Hydrothermal Syntheses and Crystal Structures of Two New Polyoxometalate-based Charge Transfer Salts

Chunhua Zhang[a,b], Fengyan Li[a], and Lin Xu[a]

[a] Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, P. R. China
[b] Department of Chemistry, Baicheng Teacher's College, Baicheng 137000/P.R. China

Reprint requests to Prof. Dr. L. Xu. Fax: +86-431-/5099668. E-mail: linxu@nenu.edu.cn

Z. Naturforsch. **61b,** 1377 – 1382 (2006); received April 4, 2006

Two new charge transfer salts based on Keggin polyoxoanions, $[Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}] \cdot 3.5\,H_2O$ (**1**) and $[Hpy]_4[GeMo_{12}^{VI}O_{40}] \cdot 2H_2O$ (**2**) (en = ethylenediamine, py = pyridine), have been synthesized and characterized by single crystal X-ray diffraction, elemental analyses, IR spectra, UV/vis spectra, cyclic voltammograms and X-ray photoelectron spectra. The IR spectra and solid reflectance electronic spectra of the title compounds indicate that interactions exist between the polyanions and the organic substrates, which are probably caused by charge transfer.

Key words: Polyoxometalates, Charge Transfer Salts, Hydrothermal Synthesis, Crystal Structure

Introduction

As a diverse family of inorganic cluster systems, the polyoxometalates are noted for their fascinating structural, catalytic, magnetic, electrochemical, medical, and photophysical properties [1 – 8]. Many reports have shown that such properties are associated with structures constructed by so-called anion-cation salts or host-guest solids. Many heteropoly anions can be combined with organic π-electron donors, such as tetrathiafulvalene (TTF) [9 – 12], bis(ethylenedithio)tetrathiafulvalene (ET) [13 – 16], decamethylferrocene [4], organic amines [17, 18] to accept various specific numbers of electrons, which are delocalized over a large number of atoms of the heteropoly framework, forming heteropoly "blues" or "browns" [6]. Some of them have been studied for their magnetic, electric and anti cucumber mosaic virus (CMV) properties [19 – 23]. Also, Keggin anions may act as electron-accepting moieties to give interesting optical properties (non-linear optics or photochromism) [15, 24, 25]. So polyoxoanions are attractive precursors to prepare charge-transfer hybrid salts, which consist of organic donors and inorganic acceptors based on the polyoxometalates [11].

Though many charge transfer salts have been explored, most of them were synthesized on the routine way, therefore always powder products were obtained instead of crystals, or the crystals were not suited for crystal X-ray diffraction measurements. In this paper, we used the hydrothermal synthesis, got the new charge transfer compounds $[Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}] \cdot 3.5\,H_2O$ **(1)** and $[Hpy]_4[GeMo_{12}^{VI}O_{40}] \cdot 2\,H_2O$ **(2)**, and determined their crystal structures using single crystal X-ray diffraction. The salts were characterized by IR and UV/vis spectra, cyclic voltammetry and X-ray photoelectron spectra (only for compound **1**).

Results and Discussion

Hydrothermal synthesis

The isolation of compounds **1** and **2** depends on the use of hydrothermal techniques, and the choice of the starting materials is vital for the successful preparation of the compounds. Attempts to synthesize compounds without the transition metal salts ($CoCl_2$ or $FeCl_3$) proved to be unsuccessful to obtain single crystals of good quality, although the effect of the salts is not understood. The reactions can be illustrated by the equations:

$$H_3PMo_{12}O_{40} + 3en + H^+ + 3.5H_2O = [Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}] \cdot 3.5H_2O \ (\mathbf{1})$$

$$H_4GeMo_{12}O_{40} + 4py + 2H_2O = [Hpy]_4[GeMo_{12}O_{40}] \cdot 2H_2O \ (\mathbf{2})$$

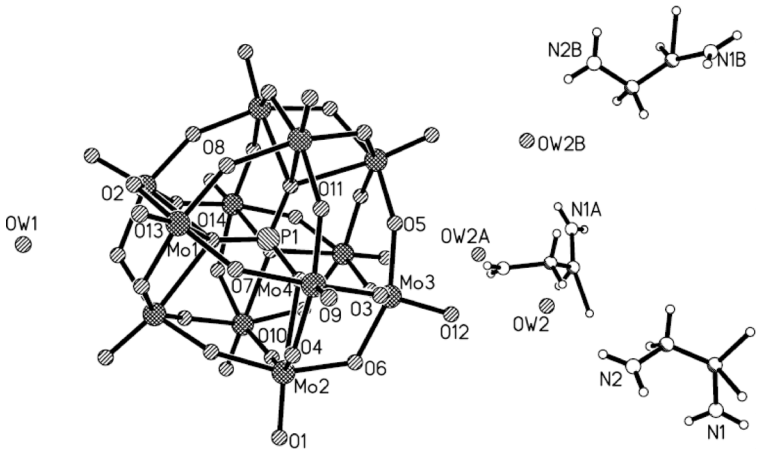

Fig. 1. Crystal structure of $[Hen]_2[H_2en]$-$[PMo_{11}^{VI}Mo^{V}O_{40}] \cdot 3.5\,H_2O$ (**1**).

Description of the crystal structures

A single crystal X-ray analysis revealed that compound **1** consists of a $[PMo_{11}^{VI}Mo^{V}O_{40}]^{4-}$ heteropolyanion, two $[Hen]^{+}$cations, a $[H_2en]^{2+}$ cation and crystal water molecules (see Fig. 1). Compound **2** is composed of a $[GeMo_{12}^{VI}O_{40}]^{4-}$polyanion, four $[Hpy]^{+}$ cations and two crystal water molecules (see Fig. 2). The title complexes both have the well-known α-Keggin structure, based on a central PO_4 (GeO_4) tetrahedron surrounded by 12 MoO_6 octahedra arrayed in four groups of three edge-sharing

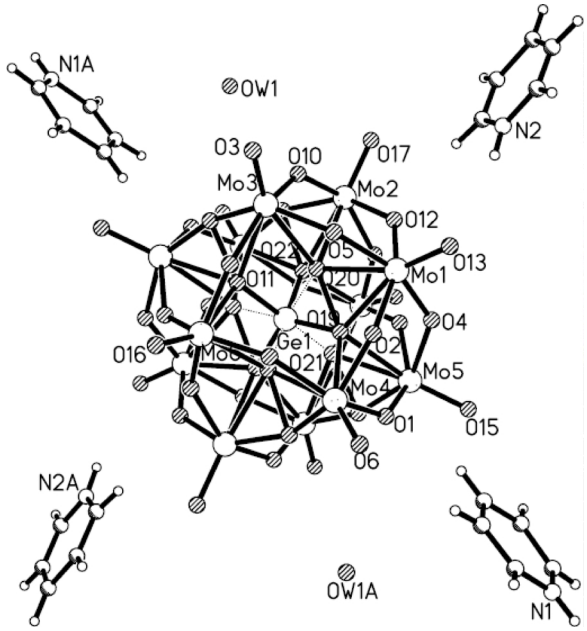

Fig. 2. Crystal structure of $[Hpy]_4[GeMo_{12}^{VI}O_{40}] \cdot 2\,H_2O$ (**2**).

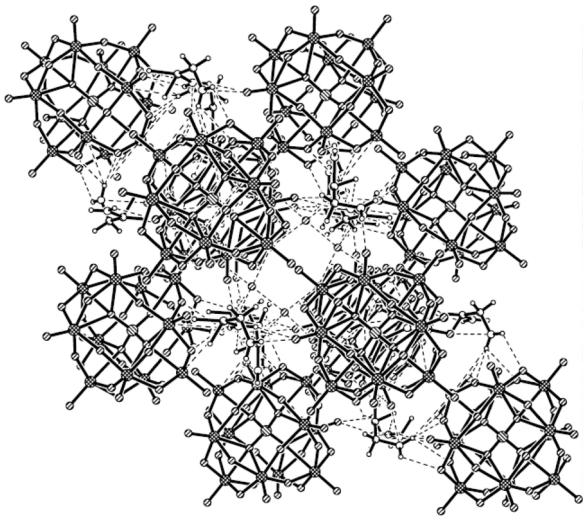

Fig. 3. View of the packing of molecules **1** along the *a*-axis.

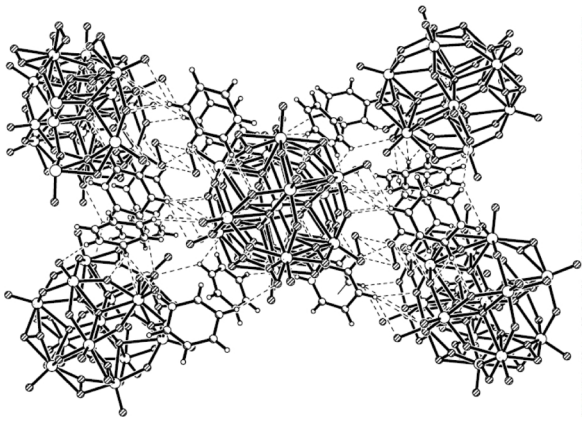

Fig. 4. View of the packing of molecules **2** down the *a*-axis.

Table 1. Crystal data and structure refinement.

	1	**2**
Molecular formula	$C_6H_{33}N_6PMo_{12}O_{43.5}$	$C_{20}H_{28}N_4PMo_{12}O_{42}$
Formula weight	2067.62	2220.34
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.7103
Space group	$R\bar{3}$	$P2_1/n$
Crystal system	rhombohedral	monoclinic
a [Å]	13.212(15)	10.975(2)
b [Å]	13.212(15)	19.563(4)
c [Å]	13.212(15)	12.334(3)
α [°]	75.96(17)	90
β [°]	75.96(17)	99.80(3)
γ [°]	75.96(17)	90
V [Å^3]	2128.7(4)	2609.6(9)
Z, ρ_c [g·cm^{-3}]	3, 1.61	2, 2.83
μ [mm^{-1}]	1.8	3.5
$F(000)$	976	2096
Reflections collected	3235	10790
Independent reflections	1786 ($R_{int} = 0.0157$)	5540 ($R_{int} = 0.0363$)
Data / restraints / parameters	1786 / 4 / 205	5540 / 0 / 421
Goodness-of-fit on F^2	1.118	1.064
Final R indices [$I \geq 2\sigma(I)$][a]	$R1 = 0.0311$, $wR2 = 0.0846$	$R1 = 0.0612$, $wR2 = 0.1597$
R indices (all data)[a]	$R1 = 0.0361$, $wR2 = 0.0875$	$R1 = 0.0871$, $wR2 = 0.1725$

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

Table 2. Selected bond lengths (Å) and angles (°) for compound **1**.

Mo(1)-O(13)	1.684(5)	Mo(1)-O(8)	1.883(5)
Mo(1)-O(7)	1.883(5)	Mo(1)-O(2)$^{\#2}$	1.934(5)
Mo(1)-O(2)	1.946(5)	Mo(1)-O(14)	2.435(5)
Mo(2)-O(1)	1.684(5)	Mo(2)-O(6)	1.892(5)
Mo(2)-O(10)	1.905(5)	Mo(2)-O(4)	1.926(5)
Mo(2)-O(8)$^{\#2}$	1.951(5)	Mo(2)-O(11)$^{\#2}$	2.438(5)
Mo(3)-O(12)	1.679(5)	Mo(3)-O(5)$^{\#2}$	1.902(5)
Mo(3)-O(5)	1.914(5)	Mo(3)-O(6)	1.949(5)
Mo(3)-O(3)	1.952(5)	Mo(3)-O(11)	2.432(4)
Mo(4)-O(9)	1.682(5)	Mo(4)-O(3)	1.885(5)
Mo(4)-O(10)$^{\#2}$	1.899(5)	Mo(4)-O(4)	1.928(5)
Mo(4)-O(7)	1.954(5)	Mo(4)-O(11)$^{\#2}$	2.438(5)
P(1)-O(11)$^{\#1}$	1.535(5)	P(1)-O(11)	1.535(5)
P(1)-O(11)$^{\#2}$	1.535(5)	P(1)-O(14)	1.537(8)
O(11)$^{\#1}$-P(1)-O(11)	109.61(18)	O(11)$^{\#1}$-P(1)-O(11)$^{\#2}$	109.61(18)
O(11)-P(1)-O(14)	109.33(19)	O(11)$^{\#1}$-P(1)-O(14)	109.33(19)
O(13)-Mo(1)-O(14)	168.5(2)	O(8)-Mo(1)-O(2)$^{\#2}$	157.0(2)
O(13)-Mo(1)-O(8)	104.3(2)	O(13)-Mo(1)-O(2)	99.2(2)
O(8)-Mo(1)-O(7)	88.8(2)	O(2)$^{\#2}$-Mo(1)-O(14)	72.92(18)

Mo_3O_{13} octahedra. The groups of Mo_3O_{13} are linked to each other and to the central PO_4 (GeO_4) tetrahedron by sharing corners. In compound **1**, the Mo-O distances in the MoO_6 octahedron are in the range of 1.679(5)–1.684(5) Å for Mo-O_d, 1.883(5)–1.954(5) Å for Mo-$O_{b,c}$, 2.432(4)–2.438(5) Å for Mo-O_a. The O-Mo-O angles are 72.49(17)–172.1(2)°. The distances P-O_a are 1.535(5)–1.537(8) Å, and O-P-O angles are 109.33(19)–109.61(18)°, which corresponds to an almost ideal tetrahedral coordination.

Table 3. Selected bond lengths (Å) and angles (°) for compound **2**.

Mo(1)-O(13)	1.653(8)	Mo(1)-O(4)	1.851(7)
Mo(1)-O(12)	1.863(9)	Mo(1)-O(5)	1.944(7)
Mo(1)-O(2)	1.971(8)	Mo(1)-O(22)	2.307(11)
Ge(1)-O(22)	1.632(10)	Ge(1)-O(19)	1.657(11)
Ge(1)-O(21)	1.814(10)	Ge(1)-O(20)	1.837(11)
O(22)-Ge(1)-O(21)	108.5(5)	O(22)-Ge(1)-O(20)$^{\#1}$	109.3(5)
O(19)$^{\#1}$-Ge(1)-O(21)	108.2(5)	O(19)$^{\#1}$-Ge(1)-O(20)$^{\#1}$	108.6(5)
O(13)-Mo(1)-O(4)	101.3(6)	O(4)-Mo(1)-O(5)	158.1(5)
O(13)-Mo(1)-O(5)	99.8(5)	O(13)-Mo(1)-O(2)	99.2(2)
O(12)-Mo(1)-O(19)	96.6(5)	O(4)-Mo(1)-O(19)	65.9(4)

In compound **2**, the Mo-O distances can be classified as three sets: Mo-O_d: 1.642(7)–1.653(8) Å, Mo-$O_{b,c}$: 1.734(13)–2.087(11) Å, Mo-O_a: 2.222(10)–2.471(11) Å, while the bond angles vary from 65.2(4)–171.3(5)°. The packing of the molecules of the title compounds is shown in Figs. 3 and 4. The values of bond valence sum (BVS) calculations [27], based on the observed bond length data, are listed in Table 4. The BVS calculations for Mo atoms [Mo(1)–Mo(4)] of compound **1** give values of 6.03, 5.94, 5.86 and 5.98, respectively. The calculated average value for the oxidation state of molybdenum is 5.95 (expected: 5.92 for $Mo_{11}^{VI}Mo^{V}$). In compound **2**, the BVS values of the Mo atoms [Mo(1)–Mo(6)] are 6.01, 5.92, 6.16, 6.04, 5.88 and 5.99, showing that all Mo centers are in the +6 oxidation state.

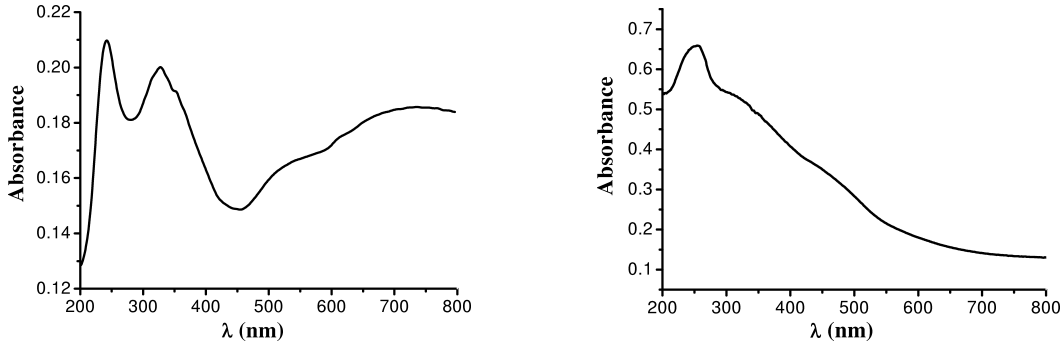

Fig. 5. Electronic spectra of solid $[Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}]\cdot 3.5H_2O$ (left) and $[Hpy]_4[GeMo_{12}^{VI}O_{40}]\cdot 2H_2O$ (right).

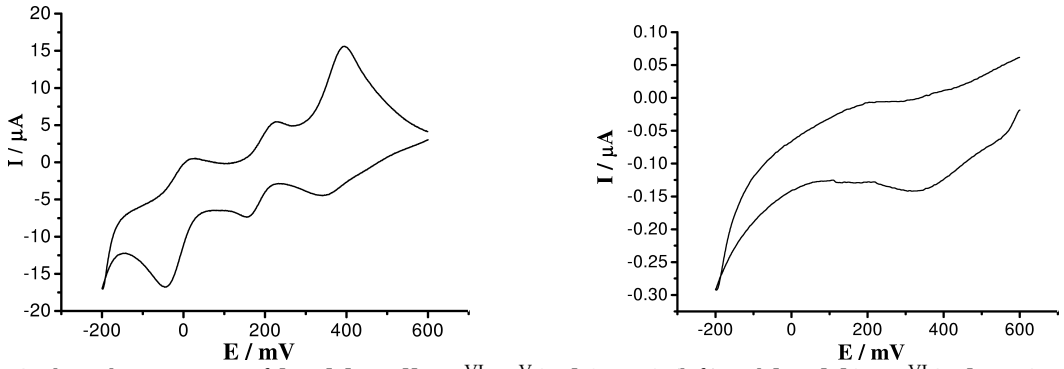

Fig. 6. Cyclic voltammograms of $[Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}]\cdot 3.5H_2O$ (left) and $[Hpy]_4[GeMo_{12}^{VI}O_{40}]\cdot 2H_2O$ in 0.5 M H_2SO_4 (right) at a modified CPE.

Table 4. Bond valence sum values.

Atom	Valence	Atom	Valence
Compound **1**		Compound **2**	
Mo1	6.03	Mo1	6.01
Mo2	5.94	Mo2	5.92
Mo3	5.86	Mo3	6.16
Mo4	5.98	Mo4	6.04
		Mo5	5.88
		Mo6	5.99

IR spectra

In the IR spectra of compounds **1** and **2**, there are four characteristic vibrations resulting from heteropolyanions with the Keggin structure: ν_{as}(X-O_a), ν_{as}(Mo=O_d), ν_{as}(Mo-O_b) and ν_{as}(Mo-O_c) (X = P or Ge). The peaks were observed at 1055, 956 and 769 cm^{-1} for **1**, 968, 851, 832 and 744 cm^{-1} for **2**. Comparing the IR spectrum of compound **1** with that of α-$H_3PMo_{12}O_{40}$ [26], the vibrational band of the P-O_a and Mo=O_d bonds have a red-shift from 1065 to 1055 cm^{-1} and from 970 to 956 cm^{-1}. The vibrational bands of the Mo-O_b and Mo-O_c bonds have merged together at 768 cm^{-1}, due to the interactions between the polyanions and the organic substrates. In contrast to the IR spectrum of α-$H_4GeMo_{12}O_{40}$, in the spectrum of compound **2** the peaks all have a small red-shift or a blue shift. The results indicate that the polyanions in the title compounds still retain the Keggin structure, but due to the interaction with the organic cations, they are somewhat distorted. This is in agreement with the results of the single crystal X-ray diffraction analysis.

Electronic spectra

Fig. 5 shows the reflectance electronic spectra of the title compounds. The bands at 242 and 331 nm for **1**, 254 and 327 nm for **2**, belong to O-Mo and d-d transitions of MoO_6 octahedra, respectively [28]. The band at 728 nm is attributed to the intervalence charge transfer (IVCT) band ($Mo^{V} \rightarrow Mo^{VI}$) of $[PMo_{12}O_{40}]^{4-}$, which indicates that electron transfer occurs between the organic substrate and the polyoxoanion, converting $[PMo_{12}O_{40}]^{3-}$ to the heteropoly blue $[PMo_{12}O_{40}]^{4-}$ [6]. No IVCT bond was found in the spectrum of compound **2**, which suggests that

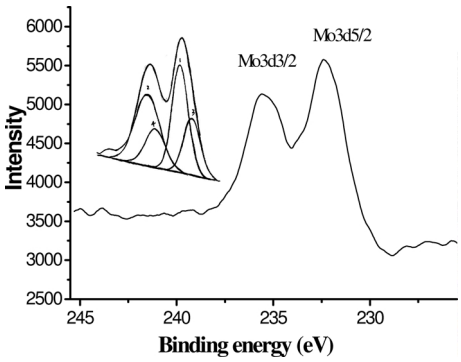

Fig. 7. XPS spectrum of compound **1**.

the interactions between the polyanion and the organic substrate in compound **2** are relatively weak.

Electrochemical behavior

The title compounds were embedded into a bulk-modified carbon paste electrode (CPE). The electrochemical studies were carried out in 0.5 M H_2SO_4 aqueous solution, because the polyanion is unstable in neutral and basic aqueous solution. Fig. 6 shows the cyclic voltammograms in 0.5 M H_2SO_4 at a modified CPE. It can be seen from Fig. 6 (left) that in the potential range +800 to −200 mV, there are three redox peaks, among which only the second pair of peaks are quasireversible with an $E_{1/2}$ value of 0.19 V. As to the CV curve of compound **2** (Fig. 6 (right)), there is only one reduction peak at $E = 0.33$ V, which suggests that compound **2** is not very stable and decomposes upon reduction.

X-Ray photoelectron spectrum (XPS)

In the X-ray photoelectron spectrum (XPS) of compound **1**, there are two overlapping peaks at 231.4 and 234.5 eV (as shown in Fig. 7), which reveals that the mixed valences of Mo(V) and Mo(VI) coexist in compound **1**. This is in accordance with the BVS calculation.

Conclusion

Two new charge transfer salts based on Keggin polyoxoanions, $[Hen]_2[H_2en][PMo_{11}{}^{VI}Mo^{V}O_{40}]\cdot 3.5H_2O$ (**1**) and $[Hpy]_4[GeMo_{12}{}^{VI}O_{40}]\cdot 2H_2O$ (**2**), have been synthesized and structurally characterized. Compounds **1** and **2** are further examples of charge transfer salts based on polyoxometalates. The successful preparation of these compounds shows that hydrothermal synthesis is an effective way to get new materials of high single crystal quality.

Experimental Section

Materials and methods

All chemicals were of reagent grade and used without further purification. High purity graphite powder (average particle 1 – 2 μm) was obtained from Aldrich, $H_3PMo_{12}O_{40}\cdot nH_2O$ and $H_4GeMo_{12}O_{40}\cdot nH_2O$ were prepared according to the literature method [26].

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The IR spectra were obtained in the range 400 – 4000 cm^{-1} on an Alpha centaure FT/IR spectrophotometer using KBr pellets. Diffuse reflectance UV/vis spectra were obtained with a Varian Cary 500 UV/vis NIR spectrometer. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode cell, consisting of a modified carbon paste electrode (CPE) as the working electrode, a Ag/AgCl reference electrode and a Pt gauze counter electrode was used. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a MgK_α (1253.6 eV) achromatic X-ray source.

*Synthesis of $[Hen]_2[H_2en][PMo_{11}^{VI}Mo^{V}O_{40}]\cdot 3.5H_2O$ **(1)***

Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of $H_3PMo_{12}O_{40}\cdot 12H_2O$ (0.186 g), $CoCl_2$ (0.034 g), en (1 mL) and water (10 mL) was stirred and then sealed in a 15 mL teflon-lined autoclave, which was heated to 180 °C for 6 d. After slow cooling to r. t. at a rate of 10 °C h^{-1}, dark blue block crystals of compound **1** were separated as a major phase (70% yield based on Mo) together with an unidentified yellow powder. Elemental analysis for $C_6H_{33}N_6PMo_{12}O_{43.5}$ (2067.62): calcd. C 3.48, H 1.59, N 4.06; found C 3.50, H 1.58, N 4.05.

*Synthesis of $[Hpy]_4[GeMo_{12}^{VI}O_{40}]\cdot 2H_2O$ **(2)***

A mixture of $H_4GeMo_{12}O_{40}\cdot 12H_2O$ (0.200 g), $FeCl_3\cdot 6H_2O$ (0.027 g), pyridine (1 mL) and water (10 mL) was stirred and then sealed in a 15 mL teflon-lined autoclave, which was heated to 180 °C for 6 d. After slow cooling to r. t. at a rate of 10 °C h^{-1}, orange block crystals of compound **2** were separated as a major phase (80% yield based on Mo). Elemental analysis for $C_{20}H_{28}N_4PMo_{12}O_{42}$ (2220.34): calcd. C 10.81, H 1.26, N 2.52; found C 10.76, H 1.36, N 2.50.

X-ray crystallography

The structures of compounds **1** and **2** were determined by single crystal X-ray diffraction. Data were collected on

a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) and oscillation scans technique in the range of $2.51 < \theta < 27.44°$ for compound **1** and $2.15 < \theta < 27.46°$ for compound **2**. Empirical absorption corrections were applied. The structures were solved by Direct Methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 program package. All the non-hydrogen atoms in compounds **1** and **2** were refined anisotropically. Some oxygen atoms and the GeO_4 tetrahedron in **2** are disordered over two locations. The occupancies for them over two sites are 0.5, respectively. Crystal data for **1** and **2** are summarized in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-242395, 242396. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors are thankful for financial supports from the National Natural Science Foundation of China (Grant No. 20371010) and the State Key Laboratory for Structural Chemistry of Unstable and Stable Species in Peking University (No. 03-12).

[1] C. L. Hill, Chem. Rev. **98**, 1 (1998).
[2] M. Misono, Catal. Rev. Sci. Eng. **29**, 269 (1987).
[3] F. Bussereau, M. Picard, C. Malik, A. Teze, J. Blancou, Ann. Inst. Pasteur/Virol. **32**, 33 (1988).
[4] L. Ouahab, Chem. Mater. **9**, 1909 (1997).
[5] M. T. Pope, A. Müller, Angew. Chem. **103**, 56 (1991); Angew. Chem., Int. Ed. Engl. **30**, 34 (1991).
[6] M. T. Pope, Heteropoly and Isopolyoxometalates, Springer, Berlin (1983).
[7] M. T. Pope, A. Müller, Polyoxometalates: From Platonic Solid toAnti-Retro viral Activity, Kluwer, Dordrecht (1994).
[8] A. M. Khenkin, R. Neumann, J. Am. Chem. Soc. **124**, 4198 (2002).
[9] A. Mhanni, L. Ouahab, O. Pena, D. Grandjean, C. Garrigou-Lagrange, P. Delhaes, Synth. Met. **41 – 43**, 1703 (1991).
[10] D. Attanasio, C. Bellitto, M. Bonamico, V. Fares, S. Patrizo, Synth. Met. **41 – 43**, 2289 (1991).
[11] L. Ouahab, M. Bencharif, A. Mhanni, D. Pelloquin, J. F. Halet, O. Pena, J. Padiou, D. Grandjean, C. Garrigou-Lagrange, J. Amiell, P. Delhaes, Chem. Mater. **4**, 666 (1992).
[12] L. Ouahab, Chem. Mater. **9**, 1909 (1997).
[13] A. Davidson, K. Boubekeur, A. Penicaud, P. Auban, C. Lenoir, P. Batail, G. Herve, J. Chem. Soc., Chem. Commun. 1373 (1989).
[14] C. J. Gomez-Garcia, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Ouahab, L. Ducasse, C. Sourisseau, P. Delhaes, Inorg. Chem. **34**, 4139 (1995).
[15] C. J. Gomez-Garcia, L. Ouahab, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Delhaes, Angew. Chem., Int. Ed. Engl. **33**, 223 (1994); Angew. Chem. **106**, 234 (1994).
[16] C. J. Gomez-Garcia, L. Ouahab, C. Gimenez-Saiz, S. Triki, E. Coronado, L. Ducasse, P. Le Magueres, L. Ouahab, P. Delhaes, Synth. Met. **70**, 783 (1995).
[17] D. Attanasio, M. Bonamico, V. Fares, P. Imperatori, L. Suber, J. Chem. Soc., Dalton Trans. 3221 (1990).
[18] P. Magueres, S. M. Hubig, S. V. Lindeman, P. Veya, J. K. Kochi, J. Am. Chem. Soc. **122**, 10073 (2000).
[19] E. Coronado, C. J. Gomez-Garcia, Comments Inorg. Chem. **17**, 255 (1995).
[20] E. Coronado, C. J. Gomez-Garcia, Chem. Rev. **98**, 327 (1998).
[21] J. M. Clemente-Juan, E. Coronado, Coord. Chem. Rev. **193 – 195**, 361 (1999).
[22] L. Ouahab, Coord. Chem. Rev. **178 – 180**, 1501 (1998).
[23] L. H. Bi, Q. Z. He, Q. Jia, E. B. Wang, J. Mol. Struct. **597**, 83 (2001).
[24] L. Zhang, Y. Zhou, Z. Yu, G. Fang, X. You, J. Mol. Struct. **570**, 83 (2001).
[25] J. A. Gamelas, A. M. Cavaleiro, E. M. Gomes, M. Belsley, E. Herdtweck, Polyhedron **21**, 2537 (2002).
[26] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenoy, Inorg. Chem. **22**, 207 (1983).
[27] L. D. Brown, D. Altermatt, Acta. Crystallogr., Sect. B **41**, 244 (1985).
[28] B. Z. Wan, J. H. Lunsford, Inorg. Chim. Acta. **65**, 129 (1982).