Mo^{VI}_{6}O_{40}(V^{IV}O)_{2}]^{5-}$,[11] $[SiMo_{14}O_{44}]^{4-}$,[14] and $[As^{III}_{2}As^{V}Mo_{8}V^{IV}_{4}O_{40}]^{5-}$,[21,16] and tetracapped $[PMo^{VI}_{5}Mo^{V}_{3}V^{IV}_{8}O_{44}]^{6-}$ and $[PMo^{VI}_{6}Mo^{V}_{2}V^{IV}_{8}O_{44}]^{5-}$.[17] However, the capping metals in these compounds were only restricted to Mo, V, or As atoms which possess high oxidation states. To our knowledge, the polyoxometalate clusters with divalent first-row transition metal as capping atoms have been rarely reported.[22]

Furthermore, heteropolyoxoanion-supported inorganic−organic hybrid solids have been scarcely reported, perhaps due to the difficulty in modifying the surface of hereropolyoxoanions. Moreover, such reported compounds as $[PW_{12}O_{40}Ni(2,2'\text{-bipy})_{2}(H_{2}O)]^{3-}$[23] and $[CpRh{\cdot}SiW_{9}Nb_{3}O_{40}]^{5-}$[24] were only decorated by one transition metal complex. In fact, it is very difficult to find appropriate heteropolyoxometalates that contain sufficient charge density at their surface oxygen atoms so that they can be covalently bonded to more than one chemical group.

In general, two strategies may be exploited to increase the surface charge density and activate the surface oxygen atoms of heteropolyoxoanions:[25] (a) reduce the metal centers from high oxidation state to low oxidation state by introducing strong reducing regents, from Mo(VI) to Mo(V), for instance; or (b) replace metal centers with high oxidation state by another lower-valence metal, for example, from Mo(VI) to V(IV). However, usually the highly reduced polyoxoanions are unstable and inclined to be oxidized in ambient atmosphere. Therefore, it is still a great challenge to obtain stable existing reduced polyoxometalates. Herein, during the course of our attempts to synthesize polyoxometalate-based solid materials,[26−31] we report three novel highly reduced and capped Keggin-heteropolyoxoanion derivatives in terms of the exploitation of hydrothermal techniques and the two strategies already mentioned, $[PMo^{VI}_{6}Mo^{V}_{2}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_{2}(H_{2}O)\}_{4}][PMo^{VI}_{4}Mo^{V}_{4}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_{2}(H_{2}O)\}_{2}]{\cdot}4H_{2}O$ (**1**), $[Cu^{I}(phen)_{2}]_{4}[PMo^{VI}_{8}V^{IV}_{6}O_{42}\{Cu^{I}(phen)\}_{2}]{\cdot}H_{5}O_{2}$ (**2**), and $[Ni(phen)_{3}][PMo^{VI}_{9}Mo^{V}_{3}\ O_{40}\{Ni(phen)\}_{2}]$ (**3**) (2,2′-bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline). In their structures, capping atoms play a great role in stabilizing the highly reduced heteropolyoxoanions and making the surface of heteropolyoxoanions more easily decorated by transition metal complexes. Attractively, in the structure of **1**, heteropolyoxocations and heteropolyoxoanions were coexistently involved in the same crystal because of the modifying effect of transition metal complexes; compound **3** unprecedentedly incorporates a divalent transition metal into the framework as a capping atom and provides a new mode of supporting organic groups as well. Also, hydrogen bonds and $\pi-\pi$ interactions contribute to the building of these architectures. Furthermore, the successful syntheses of these new POM derivatives not only enriched the modifying chemistry of POMs but also may provide more favorable models for catalyst study.

Experimental Section

Materials. All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 20 mL Teflon-lined autoclaves under autogenous pressure. The reactants were neutralized to pH ≈ 4 with 8 M $H_{3}PO_{3}$ under continuous stirring before heating. The reaction vessels were filled to approximately 60% volume capacity. Water used in the reactions is distilled water.

Synthesis of $[PMo^{VI}_{6}Mo^{V}_{2}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_{2}(H_{2}O)\}_{4}][PMo^{VI}_{4}Mo^{V}_{4}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_{2}(H_{2}O)\}_{2}]{\cdot}4H_{2}O$ (1). A mixture of $NH_{4}VO_{3}$ (0.40 g, 3.42 mmol), $Na_{2}MoO_{4}{\cdot}2H_{2}O$ (0.60 g, 2.48 mmol), $CoCl_{2}{\cdot}6H_{2}O$ (0.30 g, 1.26 mmol), 2,2′-bipy (0.40 g, 2.56 mmol), and water (10.0 g, 555.6 mmol) neutralized to pH = 4.2 with $H_{3}PO_{3}$ was heated at 160 °C for 7 days. After slow cooling to room temperature, black block crystals of **1** were separated as a major phase (70% yield on V) together with a small amount of an unidentified brown powder. Anal. Calcd for compound **1**: C, 22.81; H, 2.01; N, 5.32; P, 0.98; Mo, 24.30; V, 12.90; Co, 5.60 (%). Found: C, 22.90; H, 2.16; N, 5.20; P, 0.89; Mo, 24.41; V, 12.79; Co, 5.73 (%).

Synthesis of $[Cu^{I}(phen)_{2}]_{4}[PMo^{VI}_{8}V^{IV}_{6}O_{42}\{Cu^{I}(phen)\}_{2}]{\cdot}H_{5}O_{2}$ (2). A mixture of $NH_{4}VO_{3}$ (1.00 g, 8.55 mmol), $Na_{2}MoO_{4}{\cdot}2H_{2}O$ (0.60 g, 2.48 mmol), $CuCl_{2}{\cdot}2H_{2}O$ (0.30 g, 1.76 mmol), 1,10-phen·$H_{2}O$ (0.40 g, 2.02 mmol), and water (10.0 g, 555.6 mmol) neutralized to pH = 4.4 was heated at 160 °C for 7 days. After slow cooling to room temperature, compound **2** was isolated as black blocks in 80% yield (based on V) along with a small amount of an unidentified brown powder. Anal. Calcd for compound **2**: C, 36.07; H, 2.14; N, 7.01; P, 0.78; Mo, 19.21; V, 7.65; Cu, 9.54 (%). Found: C, 35.95; H, 2.21; N, 7.12; P, 0.68; Mo, 19.34; V, 7.54; Cu, 9.67 (%).

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(11) Chen, Q.; Hill, C. L. *Inorg. Chem.* **1996**, *35*, 2403.

(12) Khan, M. I.; Zubieta, J. *Inorg. Chim. Acta* **1992**, *193*, 17.

(13) Xu, Y.; Xu, J. Q.; Yang, G. Y.; Wang, T. G.; Xing, Y.; Lin, Y. H.; Jia, H. Q. *Polyhedron* **1998**, *17*, 2441.

(14) Dolbecq, A.; Cadot, E.; Eisner, D.; Sécheresse, F. *Inorg. Chem.* **1999**, *38*, 4217.

(15) Luan, G. Y.; Li, Y. G.; Wang, E. B.; Han, Z. B. *Inorg. Chem. Commun.* **2001**, *4*, 632.

(16) Müller, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 599.

(17) Xu, Y.; Zhu, D. R.; Guo, Z. J.; Shi, Y. J.; Zhang, K. L.; You, X. Z. *J. Chem. Soc., Dalton Trans.* **2001**, 772.

(18) Huang, G. Q.; Zhang, S. W.; Wei, Y. G.; Shao, M. C. *Polyhedron* **1993**, *12*, 1483.

(19) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *212*, 199.

(20) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2924.

(21) Luan, G. Y.; Li, Y. G.; Wang, E. B.; Han, Z. B.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *Inorg. Chem. Commun.* **2001**, *4*, 632.

(22) Müller, A.; Beugholt, C.; Kögerler, P.; Bögge, H.; Bud'ko, S.; Luban, M. *Inorg. Chem.* **2000**, *39*, 5176.

(23) Xu, Y.; Xu, J. Q.; Zhang, K. L.; Zhang, Y.; You, X. Z. *Chem. Commun.* **2000**, 153.

(24) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274.

(25) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77.

(26) Guo, Y. H.; Hu, C. W.; Wang, X. L.; Wang, E. B.; Zhou, Y. N.; Feng, S. H. *Chem. Mater.* **2001**, *13*, 4058.

(27) Hu, C. W.; He, Q. L.; Zhang, Y. H.; Liu, Y. Y.; Zhang, Y. F.; Tang, T. D.; Zhang, J. Y.; Wang, E. B. *Chem. Commun.* **1996**, 121.

(28) You, W. S.; Wang, E. B.; Xu, Y.; Li, Y. G.; Xu, L.; Hu, C. W. *Inorg. Chem.* **2001**, *40*, 5648.

(29) Bi, L. H.; Wang, E. B.; Peng, J.; Huang, R. D.; Xu, L.; Hu, C. W. *Inorg Chem.* **2000**, *39*, 671.

(30) Bi, L. H.; Huang, R. D.; Peng, J.; Wang, E. B. *J. Chem. Soc., Dalton Trans.* **2001**, 121.

(31) Peng, J.; Li, W. Z.; Wang, E. B.; Bai, Q. L. *J. Chem. Soc., Dalton Trans.* **2001**, 3668−3671.

Table 1. Crystal Data and Structural Refinement for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{120}H_{126}Co_6Mo_{16}$-$N_{24}O_{103}P_2V_{16}$	$C_{120}H_{85}Cu_6Mo_8$-$N_{20}O_{44}PV_6$	$C_{60}H_{40}Mo_{12}$-$N_{10}Ni_3O_{40}P$
fw	3159.02	3996.45	2899.40
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	15.6727(2)	14.565(4)	14.804(3)
b (Å)	17.3155(3)	15.899(3)	22.137(4)
c (Å)	19.5445(2)	16.246(4)	25.162(5)
α (deg)	86.1520(1)	116.289(2)	90
β (deg)	81.2010(1)	103.084(2)	98.59(3)
γ (deg)	63.5970(1)	94.796(2)	90
V (Å^3)	4694.82(1)	3211.6(1)	8154(3)
Z	1	1	4
D_c (g cm^{-3})	2.235	2.066	2.362
μ (mm^{-1})	2.415	2.240	2.567
R1[a]	0.0443	0.0555	0.0537
wR2[b]	0.1315	0.1202	0.1080

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Synthesis of $[Ni(phen)_3][PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]$ (3). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.00 g, 0.81 mmol), $NiCl_2\cdot 6H_2O$ (0.20 g, 0.84 mmol), 1,10-phen·H_2O (0.20 g, 1.01 mmol), and water (10.0 g, 555.6 mmol) neutralized to pH = 3.8 was heated at 160 °C for 7 days. After slow cooling to room temperature, little black crystals of compound **3** were collected in 50% yield (based on Mo) together with a small amount of an amorphous brown powder. Anal. Calcd for compound **3**: C, 24.86; H, 1.39; N, 4.83; P, 1.18; Mo, 39.71; Ni, 6.21 (%). Found: C, 25.02; H, 1.48; N, 4.71; P, 1.07; Mo, 39.86; Ni, 6.07 (%).

X-ray Crystallography. The data for compounds **1** and **3** were collected on a Rigaku R-AXIS RAPID imaging-plate X-ray diffractometer, while the measurement for compound **2** was performed on a Siemens P4 four-circle diffractometer. In all cases, the data were collected at 293 K, and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used.

The structures for compounds **1**−**3** were solved by direct methods using the program SHELXS-97[32] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97[33] program package. All of the non-hydrogen atoms were refined anisotropically except for several oxygen and carbon atoms. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions, and those attached to oxygen atoms were not located. A summary of the crystallographic data and structural determination for **1**−**3** is provided in Table 1. Selected bond lengths and angles for **1**−**3** are listed in the Supporting Information.

The CCDC reference numbers are 191850 for compound **1**, 191851 for compound **2**, and 191852 for compound **3**.

Physical Measurements. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. P, Mo, V, Co, Cu, and Ni were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. A diffuse reflectance UV−vis spectrum ($BaSO_4$ pellet) was obtained from the solid state with a Varian Cary 500 UV−vis−NIR spectrometer. An EPR spectrum was recorded on a Japanese JES-FE3AX spectrometer at room temperature. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}.

Results and Discussion

Synthesis. The isolations of compounds **1**−**3** depended on the exploitation of hydrothermal techniques. Hydrothermal reactions in the presence of organic ligand molecules, which cause a reaction that shifts from the kinetic to the thermodynamic domain as compared to traditional aqueous reactions, have been established as versatile methods for the isolation of new materials with diverse structural architectures.[9,34−37] Besides well-established V−O−L and Mo−O−L systems, the hydrothermal reactions of Mo−P−O−L and Mo−V−P−O−L systems are receiving more and more attention, especially for those heteropolyanion clusters attached to organic groups.[23] This may be due to the fact that, in the typical hydrothermal reactions in the temperature range 120−260 °C under autogenous pressure, differential solubility problems arising from the mixture of organic and inorganic starting materials are minimized,[38] and the self-assembly of the product from soluble precursors is exploited. However, hydrothermal synthesis is a relatively complex process, so the elements of mechanistic control are generally absent and the final products under a given set of conditions are often unpredictable. Generally, many factors can affect the reaction, such as starting materials, pH, temperature, filling volume, and stoichiometry.

Compounds **1**−**2** were both separated from the hydrothermal reactions of NH_4VO_3, $Na_2MoO_4\cdot 2H_2O$, $CoCl_2\cdot 2H_2O$ ($CuCl_2\cdot 2H_2O$), 2,2′-bipy (1,10-phen·H_2O), H_3PO_3, and water at 160 °C for 7 days, respectively, while compound **3** was prepared by the hydrothermal reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $NiCl_2\cdot 6H_2O$, 1,10-phen·H_2O, H_3PO_3, and water in similar conditions to those of compounds **1**−**2**. By plenty of parallel experiments, it was found that starting materials play a great role in the isolations of these three compounds: (1) The organonitrogen ligand is significant. For compound **1**, if 2,2′-bipy was substituted by phen, another novel compound reported by our group would be synthesized, which was constructed from the organic−inorganic hybrid $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$ complex and highly reduced bicapped pseudo-Keggin $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$ polyoxoanions connected into an extended 2D network through hydrogen bonds, combining polyoxometalates with metal phosphites for the first time.[37] This example also shows that the steric constraints imposed by the phenanthroline ligand are quite distinct from those of the 2,2′-bipy. Furthermore, if 2,2′-bipy was replaced by 4,4′-bipy, we could only get some homogenized blue slurry. (2) The divalent transition metal is significant. As we know, transition metal cations can efficiently influence the formation of structural materi-

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(32) Sheldrick, G. M. *SHELXS 97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(33) Sheldrick, G. M. *SHELXL 97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(34) Lu, Y.; Wang, E. B.; Yuan, M.; Luan, G. Y.; Li, Y. G.; Zhang, H.; Hu, C. W.; Yao, Y. G.; Qin, Y. Y.; Chen, Y. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3029.

(35) Xu, L.; Sun, Y. Q.; Wang, E. B.; Shen, E. H.; Liu, Z. R.; Hu, C. W.; Xing, Y.; Lin, Y. H.; Jia, H. Q. *New. J. Chem.* **1999**, *23*, 1041.

(36) Li, Y. G.; Wang, E. B.; Zhang, H.; Luan, G. Y.; Hu, C. W. *J. Solid State. Chem.* **2002**, *163*, 10.

(37) Yuan, M.; Li, Y. G.; Wang, E. B.; Lu, Y.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *J. Chem. Soc., Dalton Trans.* **2002**, 2916.

(38) Hagrman, P. J.; LaDuca, R. L., Jr.; Koo, H. J.; Rarig, R., Jr.; Haushalter, R. C.; Whangbo, M. H.; Zubieta, J. *Inorg. Chem.* **2000**, *39*, 4311.

als. We once tried to replace $CoCl_2{\cdot}2H_2O$ with $MnCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ in the synthesis of compound **2** and replace $NiCl_2{\cdot}6H_2O$ with $CuCl_2{\cdot}2H_2O$ in the preparation of compound **3**, but all attempts failed, showing the effect of a third divalent transition metal to such a reaction system. (3) The phosphorus (+3) acid is also important. It serves as a strongly reductive reagent in the reactions and leads to the formation of highly reduced polyoxoanions that can easily be modified on the surface. (4) The molybdenum source is significant. For the synthesis of compound **3**, the molybdenum source must be the isopolymolybdate cluster; if it was replaced by simple sodium molybdate, we would only find a large sum of black powders. The reason may lie in the fact that the isopolymolybdate can slowly release molybdenum sources and then contribute to the formation of large single crystals. In addition, we also found that the reactions of Mo−V−P system were not sensitive to reaction temperature. If the reaction temperature was set 10 °C above or below 160 °C, the expected crystals remained to be formed. However, if the pH of the reaction was lower or higher than 4, polycrystals were obtained.

Crystal Structures. The structures of **1**−**3** are all built on reduced heteropolyoxoanions and divalent transition metal complexes.

The crystal of **1** contains a tetracapped tetrasupporting $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$ heteropolyoxocation, tetracapped bisupporting $[PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]^{3-}$ heteropolyoxoanion, and lattice water molecules. As shown in Figure 1a, the novel eiconuclear polyoxocation $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$ consists of a highly reduced tetracapped pseudo-Keggin $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]^{5-}$ unit and four $\{Co(2,2'\text{-bipy})_2(H_2O)\}$ fragments. The $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]^{5-}$ cluster is very similar to that in $[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]{\cdot}tea{\cdot}H_2O$ and $[Co(tea)_2]Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]{\cdot}8H_2O$ (tea = triethylenediamine).[17] Its structure is essentially built on the well-known α-Keggin structure with four additional five-coordinating terminal $\{VO\}^{2+}$ units and contains a distorted central P^{5+} as a guest in the $[Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}]^{2-}$ host cage. All vanadium atoms show a distorted $\{VO_5\}$ square pyramidal environment with V−O distances in the range 1.605(4)−1.999(5) Å and bond angles 65.60(2)−162.19(2)°. All molybdenum atoms have a distorted $\{MoO_6\}$ octahedral environment with Mo−O distances 1.655(4)−2.520(7) Å and bond angles 62.9(2)−161.3(3)°. The disordered PO_4 tetrahedron was located in the center of the host cage with P−O distances of 1.511(7)−1.572(6) Å and O−P−O angles 107.3(4)−110.0(4)°. In the Keggin part $[PMo^{VI}_6Mo^{V}_2V^{IV}_4O_{40}]$, each trimetallic group is composed of one V and two Mo atoms; four $\{MoO_6\}$ octahedra form a $\{Mo_4O_{18}\}$ ring via the corner- and edge-sharing modes, as shown in Figure 1b. Thus, in the whole $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]^{5-}$ cluster, eight $\{VO_5\}$ square pyramids are bonded into a central belt by sharing square edges with two $\{Mo_4O_{18}\}$ rings above and below the $\{V_8\}$ belt through corner- and edge-sharing modes. In addition, the polyoxoanion reveals a high negative charge due to the introduction of strong reductive reagent H_3PO_3. The valence sum calculations[39,40] give values 5.70−5.87 Å for Mo(5)−Mo(8) (2×), the average value of which is 5.77 Å (the expected average value for $Mo^{VI}_6Mo^{V}_2$ is 5.75 Å), and also give values 3.96−4.18 Å for V atoms with an average value of 4.08 Å. The calculated results reveal that, in the structure of the polyoxocation of **1**, all V centers are

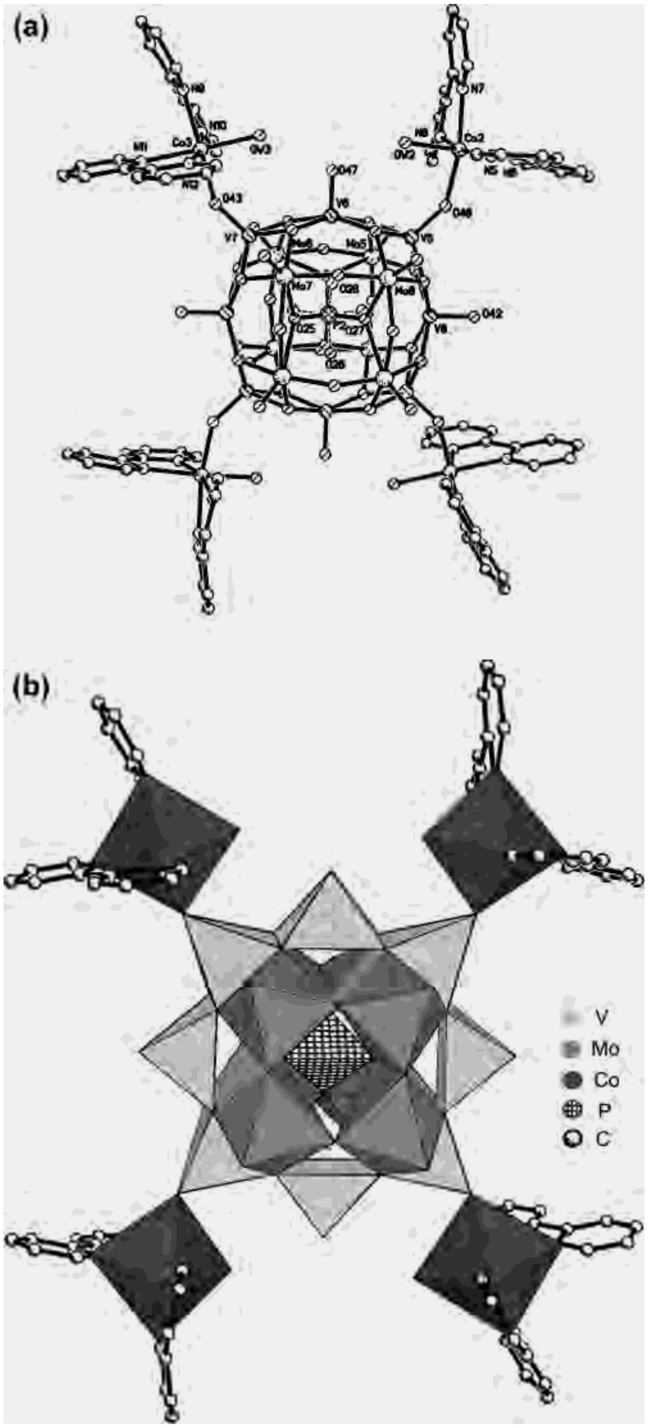

Figure 1. (a) View of the polyoxocation in **1**, $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$, showing the tetracapping and tetrasupporting connection mode and disordered P tetrahedron. (b) Polyhedral representation of the polyoxocation in **1**, exhibiting the V8 belt.

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(39) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(40) O'Keeffe, M.; Navrotsky, A. *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Acadamic Press: New York, 1981; Vol. II, p 1.

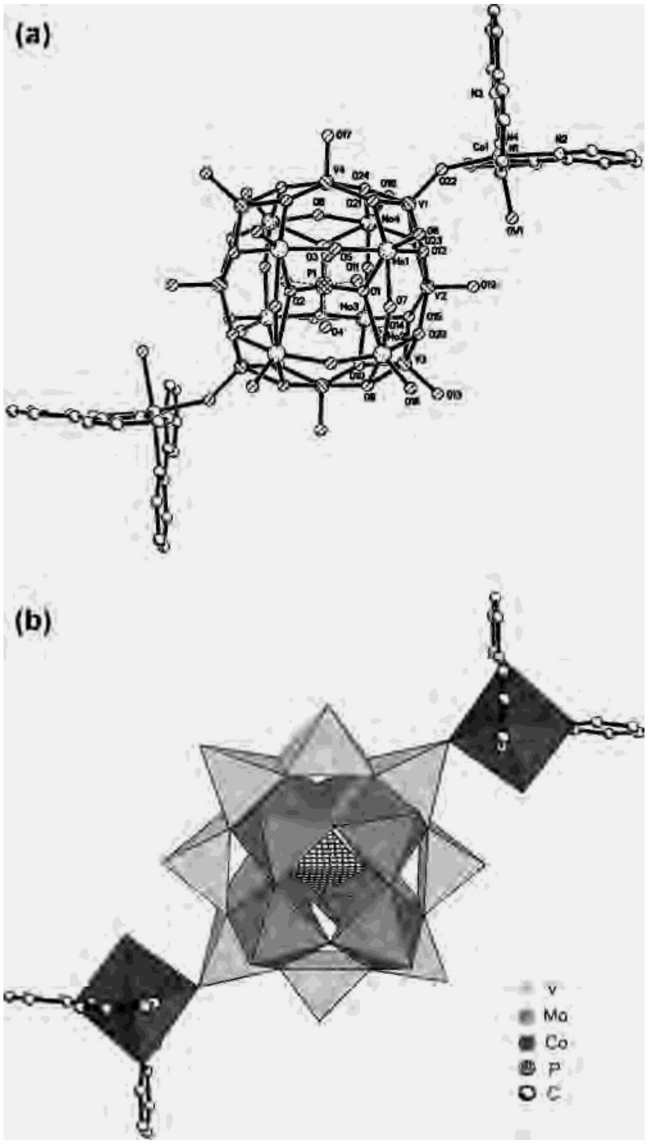

Figure 2. (a) View of the polyoxoanion in **1**, $[PMo^{VI}_4Mo^V_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3-}$, showing the tetracapping and bisupporting connection mode. (b) Polyhedral representation of the polyoxoanion in **1**, showing the coordination environments around Mo, V, and Co atoms.

in the +4 oxidation state, while two out of eight Mo centers are in the +5 oxidation state with two electrons delocalized within the two $\{Mo_4O_{18}\}$ rings, which was consistent with the formula of the polyoxocation. Such mixed-valence Mo atoms have once been found in three-electron-reduced $[Ni(tea)_2]_3[PMo^{VI}_5Mo^V_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ and two-electron-reduced $[Co(tea)_2]Na[PMo^{VI}_6Mo^V_2V^{IV}_8O_{44}]\cdot 8H_2O$.[17]

It is noteworthy that each $[PMo^{VI}_6Mo^V_2V^{IV}_8O_{44}]^{5-}$ unit acts as a ligand covalently bonded to four $\{Co(2,2'\text{-bipy})\}$ subunits through the terminal oxygen atoms of the four capping V atoms. Each Co atom is coordinated by four nitrogen atoms from two 2,2′-bipy ligands with Co−N distances of 2.108(5)−2.147(5) Å and N−Co−N angles of 75.6(2)−173.9(2)°, one oxygen atom from the $[PMo^{VI}_6Mo^V_2V^{IV}_8O_{44}]^{5-}$ anion, and a terminal ligand water molecule with Co−OW distances of 2.144(4) and 2.109(5) Å to finish its distorted octahedral coordination environment.

As shown in Figure 2a,b, the octadenuclear polyoxoanion $[PMo^{VI}_4Mo^V_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]^{3-}$ of **1** consists of a tetracapped $[PMo^{VI}_4Mo^V_4V^{IV}_8O_{44}]^{7-}$ and two $\{Co(2,2'\text{-bipy})\}$ fragments. Its structure is very similar to the $[PMo^{VI}_6Mo^V_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$ polyoxocation as already described. The main differences between them consist of the charge distribution of the $[PMo_8V_8O_{44}]$ cluster and the number of supporting transition metal complexes on its surface. The valence sum calculations[39,40] establish that all the V centers are in the +4 oxidation state with a calculated average value of 4.08, and there are four reduced Mo^{5+} centers (calculated average value, 5.54; expected for $[Mo^{VI}_4Mo^V_4]$, 5.50) with four electrons delocalized within two $\{Mo_4O_{18}\}$ rings. In comparison, the $[PMo^{VI}_6Mo^V_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]^{3+}$ cation supports four $\{Co(2,2'\text{-bipy})\}$ complexes and exhibits a net valence of +3, while the $[PMo^{VI}_4Mo^V_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]^{3-}$ anion supports two $\{Co(2,2'\text{-bipy})\}$ complexes and possess a net valence of −3, meeting with the need of charge balance.

Another noteworthy feature in **1** is that both polyoxocations and polyoxoanions are both presented in the same crystal at the same time. This may be caused by the modifying effect of the transition metal complexes on the surface of polyoxometalates. Such a case once occurred in $K_3[\epsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_{4.25}Cl_{0.75}\}_4][\alpha\text{-}PMo_{12}O_{40}]\cdot 28H_2O$ in which columns of ϵ-Keggin cations alternate with columns of α-Keggin anions.[41] Furthermore, through the linkages of $\pi-\pi$ stacking interactions and hydrogen bond contacts, an extended three-dimensional supramolecular network in the solid of **1** was formed.

The crystal of **2** consists of bicapped bisupporting mixed-metal hexadenuclear clusters $[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^I(phen)\}_2]^{5-}$, $\{Cu(phen)_2\}^+$ countercations, and lattice water molecules, which are held together into an extended one-dimensional network via $\pi-\pi$ interactions. As shown in Figure 3a, the $[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^I(phen)\}_2]^{5-}$ polyoxoanion is constructed from a $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ tetradenuclear cluster decorated by $\{Cu(phen)\}^+$ units. The $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ cluster can also be regarded as an α-Keggin core $\{PMo_8V_4O_{40}\}$ with square pyramidal $\{VO\}$ units capping two opposite pits. Two $\{Mo_4O_{18}\}$ rings composed of four $\{MoO_6\}$ octahedra, just as described in **1**, are connected with four $\{VO_5\}$ pyramids through corner-sharing mode from above and below the center, respectively. Thus, the polyoxoanion exhibits an unusual phosphorus-centered regular arrangement of vanadium and molybdenum oxide layers, as occurred in $[Co_4(phen)_8(H_2O)_2(HPO_3)_2](H_3O)_3[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]$.[37] The valence sum calculations[39,40] confirm that all the V centers are in the +4 oxidation state (calculated average value 4.03) and all the Mo centers are in +6 oxidation state (calculated average value 6.05), leading the polyoxoanion to be formulated as $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$, similar to that in $[Co_4(phen)_8(H_2O)_2(HPO_3)_2](H_3O)_3[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]$.[37] Interestingly, each $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ unit forms a covalent interaction with two $\{Cu(phen)\}^+$ fragments via the terminal oxygen atoms of the capping vanadium atoms from the

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(41) Mialane, P.; Dolbecq, A.; Lisnard, L.; Mallard, A.; Marrot, J.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2398.

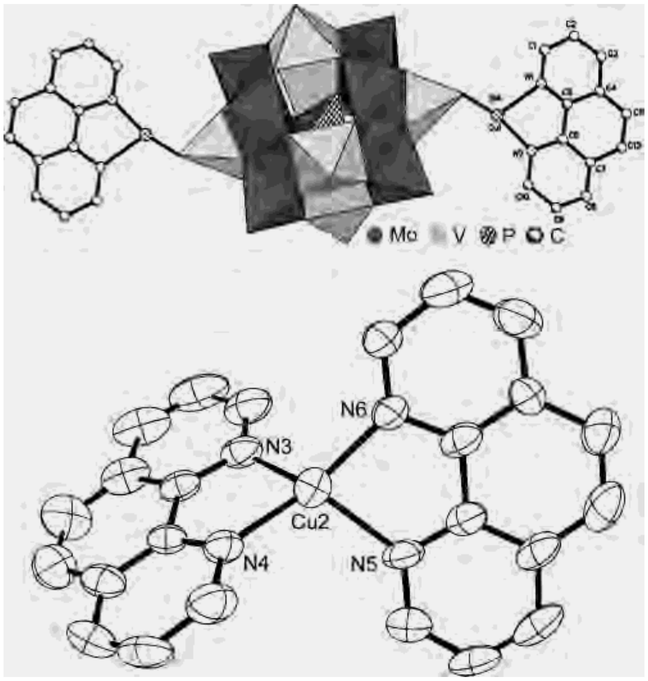

Figure 3. (a) Polyhedral representation of the polyoxoanion $[PMo^{VI}_8V^{IV}_6O_{42}\{Cu(phen)\}_2]^{5-}$ in **2**, showing the coordination environment of Cu^+ and the alternating vanadium and molybdenum oxide layers. (b) ORTEP drawing of the countercation in **2** depicted at the 50% probability level, showing the coordination environment of Cu^+.

$[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ anion with Cu^I-O distance of 1.836(6) Å. Another unusual feature in **2** is that there are two types of copper(I) coordination environments (as shown in Figure 3a,b): Cu(1) is linked to a terminal oxygen atom of a capping vanadium center in the $[PMo^{VI}_8V^{IV}_6O_{42}]^{7-}$ anion and two nitrogen atoms from one phen ligand [Cu−N, 1.917(9) and 2.177(7) Å], obviously forming a "T"-shaped coordination geometry in the form of $\{OCuN_2\}$, whereas Cu(2) ion is coordinated by four nitrogen atoms from two phen ligands [Cu−N, 1.990(9)−2.084(1) Å], exhibiting a distorted tetrahedral geometry in the form of $\{CuN_4\}$, which serves as countercation in the crystal structure. In comparison with the Cu−O distance in $[\{Cu^I(py)_3\}_2\{Cu(py)_2\}_2(\alpha\text{-}Mo_8O_{26})]$,[42] the Cu−O distance in **2** is much shorter, showing that the $\{Cu^I(phen)\}$ units are more strongly bonded to the polyoxoanions. Furthermore, two lattice water molecules are protonated because of the need of the charge balance. The hexadenuclear heterometallic polyoxoanions of **2** are stabilized and further extended into an interesting one-dimensional supramolecular array via $\pi-\pi$ interactions.

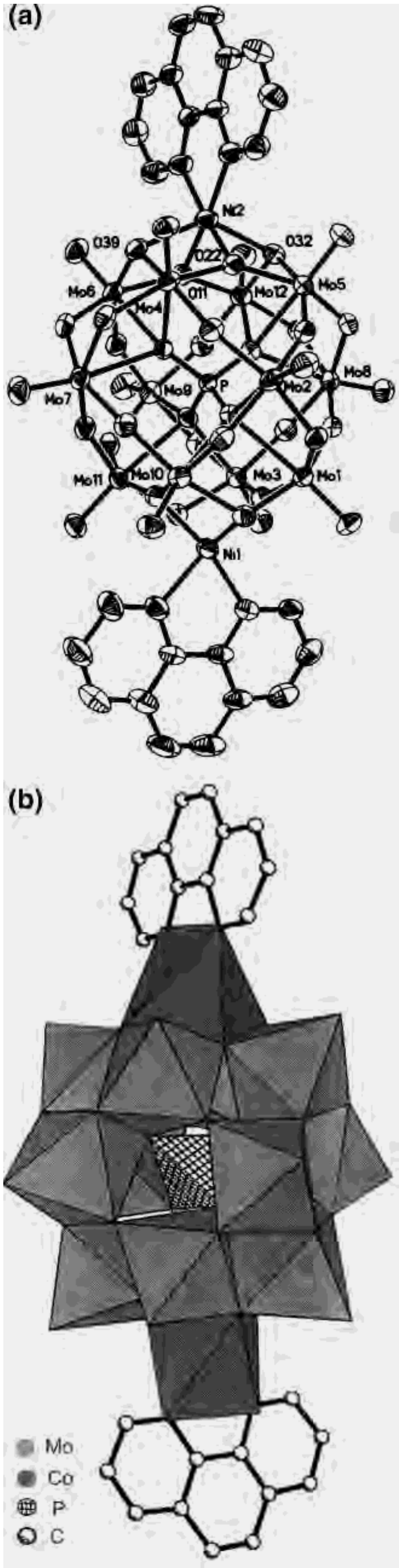

Figure 4. (a) ORTEP drawing of compound **3** depicted at the 50% probability level, showing the atom-labeling scheme. (b) Polyhedral representation of the polyoxoanion in **3**, $[PMo^{VI}_9Mo^V_3O_{40}\{Ni(phen)\}_2]^{2-}$.

During the course of our attempts to synthesize new Keggin derivatives, a novel bicapped compound $[Ni(phen)_3][PMo^{VI}_9Mo^V_3O_{40}\{Ni(phen)\}_2]$ (**3**) with two Ni atoms as caps has been obtained. As shown in Figure 4a,b, the novel polyoxoanion $[PMo^{VI}_9Mo^V_3O_{40}\{Ni(phen)\}_2]^{2-}$ consists of a reduced Keggin heteropolyanion $[PMo^{VI}_9Mo^V_3O_{40}]^{6-}$ and two-$\{Ni(phen)\}$ complexes. As in other well-known Keggin structures, the highly reduced polyoxoanion is constructed from a central PO_4 tetrahedron which shares its oxygen atoms with four $\{Mo_3O_{13}\}$ groups, each of which is made up of three edge-sharing $\{MoO_6\}$ octahedral. The $\{Mo_3O_{13}\}$ subunits are joined to each other by corner-sharing mode. The valence

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(42) Chae, H. K.; Klemperer, W. G.; Day, V. W. *Inorg. Chem.* **1989**, *28*, 1423.

sum calculations[39,40] provide values in the range 5.66−5.86 for Mo atoms to give an average value of 5.77 (the expected average value for $Mo^{VI}_9Mo^{V}_3$ is 5.75). The calculated results show 3 out of 12 Mo atoms in +5 oxidation states with three electrons delocalized within the whole metal−oxide cluster, which is also in agreement with the formula of the classic Keggin-polyoxoanion, $[PMo^{VI}_9Mo^{V}_3O_{40}]^{6-}$. An unusual feature of the structure is that the Keggin polyoxoanion is capped by two divalent Ni atoms through four bridging oxo groups on two opposite $\{Mo_4O_4\}$ faces or pits, while in the case of $[Mo^{V}_{12}O_{30}(\mu\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4]$,[22] the Ni^{2+} was bonded to the polyoxometalate framework through three oxo groups. The Ni^{2+} in **3** is coordinated by two nitrogen atoms from one 2,2′-bipy ligand and four bridging oxygen atoms from the Keggin unit with Ni−N distances of 2.049(5)−2.113(6) Å and Ni−O distances of 2.012(4)−2.197(4) Å, respectively. The structure of $[PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]^{2-}$ can also be described as a reduced Keggin polyoxoanion supporting two {Ni(phen)} units through four bridging oxo groups which connect two adjacent molybdenum sites. In contrast to the first reported α-Keggin heteropolyanion coordinated to a transition metal complex, $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$,[23] the crystal of **3** has three specific characteristics: (1) The net valence of the Keggin polyoxoanion in **3** is −6 while it was −5 in the former compound. (2) The Keggin anion in **3** supports two transition metal complexes in the opposite directions whereas the polyoxoanion in the former compound only supports one. (3) For **3**, the transition metal complex and the heteropolyanion are bridged via four bridging atoms, strengthening the interaction between them, which is obviously stronger than that in the former compound with only one terminal atom as bridge. Such a kind of connection mode is often observed between the capping vanadium(IV) atom and the basic POM part while it is very unusual for a divalent transition metal.

Characterization. In the IR spectra, vibration modes for $\nu(P{-}O_a)$, $\nu(M{=}O_d)$, $\nu(M{-}O_b{-}M)$, and $\nu(M{-}O_c{-}M)$ (M = V or Mo) are observed at 1046, 949, 870, 767 cm^{-1}, **1**; 1049, 926, 844, 769 cm^{-1}, **2**; 1049, 940, 870, 774 cm^{-1}, **3**.[11] The characteristic absorption bands of organonitrogen ligands occur at 1597, 1573, 1490, 1471, 1046, cm^{-1}, **1**; 1582, 1517, 1493, 1342 cm^{-1}, **2**; 1584, 1516, 1426, 1344 cm^{-1}, **3**.[43] The IR data show that the $\nu(M{=}O_d)$ bands in compounds **1** and **3** are at higher energy than that in compound **2**, as anticipated for more reduced molybdenum sites.[38] In the UV−vis spectra, the oxygen-to-metal charge transfer absorption maxima occur at 252, 293 nm, **1**; 258, 346 nm, **2**; 261, 342 nm, **3**, and the characteristic combination d−d and intervalence charge transfer (IVCT) absorption maxima are observed at 675 and 691 nm for compounds **1** and **3**, respectively.[11] The absence of IVCT absorption for **2** further confirms that all the molybdenum atoms are in the high +6 oxidation state. The EPR spectra for both compounds **1** and **2** exhibit the V^{4+} signal with $g = 1.9684$, $A = 400$ G and $g = 2.0984$, $A = 180$ G, respectively, and the EPR spectrum for compound **3** shows the Mo^{5+} signal with $g = 1.9262$, $A = 70$ G. All these results further confirm the structure analysis.

The TG curves (see Supporting Information) for compounds **1**−**3** also support their chemical compositions. The weight loss at 50−200 °C is considered as the loss of lattice water and ligand water molecules, 4.69% (calcd 4.28%), **1**; 1.52% (calcd 0.93%), **2**; 0.32% (calcd 0), **3**, while the weight loss at 250−620 °C is ascribed to decomposition of organoamine ligands, 28.76% (calcd 29.66%), **1**; 45.40% (calcd 45.09%), **2**; 30.24% (calcd 31.08%), **3**.

Conclusions

In this paper, we have prepared and structurally characterized three novel POM derivatives. As for **1** and **2**, they have four common interesting structural features: (1) the presence of mixed molybdenum−vanadium polyoxometalate units; (2) the capping by vanadium(IV) atoms; (3) covalent bonds to divalent transition metal complexes through the terminal oxo groups of the capping vanadium atoms; and (4) the formation of extended supramolecular networks via hydrogen bond contacts or $\pi-\pi$ stacking interactions. It is noted that the structure of **1** contains two kinds of structural polyoxometalates as cation and anion, respectively. The structure of **3** is different from the other two compounds already mentioned. It is derived from the classic Keggin $[PMo_{12}O_{40}]$ cluster covalently bonded to two divalent transition metal complexes via four bridging oxo groups of the normal molybdenum atoms from the Keggin part. Extraordinarily, these two transition metal complexes in **3** can be not only regarded as caps on the Keggin part but also considered to be supported on the surface of the heteropolyanion in a new mode different from the routine supported compounds. It is noted that, in the structures of **1**−**3**, the capping V or Ni atoms keep the high polyoxoanions in a stabilized state and ensure that the surfaces of polyoxoanions are easily decorated by more transition metal complexes. Furthermore, the successful syntheses of these three novel POM derivatives prove again the advantages of hydrothermal techniques in designing new kinds of structural inorganic−organic hybrid solids. Also, just as Drs. Gouzerh and Proust anticipated, the surface of the polyoxometalates can be activated by exploiting lower valent metals than Mo(VI) or W(VI), and then, more favorable models for catalyst study may be obtained by changing mixed metals, organoamines, and divalent transition metal, and may further enrich the modifying chemistry of POMs.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (20171010).

Supporting Information Available: X-ray crystallographic files in CIF format for structures **1**−**3** (CCDC numbers 191850−191852), five additional figures, and three additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Rarig, R. S., Jr.; Lam, R.; Zavalij, P. Y.; Ngala, J. K.; LaDuca, R. L., Jr.; Greedan, J. E.; Zubieta, J. *Inorg. Chem.* **2002**, *41*, 2124.