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A Novel Organic–Inorganic Hybrid Based on an 8-Electron-Reduced Keggin Polymolybdate Capped by Tetrahedral, Trigonal Bipyramidal, and Octahedral Zinc: Synthesis and Crystal Structure of $(CH_3NH_3)(H_2bipy)[Zn_4(bipy)_3(H_2O)_2Mo^{V}{}_8Mo^{VI}{}_4O_{36}(PO_4)]\cdot 4H_2O$

Chong Lei, Jiang-Gao Mao,* Yan-Qiong Sun, and Jun-Ling Song

State Key Laboratory of Structure Chemistry, Fujian Institute for Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

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Hydrothermal reaction of H_3PO_3, CH_3NH_2, zinc(II) acetate, 4,4′-bipyridine (bipy), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 180 °C led to a novel organic–inorganic layered hybrid, $[CH_3NH_3][H_2bipy][Zn_4(bipy)_3(H_2O)_2Mo^{V}{}_8Mo^{VI}O_{36}(PO_4)]\cdot 4H_2O$ (**1**). Its structure was established by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$ with cell parameters of $a = 17.3032(2)$, $b = 17.8113(3)$, and $c = 23.4597$ (4) Å, $\beta = 106.410(1)°$, $V = 6935.6(2)$ Å^3, and $Z = 4$. The structure of compound **1** features a novel 2D layer built from the 8e-reduced tetracapped Keggin $[Zn_4Mo_{12}O_{36}(PO_4)]^{3-}$ anions, which are further interconnected by bridging bipy ligands. The four zinc(II) ions are in tetrahedral, trigonal bipyramidal, and octahedral coordination geometries, respectively.

Introduction

Polyoxometalates (POMs) are one of the most widely used inorganic components due to their extreme variability of compositions, molecular characteristics, properties, and applications.[1] Recently, a lot of research efforts have been focused on the functionalization of POMs with transition metal complex or lanthanide complex moieties, the coordination transition metal or lanthanide metal complex cation serves to provide charge-compensation, space-filling, and structure-directing roles. For most cases, the transitional metal and the rare earth ions are found to be either sandwiched between two polymolybdate anions or positioned as a capping atom on the cluster unit.[2−5] Diphosphonic acids have been reported recently to be able to form a number of organic−inorganic hybrids containing polyoxomolybdate anions interconnected by transitional metal complex moieties.[6] Examples of the organic−inorganic hybrid built from Keggin polyoxometalates and transition metal complexes are still rare, though a number of isolated Keggin units have been reported.[7−10] We have recently reported a novel zinc(II) complex with *N*-(phosphonomethyl)-*N*-methylglycine, $MeN(CH_2CO_2H)(CH_2PO_3H_2)$, which contains an unusual

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* To whom correspondence should be addressed. E-mail: mjg@ms.fjirsm.ac.cn.

[1] (a) *Polyoxometalate Chemistry for Nanocomposite Design*; Pope, M. T., Yamase, T., Eds.; Kluwer: Dordrecht, The Netherlands, 2002. (b) *Polyoxometalates: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 2001.

[2] (a) Hagrman, D.; Zapf, P. J.; Zubieta, J. *Chem. Commun.* **1998**, 1283. (b) Zhou, Y.-S.; Zhang, L.-J.; You, X.-Z.; Natarajan, S. *J. Solid State Chem.* **2001**, *159*, 209. (c) Meyer, L. A.; Haushalter, R. C. *Inorg. Chem.* **1993**, *32*, 1579. (d) Rarig, Jr. R. S.; Zubieta, J. *J. Solid State Chem.* **2002**, *167*, 370. (e) Rarig, R. S., Jr.; Bewley, L.; Golub, V.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem. Commun.* **2003**, *6*, 539.

[3] (a) Wu, C.-D.; Lu, C.-Z.; Zhuang, H.-H.; Huang, J.-S. *Inorg. Chem.* **2002**, *41*, 5636. (b) Yuan, M.; Wang, E.; Lu, Y.; Li, Y.; Hu, C.; Hu, N.; Jia, H. *Inorg. Chem. Commun.* **2002**, *5*, 505. (c) Peloux, C. du; Dolbecq, A.; Mialane, P.; Marrot, J.; Rivière, E.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2455. (d) Xu, L.; Sun, Y.; Wang, E.; Shen, E.; Liu, Z.; Hu, C.; Xing, Y.; Lin, Y.; Jia, H. *New J. Chem.* **1999**, *23*, 1041. (e) Xu, L.; Sun, Y.; Wang, E.; Shen, E.; Liu, Z.; Hu, C.; Xing, Y.; Lin, Y.; Jia, H. *J. Solid State Chem.* **1999**, *146*, 533.

[4] (a) Wu, C.-D.; Lu, C.-Z.; Zhuang, H.-H.; Huang, J.-S. *J. Am. Chem. Soc.* **2002**, *124*, 3836. (b) Lu, C.-Z.; Wu, C.-D.; Zhuang, H.-H.; Huang, J.-S. *Chem. Mater.* **2002**, *14*, 2649. (c) Wu, C.-D.; Lu, C.-Z.; Lin, X.; Zhuang, H.-H.; Huang, J.-S. *Inorg. Chem. Commun.* **2002**, *5*, 664. (d) Hagrman, D.; Zubieta, J. *Chem. Commun.* **1998**, 2005; Brukholder, E.; Zubieta, J. *Chem. Commun.* **2001**, 2056.

[5] (a) Mundi, L. A.; Haushalter, R. C. *Inorg. Chem.* **1992**, *31*, 3050. (b) Yuan, M.; Wang, E.; Lu, Y.; Li, Y.; Hu, C.; Hu, N.; Jia, H. *Inorg. J. Solid State Chem.* **2003**, *170*, 192. (c) Zhou, Y.; Zhang, L.; You, X.; Natarajan, S. *Inorg. Chem. Commun.* **2001**, *4*, 699.

[6] (a) Finn, R. C.; Rarig, R. S.; Zubieta, J. *Inorg. Chem.* **2002**, *41*, 2109. (b) Finn, R. C.; Burkholder, E.; Zubieta, J. *Chem. Commun.* **2001**, 1852. (c) Finn, R. C.; Zubieta, J. *Inorg. Chem.* **2001**, *40*, 2466.

[7] (a) Reinoso, S.; Vitoria, P.; Lezama, L.; Luque, A.; Gutiérrez-Zorrilla, J. M. *Inorg. Chem.* **2003**, *42*, 3709. (b) Yang, W.; Lu, C.; Zhuang, H. *J. Chem. Soc., Dalton Trans.* **2002**, 2879. (c) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2924. (d) Bu, W.-M.; Ye, L.; Yang, G.-Y.; Gao, J.-S.; Fan, Y.-G.; Shao, M.-C.; Xu, J.-Q. *Inorg. Chem. Commun.* **2001**, *4*, 1.

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oxo-bridged $Zn_6(Zn)$-centered octahedral cluster unit.[11] In our attempt to prepare a polymolybdate with zinc carboxylate phosphonate moiety by hydrothermal reaction, we obtained a novel tetracapped 8e-reduced Keggin polymolybdate instead, $[CH_3NH_3][H_2bipy][Zn_4(bipy)_3(H_2O)_2Mo^{V}{}_8Mo^{VI}{}_4O_{36}(PO_4)]\cdot 4H_2O$ (**1**). Herein we report its synthesis, characterization, and crystal structure.

Experimental Section

Materials and Methods. All chemicals and solvents were of reagent grade and used as received. $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ was synthesized by a Mannich type reaction according to procedures previously described.[11] Elemental analyses were performed on a German Elementary Vario EL III instrument. Mo, Zn, and P analyses were carried out with an ICPQ-100 spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range 4000−400 cm^{-1}. Thermogravimetric analyses were carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C/min under a nitrogen atmosphere. The XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated Cu Kα radiation in the angular range $2\theta = 5-70°$ with a step size of 0.02° and a counting time of 3 s/step. Magnetic susceptibility measurements were performed with a Quantum Design SQUID magnetometer at a field of 1 T over the range 2−300 K. The diamagnetic contributions of the samples were corrected using Pascal's constants.

Synthesis of $[CH_3NH_3][H_2bipy][Zn_4(bipy)_3(H_2O)_2Mo^{V}{}_8Mo^{VI}{}_4O_{36}(PO_4)]\cdot 4H_2O$ (1). Compound **1** was initially synthesized by hydrothermal reactions of zinc(II) acetate (0.5 mmol), 4,4′-bipyridine (0.5 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.5 mmol), and $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ (0.5 mmol) as well as 10.0 mL of water in a Teflon-lined stainless steel autoclave (25 mL) at 180 °C for 4 days. Black crystals of compound **1** were obtained in a ca. 35% yield based on zinc. The compound was then resynthesized in a much higher yield (53.5%, based on zinc) by hydrothermal reaction of H_3PO_3 (0.25 mmol), CH_3NH_2 (0.25 mmol), zinc(II) acetate ((1 mmol), 4,4′-bipyridine ((1 mmol, bipy), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.5 mmol) as well as 10.0 mL of water in a Teflon-lined stainless steel autoclave (25 mL) at 180 °C (the initial and final pH values are 5.0 and 6.0, respectively) for 5 days. Anal. Found: Mo, 39.2; Zn, 8.8; P, 1.2; C, 19.62; H, 1.62; N, 4.56. Calcd for $C_{41}H_{52}N_9Mo_{12}Zn_4O_{46}P$: Mo, 40.38; Zn, 9.18; P, 1.09; C, 17.26; H, 1.82; N, 4.42. The discrepancy between the calculated and measured carbon contents is not clear. IR data (KBr, cm^{-1}): 3226 w, 3077 w, 1955 w, 1633 s, 1606 s, 1487 m, 1411 s, 1402 s, 1219 s, 1066 s, 1059 m, 991 w, 933 s, 904 m, 806 s, 777 s, 758 s, 698 m, 638 m, 592 m, 544 w, 525 w, 482 m.

X-ray Crystallography. A black crystal of compound **1** was mounted on a Bruker Smart CCD using Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator at room temperature. Intensity data were collected by using the narrow frame method with 0.3°/frame in φ at 293 K. A total of 12 126 independent reflections were collected among which 9682 reflections with $I > 2.0\sigma(I)$ were considered observed. Absorption corrections were performed by using the SADABS program.[12] The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHEXLS.[12] C21 and C22 atoms of one 4,4′-bipy ligand are disordered and each refined with two orientations (C21A, C21B, C22A, and C22B) and with isotropic thermal parameters. C41 of the methylamine was also refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. A summary of the crystallographic data is listed in Table 1. Selected bond distances and angles are given in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

Table 1. Summary of Crystal Data and Structure Refinements for Compound **1**

empirical formula	$C_{41}H_{52}Mo_{12}N_9O_{46}PZn_4$
fw	2850.65
T, K	298
space group	$P2_1/c$
a, Å	17.3032(2)
b, Å	17.8113(3)
c, Å	23.4597(4)
β, deg	106.410(1)
V, Å^3	6935.6(2)
Z	4
D_{calcd}, g/cm^{-3}	2.730
μ, mm^{-1}	3.577
GOF on F^2	1.242
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0586/0.1113
R1, wR2 (all data)[a]	0.0821/0.1245

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

Results and Discussion

The synthesis of the title compound is interesting. In our first attempt to synthesis a polymetalate containing phosphonate groups, the phosphonic acid was decomposed to provide the source of the phosphate group and also some of the Mo(VI) ions were reduced to Mo(V) ions, probably by reducing amine thus formed. The decomposing of the phosphonic acid is due to the high reaction temperature. In our rational synthesis of the target compound, H_3PO_3 was added as a reducing agent to reduce the Mo(VI) ions as well to provide a source for the phosphate anion.

The structure of **1** features a novel 2D organic−inorganic layer built from tetracapped 8e-reduced ϵ-Keggin polymolybdate anions formulated as $\{Mo^{V}{}_8Mo^{VI}{}_4O_{36}(PO_4)\}^{11-}$. As shown in Figure 1, there are 12 Mo and 4 zinc atoms in an asymmetric unit. Each Mo atom is octahedrally coordinated by six oxygen atoms. These octahedra are interconnected through edge-sharing to form a Keggin core. The phosphate group is encapsulated in the center of the polymolybdate cluster, bridging with all 12 Mo atoms, and each phosphate

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(8) (a) Kwen, H.; Tomlinson, S.; Maatta, E. A.; Dablemont, C.; Thouvenot, R.; Proust, A.; Gouzerh, P. *Chem. Commun.* **2002**, 2970. (b) Kim, G. S.; Zeng, H. D.; VanDerveer, D.; Hill, C. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3205. (c) Leclaire, A.; Borel, M. M.; Chardon, J.; Raveau, B. *Mater. Res. Bull.* **1995**, *30*, 1075.

(9) (a) Johnson, B. J. S.; Schroden, R. C.; Zhu, C. C. Stein, A. *Inorg. Chem.* **2001**, *40*, 5972. (b) Kim, G. S.; Zeng, H. D.; VanDerveer, D.; Hill, C. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3205. (c) Lemagueres, P.; Ouahab, L.; Golhen, S.; Grandjean, D.; Pena, O.; Jedaden, J. C.; Gomezgarcia, C. J.; Delhares, P. *Inorg. Chem.* **1994**, *33*, 5180.

(10) (a) Khan, M. I.; Müller, A.; Dillinger, S.; Bögge, H.; Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed.* **1993**, *32*, 1780. Müller, A.; Dillinger, S.; Krichemeyer, E.; Bögge, H.; Plass, W.; Stammler, A.; Haushaller, R. C. *Z. Naturforsch.* **1997**, *B52*, 1301.

(11) Lei, C.; Mao, J.-G.; Sun, Y.-Q.; Zeng, H.-Y.; Clearfield, A. *Inorg. Chem.* **2003**, *42*, 6157.

(12) (*a*) Sheldrick, G. M. *Program SADABS*; Universität Göttingen: Göttingen, Germany, 1995. (b) Sheldrick, G. M. *SHELXTL, Crystallographic Software Package, SHELXTL*, version 5.1; Bruker-AXS: Madison, WI, 1998.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**[a]

Zn(1)−O(21)	2.009(7)	Zn(1)−O(27)	2.059(7)
Zn(1)−O(20)	2.062(7)	Zn(1)−N(1)	2.113(9)
Zn(1)−N(3)	2.153(9)	Zn(2)−O(28)	1.993(7)
Zn(2)−O(24)	2.030(7)	Zn(2)−O(18)	2.070(7)
Zn(2)−N(2)	2.136(9)	Zn(2)−N(4)	2.147(9)
Zn(3)−O(25)	1.938(7)	Zn(3)−O(26)	1.944(7)
Zn(3)−O(23)	1.983(7)	Zn(3)−N(6)	2.016(9)
Zn(4)−O(19)	2.040(7)	Zn(4)−O(22)	2.060(7)
Zn(4)−O(14)	2.060(7)	Zn(4)−N(5)	2.093(9)
Zn(4)−O(2W)	2.173(10)	Zn(4)−O(1W)	2.346(15)
Mo(1)−O(1)	1.677(8)	Mo(1)−O(23)	1.949(7)
Mo(1)−O(27)	1.957(7)	Mo(1)−O(32)	2.010(7)
Mo(1)−O(30)	2.062(7)	Mo(1)−O(38)	2.485(7)
Mo(1)−Mo(2)	2.6144(13)	Mo(2)−O(2)	1.664(7)
Mo(2)−O(27)	1.962(7)	Mo(2)−O(23)	1.968(7)
Mo(2)−O(17)	1.971(7)	Mo(2)−O(16)	2.049(7)
Mo(2)−O(40)	2.486(7)	Mo(3)−O(3)	1.670(7)
Mo(3)−O(13)	1.953(7)	Mo(3)−O(19)	1.956(7)
Mo(3)−O(28)	1.979(7)	Mo(3)−O(33)	2.029(7)
Mo(3)−O(37)	2.547(7)	Mo(3)−Mo(4)	2.6176(13)
Mo(4)−O(4)	1.670(8)	Mo(4)−O(19)	1.958(7)
Mo(4)−O(28)	1.967(7)	Mo(4)−O(29)	2.018(7)
Mo(4)−O(35)	2.067(7)	Mo(4)−O(39)	2.566(7)
Mo(5)−O(5)	1.685(7)	Mo(5)−O(20)	1.952(7)
Mo(5)−O(18)	1.962(7)	Mo(5)−O(17)	1.986(7)
Mo(5)−O(31)	2.039(7)	Mo(5)−O(40)	2.499(6)
Mo(5)−Mo(6)	2.5903(12)	Mo(6)−O(6)	1.674(7)
Mo(6)−O(18)	1.949(7)	Mo(6)−O(20)	1.967(7)
Mo(6)−O(36)	2.023(7)	Mo(6)−O(35)	2.081(7)
Mo(6)−O(39)	2.473(6)	Mo(7)−O(7)	1.675(7)
Mo(7)−O(22)	1.955(7)	Mo(7)−O(26)	1.964(7)
Mo(7)−O(15)	2.022(7)	Mo(7)−O(30)	2.072(7)
Mo(7)−O(38)	2.489(7)	Mo(7)−Mo(8)	2.6230(13)
Mo(8)−O(8)	1.672(8)	Mo(8)−O(22)	1.958(7)
Mo(8)−O(13)	1.972(7)	Mo(8)−O(26)	1.975(7)
Mo(8)−O(34)	2.049(7)	Mo(8)−O(37)	2.508(7)
Mo(9)−O(9)	1.696(7)	Mo(9)−O(33)	1.816(7)
Mo(9)−O(34)	1.824(7)	Mo(9)−O(24)	1.997(7)
Mo(9)−O(25)	2.030(7)	Mo(9)−O(37)	2.593(7)
Mo(9)−Mo(10)	3.1725(13)	Mo(10)−O(10)	1.681(8)
Mo(10)−O(31)	1.828(7)	Mo(10)−O(16)	1.830(7)
Mo(10)−O(25)	2.001(7)	Mo(10)−O(24)	2.002(7)
Mo(10)−O(40)	2.599(7)	Mo(11)−O(11)	1.694(8)
Mo(11)−O(32)	1.816(7)	Mo(11)−O(15)	1.841(7)
Mo(11)−O(21)	1.990(7)	Mo(11)−O(14)	2.006(7)
Mo(11)−O(38)	2.617(7)	Mo(11)−Mo(12)	3.1510(13)
Mo(12)−O(12)	1.680(7)	Mo(12)−O(36)	1.823(7)
Mo(12)−O(29)	1.832(7)	Mo(12)−O(14)	1.998(7)
Mo(12)−O(21)	2.004(7)	Mo(12)−O(39)	2.600(7)
O(21)−Zn(1)−O(27)	105.0(3)	O(21)−Zn(1)−O(20)	104.5(3)
O(27)−Zn(1)−O(20)	87.2(3)	O(21)−Zn(1)−N(1)	96.8(3)
O(27)−Zn(1)−N(1)	93.3(3)	O(20)−Zn(1)−N(1)	157.8(3)
O(21)−Zn(1)−N(3)	105.2(3)	O(27)−Zn(1)−N(3)	149.7(3)
O(20)−Zn(1)−N(3)	82.4(3)	N(1)−Zn(1)−N(3)	86.1(4)
O(28)−Zn(2)−O(24)	106.0(3)	O(28)−Zn(2)−O(18)	93.8(3)
O(24)−Zn(2)−O(18)	97.9(3)	O(28)−Zn(2)−N(2)	98.6(3)
O(24)−Zn(2)−N(2)	90.5(3)	O(18)−Zn(2)−N(2)	162.5(3)
O(28)−Zn(2)−N(4)	105.0(3)	O(24)−Zn(2)−N(4)	148.9(3)
O(18)−Zn(2)−N(4)	82.1(3)	N(2)−Zn(2)−N(4)	82.8(4)
O(25)−Zn(3)−O(26)	112.4(3)	O(25)−Zn(3)−O(23)	112.3(3)
O(26)−Zn(3)−O(23)	102.4(3)	O(25)−Zn(3)−N(6)	107.5(3)
O(26)−Zn(3)−N(6)	122.5(3)	O(23)−Zn(3)−N(6)	98.7(4)
O(19)−Zn(4)−O(22)	91.6(3)	O(19)−Zn(4)−O(14)	103.0(3)
O(22)−Zn(4)−O(14)	100.0(3)	O(19)−Zn(4)−N(5)	95.2(4)
O(22)−Zn(4)−N(5)	155.2(4)	O(14)−Zn(4)−N(5)	101.7(3)
O(19)−Zn(4)−O(2W)	162.4(4)	O(22)−Zn(4)−O(2W)	82.1(3)
O(14)−Zn(4)−O(2W)	94.4(4)	N(5)−Zn(4)−O(2W)	84.3(4)
O(19)−Zn(4)−O(1W)	79.9(4)	O(22)−Zn(4)−O(1W)	77.4(4)
O(14)−Zn(4)−O(1W)	176.3(4)	N(5)−Zn(4)−O(1W)	80.3(5)
O(2W)−Zn(4)−O(1W)	82.6(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1, *x*, *y* + 1, *z*; #2, *x*, *y* − 1, *z*; #3, −*x* − 1, *y* + 1/2, −*z* − 1/2; #4, −*x* − 1, *y* − 1/2, −*z* − 1/2; #5, *x* − 1, *y*, *z*; #6, *x* + 1, *y*, *z*.

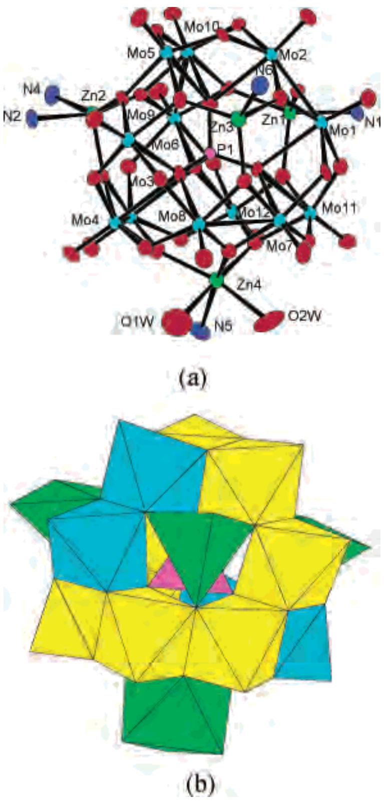

Figure 1. (a) ORTEP representation of a cluster unit in **1**. The thermal ellipsoids are drawn at 50% probability. (b) Polyhedral view of the tetracapped Keggin unit. The Mo(VI) and Mo(V) octahedra, Zn polyhedra, and phosphate group are shaded in cyan and yellow, green, and purple, respectively.

oxygen is a μ_3 metal linker. Besides the phosphate group, other tetrahedral groups such as the sulfate, arsenate, and silicate group have also been reported to be encapsulated into the Keggin units.[4,9] The surface of the Keggin assembly exhibits four cavities defined by 12-membered $\{Mo_6O_6\}$ rings. The terminal Mo−O distances range from 1.664(7) to 1.696(7) Å, and other Mo−O bonds from 1.816(7) to 2.617(7) Å (Table 2). These Mo−O distances are comparable to those reported for other polymolybdates.[2−10] Eight Mo atoms (Mo1−Mo8) are in the +5 oxidation state, forming four Mo−Mo single bonds with the Mo−Mo distances ranging from 2.590(1) to 2.623(1) Å. These Mo−Mo bonds result in the severe distortion of the MoO_6 octahedra, in which one axial Mo−O bond is significantly elongated (>2.4 Å), whereas the other axial Mo−O bond is much shorter than the equatorial Mo−O bonds. The remaining four Mo atoms (Mo9−Mo12) have a +6 oxidation state, and the Mo−Mo contacts are larger than 3.15 Å. Results of the bond valence calculations for the Mo atoms are in good agreement with our assignment: Mo9, Mo10, Mo11, and Mo12 each have total valences close to 6 (5.92−6.03), whereas those for Mo1−Mo8 are in the range 5.19−5.37.[13] On the basis of the above discussion, we conclude that the eight electrons are localized at four Mo−Mo single bonds, which is similar to ϵ-$PMo_{12}O_{40}$ Keggin ions with capping La(III) ions[14] but

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

(14) (a) Dolbecq, A.; Mialane, P.; Lisnard, L.; Marrot, J.; Secheresse, F. *Chem.—Eur. J.* **2003**, *9*, 2914. (b) Mialane, P.; Dolbecq, A.; Lisnard, L.; Mallard, A.; Marrot, J.; Secheresse, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2398.

is significantly different from the bicapped, reduced α-Keggin species $[H_4As^{III}_2As^VMo^V_8Mo^{VI}_4O_{40}]^-$, in which 4 electrons are localized and the remaining 4 are delocalized throughout the whole cluster. Hence, its Mo−Mo distances are closer to each other.[7c] Our Mo_{12} Keggin anion is also related to the ϵ-Keggin cluster in $[H_{14}Mo_{16}O_{52}]^{6-}$, where the 12 electrons of the Mo^v_{12} cluster unit are localized at 6 Mo−Mo single bonds.[10]

The Keggin polymolybdate cluster is further capped by four zinc(II) ions with tetrahedral, trigonal bipyramidal, and octahedral coordination geometries, respectively. Three oxygen atoms of a zinc polyhedron are provided by the Keggin cluster unit, and the remaining coordination sites are occupied by nitrogen atoms of the 4,4′-bipyridine ligands as well as the aqua ligands. Unlike the bicapped 8e-reduced $[As^{III}_2Mo^V_8Mo^{VI}_4O_{36}(AsO_4)]^{11-}$ Keggin species where the two As(III) groups are capping on two oppositely disposed faces defined by eight-membered $\{Mo_4O_4\}$ rings,[7c] the zinc(II) atom of **1** is capping on a face defined by 12-membered $\{Mo_6O_6\}$ ring discussed above. Zn4 is located at the bottom of the cluster unit, whereas Zn1, Zn2, and Zn3 are capping on three similar cavities on the waist of the Keggin cluster anion, resulting in a $\{Zn_3Mo_3O_6\}$ 12-member ring (Figure 1a); a similar La_3Mo_3 ring has been reported for ϵ-$PMo_{12}O_{40}$ Keggin ions with four capping La(III) ions.[14] Zn1 and Zn2 are five-coordinated by three oxygen atoms and two N atoms in a trigonal bipyramidal geometry. Zn3 is tetrahedrally coordinated by three oxygen atoms of a Keggin unit and a N atom, whereas Zn4 is octahedrally coordinated by three oxygen atoms of a cluster, two aqua ligands, and a bipy N atom. The Zn−O distances range from 1.938(7) to 2.346(15) Å, and Zn−N bond lengths fall in the range 2.016(9)−2.153(9) Å. The Zn−O(aqua) distances are significantly longer than those of Zn−O (bridging oxo) bonds (Table 2). These four zinc(II) ions form a distorted Zn_4 tetrahedron with Zn···Zn contacts ranging from 5.879(3) to 6.540(2) Å. To our knowledge, this is the first example of a Keggin unit capped by transitional metal ions with three different types of coordination geometries. A layered zinc molybdenum phosphate with octahedral and tetrahedral zinc was reported previously, in which the octahedral zinc is sandwiched between two Mo_6O_{15} cluster units to form a $ZnMo_{12}O_{30}$ unit and the tetrahedral zinc bridges with three $ZnMo_{12}O_{30}$ units.[5a] Our $[Zn_4Mo_{12}O_{36}(PO_4)]^{3-}$ cluster unit can also be viewed as derived from tetracapped ϵ-Keggin cluster $[H_{14}Mo_{16}O_{52}]^{6-}$ by breaking two of six Mo−Mo bonds and replacing four $[Mo^{VI}O_3]$ capping units with four zinc(II) ions.[10] Furthermore, the $[Zn_4Mo_{12}O_{36}(PO_4)]^{3-}$ cluster unit can be considered as the four capping La(III) ions in ϵ-$La_4PMo_{12}O_{40}$ Keggin cores being replaced by four zinc(II) ions.[14]

The above cluster units are interconnected through bidentate bridging 4,4′-bipy ligands into a 2D layer (Figure 2). Each cluster unit connects with six neighboring ones through six 4,4′-bipy ligands. These double layers are packed in such a way as to form large tunnels along *a* axis (Figure 3). These tunnels are occupied by the 1H-protonated methylamine and 2H-protonated 4,4′-bipy cations as well as the lattice water molecules. The lattice water molecules are involved in hydrogen bonding. O3w is hydrogen bonded to O5w (symmetry code: *x*, 1/2 − *y*, −1/2 + *z*) and O6w (symmetry code: −*x*, −1/2 + *y*, 1/ 2 − *z*) with O···O separations of 2.839(14) and 2.717(17) Å, respectively.

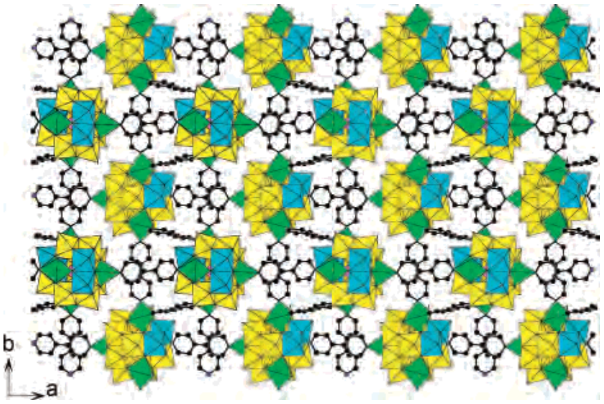

Figure 2. A ⟨001⟩ 2D double layer built from the tetracapped 8e-reduced Keggin cluster units interconnected by bridging bipy ligands in compound **1**. The Mo(VI) and Mo(V) octahedra, Zn polyhedra, and phosphate group are shaded in cyan and yellow, green, and purple, respectively. The C atoms are represented by black circles.

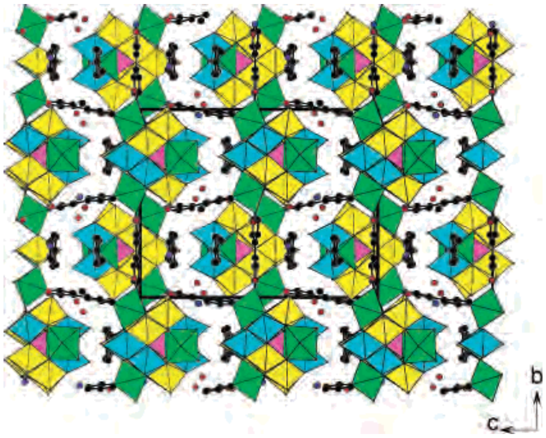

Figure 3. View of the structure of compound **1** down the *a*-axis. The Mo(VI) and Mo(V) octahedra, Zn polyhedra, and phosphate group are shaded in cyan and yellow, green, and purple, respectively. The C, N, and O atoms are represented by black, blue, and red circles, respectively.

The IR spectrum of **1** exhibits a strong band at 933 cm^{-1}, characteristic of ν(Mo═O) and features two peaks at 777 and 1066 cm^{-1} associated with ν(Mo−O−Mo) and ν(P−O), respectively. The bands at 3226 and 1606 cm^{-1} indicate the presence of water. The bands at 1606 and 1411 cm^{-1} can be assigned to the stretching bands of the pyridyl rings of 4,4′-bipy ligands.

Results of TGA measurements under an oxygen atmosphere show two major steps of weight losses. The first weight loss started at 57 °C and was completed at 165 °C, which corresponds to the release of four lattice water molecules. The weight loss of 2.8% is in good agreement with the calculated value (2.5%). Results of XRD powder diffraction indicate that the frame of the structure was retained after the removal of its four lattice water molecules. The second weight loss covered a temperature range from 230 to 870 °C, during which several process were undertaken: the release of the methylamine, aqua ligands, and protonated and coordinated 4,4′-bipyridine molecules. The final product is a mixture containing mainly $ZnMnO_4$ and MoO_3 in a molar ratio of 1:2 as well as a small amount of P_2O_5. The total weight loss of 27.1% is very close to the calculated value (25.5%).

As for its magnetic properties, since the Zn(II) and Mo(VI) ions are diamagnetic and all unpaired $5d^1$ electrons of the Mo(V) ions have been paired through Mo−Mo bonds, the title compound has no unpaired electrons and it is expected to be diamagnetic, which is supported by our experimental data. Its molar susceptibility at room temperature is measured to be -2.7×10^{-3} emu/mol, and only a very small change occurs upon decreasing temperature.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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