Inorg. Chem. **2003**, *42*, 2729–2735

Inorganic Chemistry
Article

New High-Dimensional Networks Based on Polyoxometalate and Crown Ether Building Blocks

Yangguang Li,[†] Na Hao,[†] Enbo Wang,*[,†,‡] Mei Yuan,[†] Changwen Hu,[†] Ninghai Hu,[§] and Hengqing Jia[§]

Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China, State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China, and Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

Received November 12, 2002

Three novel supramolecular assemblies constructed from polyoxometalate and crown ether building blocks, $[(DB18C6)Na(H_2O)_{1.5}]_2Mo_6O_{19}\cdot CH_3CN$, **1**, and $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]XMo_{12}O_{40}\cdot 6DMF\cdot CH_3CN$ (X = P, **2**, and As, **3**; DB18C6 = dibenzo-18-crown-6; DMF = *N,N*-dimethylfomamide), have been synthesized and characterized by elemental analyses, IR, UV–vis, EPR, TG, and single crystal X-ray diffraction. Compound **1** crystallizes in the tetragonal space group *P*4/*mbm* with $a = 16.9701(6)$ Å, $c = 14.2676(4)$ Å, and $Z = 2$. Compound **2** crystallizes in the hexagonal space group $P6_3/m$ with $a = 15.7435(17)$ Å, $c = 30.042(7)$ Å, $\gamma = 120°$, and $Z = 2$. Compound **3** crystallizes in the hexagonal space group $P6_3/m$ with $a = 15.6882(5)$ Å, $c = 29.9778(18)$ Å, $\gamma = 120°$, and $Z = 2$. Compound **1** exhibits an unusual three-dimensional network with one-dimensional sandglasslike channels based on the extensive weak forces between the oxygen atoms on the $[Mo_6O_{19}]^{2-}$ polyoxoanions and the CH_2 groups of crown ether molecules. Compounds **2** and **3** are isostructural, and both contain a novel semiopen cagelike trimeric cation $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]^{3+}$. In their packing arrangement, an interesting 2-D "honeycomblike" "host" network is formed, in which the $[XMo_{12}O_{40}]^{3-}$ (X = As and P) polyoxoanion "guests" resided.

The construction of supramolecular assemblies from organic and/or inorganic molecular building blocks has been attracting extensive interest in recent years owing to their novel and diverse topologies and potential applications in host–guest chemistry, shape-selective catalysis, absorption, electrical-conductive, magnetic, and photosensitive materials.[1–4] One of the important targets in the preparation of supramolecular assemblies is to establish the likely connections between organic and/or inorganic molecular fragments on the basis of various intermolecular interactions.[4] In this interesting molecular assembling process, hydrogen bonding of conventional OH···O and NH···O motifs has been most commonly used as supramolecular cement, yet weaker forces

---

[*] To whom correspondence should be addressed. E-mail: wangenbo@public.cc.jl.cn.

[†] Northeast Normal University.

[‡] Fujian Institute of Research on the Structure of Matter.

[§] Changchun Institute of Applied Chemistry.

(1) (a) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; p 256. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995; Chapter 9.

(2) (a) Fujita, M.; Kwon, Y. J.; Washiza, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638–2684. (c) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J. *Nature* **2000**, *404*, 982–986. (d) Coronado, E.; Galán-Mascrós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (e) Oshio, H.; Saito, Y.; Ito, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2673.

(3) (a) Lawandy, M. A.; Huang, X.; Wang, R.-J.; Li, J.; Lu, J. Y. *Inorg. Chem.* **1999**, *38*, 5410–5414. (b) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150. (c) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (d) Armentano, D.; Munno, G. D.; Lloret, F.; Palii, A. V.; Julve, M. *Inorg. Chem.* **2002**, *41*, 2007–2013. (d) Li, Y.-G.; Zhang, H.; Wang, E.-B.; Hao, N.; Hu, C.-W.; Yan, Y.; Hall, D. *New J. Chem.* **2002**, *26*, 1619–1623. (e) Li, Y.-G.; Wang, E.-B.; Zhang, H.; Luan, G.-Y.; Hu, W.-H. *J. Solid State Chem.* **2001**, *163*, 10–16.

(4) (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327. (b) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383. (c) Kumagai, H.; Arishima, M.; Kitagawa, S.; Ymada, K.; Kawata, S.; Kaizaki, S. *Inorg. Chem.* **2002**, *41*, 1989–1992. (d) Lehn, J.-M. *Science* **2002**, *295*, 2400–2403. (e) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (f) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (g) Kawata, S.; Breeze, S. R.; Wang, S.; Greedan, J. E.; Raju, N. P. *Chem. Commun.* **1997**, 717–718. (h) Dai, J.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Munakata, M. *Inorg. Chem.* **1997**, *36*, 2688. (i) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; Loye, H.-C. Z. *Inorg. Chem.* **1999**, *38*, 5027.

10.1021/ic026172+ CCC: $25.00

such as CH···O, CH···N, O···I, or even C···H and C···C have also been used.[4a-c]

Polyoxometalates (POMs), as one kind of significant metal oxide clusters with nanosizes and abundant topologies, have recently been employed as inorganic building blocks for the construction of supramolecular arrays with various organic ligands (such as N-containing ligands, amino acids, polypeptides, tetrathiafulvalenes, organometallics, and cyclopentadienyl derivatives).[5-8] These assemblies possess interesting one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) structures and exhibit potential applications in catalysis, medicine, and electrical-conductive and magnetic materials.[7b,9-11] Crown ethers, which have been widely used in the supramolecular chemistry due to their multiple functions such as molecular recognition, transportation, and catalysis,[12] have also been introduced into the POM-based supramolecular chemistry.[13-16] As a part of our work toward exploration and preparation of functional POMs, we also carried out a study of supramolecular compounds based on crown ether and POM building blocks and have synthesized a number of such compounds.[17-19] These reports demonstrate that crown ethers are capable of stabilizing crystallization water in the POMs so as to provide crystals with better quality and stability.[17] Furthermore, the crown ether−alkali metal complexes have the coordination ability to the terminal oxygen atoms of polyoxoanions.[18,19] To date, the crown ether−POM supramolecular compounds reported by other researchers and our group share a common feature in that they all exhibit discrete structures. To our knowledge, no extended 2-D or 3-D crown ether−polyoxoanion supramolecular networks with channels or porous structures have been observed yet.

In this paper, we report three novel supramolecular assemblies based on crown ether and polyoxometalate building blocks, $[(DB18C6)Na(H_2O)_{1.5}]_2Mo_6O_{19}\cdot CH_3CN$, **1**, and $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]XMo_{12}O_{40}\cdot 6DMF\cdot CH_3CN$ (X = P, **2**, and As, **3**; DB18C6 = dibenzo-18-crown-6; DMF = *N*,*N*-dimethylfomamide). Compound **1** exhibits an unusual 3-D network with sandglasslike 1-D channels. The $[Mo_6O_{19}]^{2-}$ polyoxoanions act as the joint to connect all the $[(DB18C6)Na(H_2O)_{1.5}]^+$ units together via the weak interactions between oxygen atoms of polyoxoanions and CH_2 groups of crown ethers. To our knowledge, compound **1** represents the first example of a channel-containing 3-D assembly based on the crown ether and POM building blocks. Compounds **2** and **3** are isostructural, and both contain a novel semiopen cagelike trimeric cation $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]^{3+}$. Furthermore, **2** and **3** possess an interesting “honeycomblike” 2-D “host” network, in which the $[XMo_{12}O_{40}]^{3-}$ (X = As and P) polyoxoanion “guests” resided.

Experimental Section

General Considerations. All chemicals were used as purchased without further purification. $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, $H_3PMo_{12}O_{40}\cdot 20H_2O$, and $H_3AsMo_{12}O_{40}\cdot 26H_2O$ were synthesized by the improved methods of the literature[20-22] and characterized by IR spectra and TG analyses. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; P, As, Mo, and Na were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Diffuse reflectance UV−vis spectra ($BaSO_4$ pellets) were obtained with a Varian Cary 500 UV−vis NIR spectrometer. EPR spectra were recorded on a Japanese JES−FE3AX spectrometer at 293 K. Photochromic experiments were carried out using a 500 W high-pressure mercury lamp as the light source.

Synthesis of $[(DB18C6)Na(H_2O)_{1.5}]_2Mo_6O_{19}\cdot CH_3CN$, 1. DB18C6 (0.1 g) in 10 mL of dehydrated acetonitrile was added dropwise to 10 mL of acetonitrile containing 0.19 g of $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$ and 0.017 g of NaCl with stirring for 24 h at room temperature. After filtration, the solution was allowed to stand for 5 days, and red crystals were obtained and recrystallized in a mixed DMF and water solvent (with a volume ratio 9:1). Another 2 days later, yellow

---

[5] Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

[6] *Polyoxometalate Chemistry*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, 2001.

[7] (a) Hill, C. L. *Chem. Rev.* **1998**, *98*, 1−2. (b) Coronado, E.; Gómez-García, J. *Chem. Rev.* **1998**, *98*, 273−296. (c) Rhuie, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327−357. (d) Yamase, T. *Chem. Rev.* **1998**, *98*, 307−325. (e) Baker, L. C.; Glick, D. C. *Chem. Rev.* **1998**, *98*, 3−49. (f) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199. (g) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359−387.

[8] (a) Mialane, P.; Dolbecq, A.; Lisnard, L.; Mallard, A.; Marrot, J.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2398−2401. (b) Peloux, C. D.; Mialane, P.; Dolbecq, A.; Marrot, J.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2808−2810.

[9] Hölscher, M.; Englert, U.; Zibrowius, B.; Hölderich, W. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2491−2493.

[10] (a) Han, Z. B.; Wang, E. B.; Luan, G. Y.; Li, Y. G.; Zhang, H.; Hu, N. H. *J. Mater. Chem.* **2002**, 1169−1173. (b) 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**, 2916−2920. (c) Lu, Y.; Wang, E. B.; Yuan, M.; Li, Y. G.; Xu, L.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *Solid State Sci.* **2002**, *4*, 449−453. (d) Bi, L. H.; Wang, E. B.; Peng, J.; Huang, R. D.; Xu, L.; Hu, C. W. *Inorg. Chem.* **2000**, *39*, 671−679. (e) Peng, J.; Li, W. Z.; Wang, E. B.; Bai, Q. L. *J. Chem. Soc., Dalton Trans.* **2001**, 3668−3671. (f) Guo, Y. H.; Hu, C. W.; Wang, X. L.; Wang, E. B.; Zhou, Y. N.; Feng, S. H. *Chem. Mater.* **2001**, *13* (11), 4058−4064. (g) 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**, 121−122.

[11] (a) Xu, L.; Lu, M.; Xu, B. B.; Wei, Y. G.; Peng, Z. H.; Powell, D. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4129−4132. (b) Lu, M.; Wei, Y. G.; Xu, B. B.; Cheung, C. F.-C.; Peng, Z. H.; Powell, D. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1566−1568.

[12] Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89−112.

[13] Nagano, O.; Sasaki, Y. *Acta Crystallogr., Sect. B* **1979**, *35*, 2387−2389.

[14] Neier, R.; Trojanowski, C.; Mattes, R. *J. Chem. Soc., Dalton Trans.* **1995**, 2521−2528.

[15] Drljaca, A.; Hardie, M. J.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1999**, 3639−3642.

[16] (a) Lu, X. M.; Zhu, H. J.; Liu, S. C. *Chem. J. Chin. Univ.* **1996**, *17*, 1173−1176. (b) Lu, X. M.; Zhong, R.; Liu, S. C. *Polyhedron* **1997**, *16*, 3865−3872.

[17] (a)You, W. S.; Wang, E. B.; Zhang, H.; Xu, L.; Wang, Y. B. *J. Mol. Struct.* **2000**, *554*, 141−147. (b) You, W. S.; Wang, E. B.; Xu, L.; Zhu, Z. M.; Gu, Y. P. *J. Mol. Struct.* **2002**, *605*, 41−49. (c) You, W. S.; Wang, E. B.; He, Q. L.; Xu, L.; Xing, Y.; Jia, H. Q. *J. Mol. Struct.* **2000**, *524*, 133−139.

[18] You, W. S.; Wang, E. B.; Xu, Y.; Li, Y. G.; Xu, L.; Hu, C. W. *Inorg. Chem.* **2001**, *40*, 5648−5471.

[19] Li, Y. G.; Wang, E. B.; Wang, S. T.; Lu, Y.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *J. Mol. Struct.* **2001**, *607*, 133−141.

[20] Boyer, M.; LeMeur, B. *Acad. Sci. Ser.* **1975**, *C281*, 59.

[21] Wu, H. *J. Bio. Chem.* **1920**, *43*, 189.

[22] Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194 and references there in.

tetragonal platelike crystals of **1** were isolated (yield: ca. 28% based on Mo). Anal. Calcd for $C_{42}H_{57}NO_{34}Mo_6Na_2$, **1**: C, 28.96; H, 3.30; N, 0.80; Mo, 33.05; Na, 2.64%. Found: C, 28.83; H, 3.71; N, 1.25; Mo, 33.85; Na, 2.78%. Calcd total loss was 46.85%. Found: 47.63%. IR (cm^{-1}): 3621(w), 2929(m), 1743 (w), 1592(s), 1506(s), 1454(s), 1361(w), 1330(m), 1253(s), 1216(s), 1127(s), 1061(s), 965(s), 897(s), 790(s), 677(w).

Synthesis of $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]XMo_{12}O_{40}\cdot 6DMF\cdot CH_3CN$ (X = P, 2, and As, 3). DB18C6 (0.10 g) in 10 mL of dehydrated acetonitrile was added dropwise to 10 mL of dehydrated acetonitrile solution containing 0.21 g of $H_3PMo_{12}O_{40}\cdot 20H_2O$ and 0.017 g of NaCl with stirring for 24 h at room temperature. A large amount of yellow precipitate was formed. After filtration, the precipitate was dissolved in 3 mL of *N*,*N*-dimethylfomamide, and the resulting solution was kept in ambient environment. Five days later, light-red block crystals of **2** were obtained (yield: 40% based on Mo). Anal. Calcd for $C_{80}H_{133}N_7O_{72}PMo_{12}Na_3$, **2**: C, 26.72; H, 3.73; N, 2.73; P, 0.86; Mo, 32.01; Na, 1.92. Found: C, 26.81; H, 3.68; N, 2.79; P, 0.79; Mo, 32.12; Na, 1.99. Calcd total loss was 46.69%. Found: 46.79%. IR (cm^{-1}): 3443 (s), 2927(m), 1658 (s), 1595 (w), 1505 (s), 1454(m), 1388 (m), 1358 (w), 1328(w), 1255(s), 1218(m), 1130(s), 1096(w), 1061(m), 957(s), 880(vs), 806(vs), 743(w), 662(w), 602(w).

The preparation of **3** was similar to that of **2** except that $H_3AsMo_{12}O_{40}\cdot 26H_2O$ was used (yield: 30% based on Mo). Anal. Calcd for $C_{80}H_{133}N_7O_{72}AsMo_{12}Na_3$, **3**: C, 26.40; H, 3.68; N, 2.69; As, 2.06; Mo, 31.63; Na, 1.89. Found: C, 26.51; H, 3.74; N, 2.75; As, 1.99; Mo, 31.72; Na, 1.93. Calcd total loss was 47.62%. Found: 47.41%. IR (cm^{-1}): 3440(s), 2931(m), 1668(s), 1595(w), 1506 (s), 1455(m), 1387 (m), 1358 (w), 1329(w), 1254(s), 1219(m), 1129(s), 1097(w), 1064(m), 964(s), 897(vs), 794(vs), 663(w), 602(w).

X-ray Crystallography. A yellow single crystal of **1** with dimensions 0.55 × 0.54 × 0.20 mm^3 was mounted inside a glass fiber capillary. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K in the range $2.40° < \theta < 27.47°$. Empirical absorption correction was applied (0.967 mm^{-1}). A total of 4876 (2558 unique, $R_{int} = 0.0701$) reflections were measured ($-21 \le h \le 22$, $-15 \le k \le 15$, $-18 \le l \le 18$). A light-red single crystal of **2** with dimensions 0.45 × 0.42 × 0.29 mm^3 was mounted inside a glass fiber capillary. Data were collected on a Bruker Smart Apex CCD diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K in the range $1.65° < \theta < 28.04°$ using the $\omega - 2\theta$ technique. An empirical absorption correction from ψ scan was applied (1.259 mm^{-1}). A total of 38637 (5214 unique, $R_{int} = 0.0893$) reflections were measured ($-20 \le h \le 20$, $-13 \le k \le 20$, $-38 \le l \le 34$). A light-red single crystal of **3** with dimensions 0.48 × 0.46 × 0.26 mm^3 was mounted inside a glass fiber capillary. Data were collected on a Siemens P4 four-circle diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K in the range $1.64° < \theta < 25.00°$ using the ω-scan technique. An empirical absorption correction from ψ scan was applied (1.490 mm^{-1}). A total of 9722 (3870 unique, $R_{int} = 0.0364$) reflections were measured ($-1 \le h \le 18$, $-18 \le k \le 1$, $-6 \le l \le 35$).

All structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 software.[23] Anisotropic thermal parameters were used to refine all atoms other than the C and N atoms of CH_3CN molecules and O atoms of water molecules. Hydrogen atoms were located in the Fourier difference maps. A summary of the crystallographic data and structural determination for **1**, **2**, and **3** is provided in Table 1. Selected bond lengths and angles of **1**, **2**, and **3** are listed in Tables 2 and 3, respectively. Distances involving CH···O weak interactions and OH···O hydrogen bonding interactions of **2** and **3** are shown in Table 4.

Table 1. Crystal Data and Structural Refinement for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{42}H_{57}NO_{34}Mo_6Na_2$	$C_{80}H_{133}N_7O_{72}$-$PMo_{12}Na_3$	$C_{80}H_{133}N_7O_{72}$-$AsMo_{12}Na_3$
fw	1741.51	3596.15	3640.10
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
space group	*P*4/*mbm*	*P*6$_3$/*m*	*P*6$_3$/*m*
a (Å)	16.9701(6)	15.6882(5)	15.7435(17)
b (Å)	16.9701(6)	15.6882(5)	15.7435(17)
c (Å)	14.2676(4)	29.9778(18)	30.042(7)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	120	120
V (Å^3)	4108.8(2)	6389.6(5)	6448.5(17)
Z	2	2	2
D_c (g cm^{-3})	1.408	1.869	1.875
μ (mm^{-1})	0.967	1.259	1.490
R1[a]	0.0667	0.0624	0.0645
wR2[b]	0.1997	0.1579	0.1603

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Mo(1)−O(1)	1.661(7)	Mo(1)−O(2)	1.921(7)
Mo(1)−O(4)	1.932(4)	Mo(1)−O(5)	2.3157(8)
Mo(2)−O(3)	1.671(8)	Mo(2)−O(4)	1.914(5)
Mo(2)−O(5)	2.3240(9)	Na−OW(2)	2.37(2)
Na−OW(1)	2.33(3)	Na−O(6)	2.732(8)
Na−O(7)	2.726(14)	Na−O(7′)	2.636(16)
O(1)−Mo(1)−O(2)	102.7(4)	O(1)−Mo(1)−O(4)	103.60(14)
O(1)−Mo(1)−O(5)	179.1(3)	O(2)−Mo(1)−O(4)	87.06(15)
O(3)−Mo(2)−O(4)	103.50(13)	O(3)−Mo(2)−O(5)	180.0
Mo(1)−O(4)−Mo(2)	117.1(2)	Mo(1)−O(5)−Mo(2)	90.0
OW(1)−Na−OW(2)	166.4(4)		

The CCDC reference numbers are the following: 197084 for **1**, 191702 for **2**, and 185844 for **3**.

Results and Discussion

Crystal Structure of 1. X-ray crystallography shows that compound **1** consists of one isopolyanion $Mo_6O_{19}^{2-}$, two $[(DB18C6)Na(H_2O)_{1.5}]^+$ cations, and one dissociated acetonitrile molecule. The $Mo_6O_{19}^{2-}$ isopolyanion possesses the well-known Lindqvist structure.[5] It is constructed by six MoO_6 octahedra which are connected with each other via edge-sharing oxygen atoms, and thus, it exhibits an approximate O_h symmetry (as shown in Figure 1). Three kinds of oxygen atoms exist in the cluster, that is, the terminal oxygen O_t, double-bridging oxygen O_b, and central oxygen O_c. Thus, the Mo−O bond lengths can be grouped into three sets: Mo−O_t 1.661(7)−1.671(8) Å, Mo−O_b 1.914(5)−1.932(4) Å, and Mo−O_c 2.316(8)−2.324(9) Å. The bond angle of Mo−O_b−Mo is 117.1(2)°, while that of Mo−O_c−Mo is 90°.

In the structure of **1**, each crown ether molecule has two positions owing to the crystallographic disorder of O(7), C(3), C(4), and C(5) atoms (see Figure 1). All of them have 50% occupancy over the two positions. Na^+ ions are coordinated

---

[23] (a) Sheldrick, G. M. *SHELXS 97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL 97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2** and **3**

	Compound **2**		
Mo(1)−O(3)	1.658(4)	Mo(1)−O(5)	1.823(5)
Mo(1)−O(4)	1.809(5)	Mo(1)−O(1)	2.462(7)
Mo(2)−O(6)	1.652(4)	Mo(2)−O(8)	1.815(5)
Mo(2)−O(7)	1.808(5)	Mo(2)−O(5)	1.982(5)
Mo(2)−O(1)	2.479(7)		
P−O(1)	1.536(7)	P−O(2)	1.542(12)
Na−O(9)	2.807(8)	Na−O(11)	2.653(5)
Na−O(10)	2.692(5)	Na−O(12)	2.629(9)
Na−OW(1)	2.43(2)	Na−OW(2)	2.281(11)
O(3)−Mo(1)−O(4)	103.8(3)	O(6)−Mo(2)−O(7)	103.9(3)
O(3)−Mo(1)−O(5)	103.6(3)	O(6)−Mo(2)−O(8)	102.9(3)
O(4)−Mo(1)−O(5)	95.8(2)	O(7)−Mo(2)−O(8)	96.9(3)
O(3)−Mo(1)−O(1)	158.7(2)	O(6)−Mo(2)−O(5)	99.8(2)
O(4)−Mo(1)−O(1)	95.7(3)	O(7)−Mo(2)−O(5)	86.93(19)
O(5)−Mo(1)−O(1)	65.4(2)	O(8)−Mo(2)−O(5)	155.3(3)
O(6)−Mo(2)−O(1)	158.4(2)	O(8)−Mo(2)−O(1)	96.5(3)
O(7)−Mo(2)−O(1)	64.1(3)	O(5)−Mo(2)−O(1)	63.2(2)
O(1)−P−O(2)	109.1(3)	OW(2)−Na−OW(1)	172.1(6)
	Compound **3**		
Mo(1)−O(3)	1.643(7)	Mo(1)−O(5)	1.813(8)
Mo(1)−O(4)	1.807(7)	Mo(1)−O(2)	2.433(11)
Mo(2)−O(6)	1.634(7)	Mo(2)−O(8)	1.825(8)
Mo(2)−O(7)	1.811(8)	Mo(2)−O(5)	2.014(8)
Mo(2)−O(1)	2.421(10)		
As−O(1)	1.663(19)	As−O(2)	1.667(12)
Na−O(9)	2.829(13)	Na−O(11)	2.657(9)
Na−O(10)	2.709(9)	Na−O(12)	2.623(14)
Na−OW(1)	2.47(3)	Na−OW(2)	2.284(17)
O(3)−Mo(1)−O(4)	103.4(5)	O(6)−Mo(2)−O(7)	102.8(5)
O(3)−Mo(1)−O(5)	103.3(4)	O(6)−Mo(2)−O(8)	102.8(5)
O(4)−Mo(1)−O(5)	96.7(4)	O(7)−Mo(2)−O(8)	98.5(4)
O(3)−Mo(1)−O(2)	154.8(4)	O(6)−Mo(2)−O(5)	98.9(4)
O(4)−Mo(1)−O(2)	62.8(4)	O(7)−Mo(2)−O(5)	86.2(3)
O(5)−Mo(1)−O(2)	99.4(5)	O(8)−Mo(2)−O(5)	156.1(4)
O(6)−Mo(2)−O(1)	156.2(5)	O(8)−Mo(2)−O(1)	64.2(4)
O(7)−Mo(2)−O(1)	98.9(5)	O(5)−Mo(2)−O(1)	92.0(4)
O(2)−As−O(1)	109.8(4)	OW(2)−Na−OW(1)	171.0(9)

Table 4. Distances Involving OH···O Hydrogen Bonding and CH···O Weak Interactions of **2** and **3**[a]

A	H	B	A−H distance/Å	H···B distance/Å	A···B distance/Å
O(2WA)		O(13)			2.920 (2.964)
O(3W)		O(1W)			2.739 (2.733)
C(1)	H(1)	O(6)	0.970 (0.970)[a]	2.773 (2.768)	3.261 (3.254)
C(12)	H(12)	O(3)	0.970 (0.970)	2.741 (2.854)	3.051 (3.132)
C(10A)	H(10)	O(13)	0.970 (0.970)	2.650 (2.654)	3.357 (3.352)

[a] The values in the parentheses are the H-bond distances of **3**.

to oxygen atoms of the DB18C6 molecule with Na−O(crown ether) distances of 2.636(16)−2.732(8) Å and also to the oxygen atoms of water molecules with an average Na−OW bond length of 2.35 Å. The OW(2) also has two positions due to the crystallographic disorder and has 25% occupancy over each site, suggesting that the OW(2) has the half coordination possibility with each Na^+ cation. Thus, the two Na^+ ions in compound **1** have two kinds of coordination environments, that is, the seven- and eight-coordination modes.

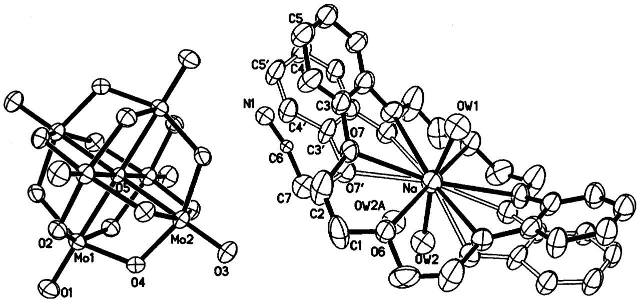


Figure 1. ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

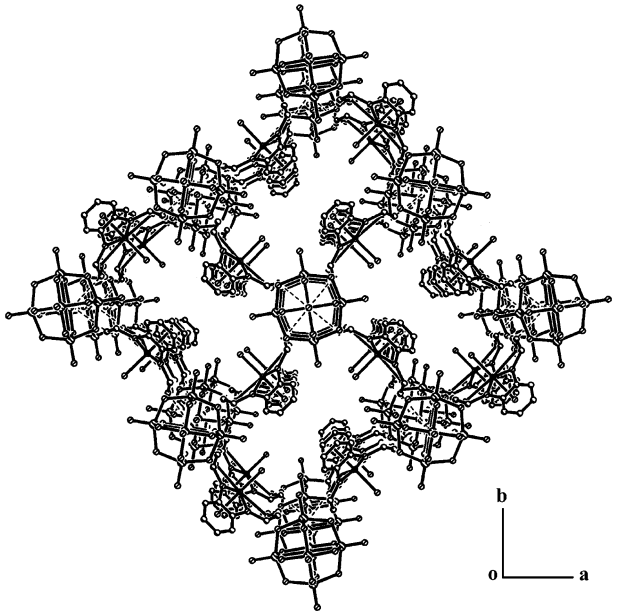


Figure 2. 3-D network of **1** with 1-D sandglasslike channels along the *c* axis. The acetonitrile molecules are omitted for clarity.

The most unusual structural feature of compound **1** is that a 3-D supramolecular network with 1-D sandglasslike channels is formed (see Figure 2). In this 3-D architecture, the polyoxoanion $Mo_6O_{19}^{2-}$ acts as the joint to connect eight $[(DB18C6)Na(H_2O)_{1.5}]^+$ building blocks through the unusual weak interactions (O(3)···C(1) 3.486 Å).[4a] The 1-D sandglasslike channels are parallel with the *c* axis and possess dimensions of 7.77 × 0.97 $Å^2$. The dissociated CH_3CN molecules are filled in these channels. Compared with previously reported supramolecular compounds based on crown ether and polyoxoanion building blocks,[13−19] compound **1** represents the first 3-D extended network with channels.

Crystal Structures of 2 and 3. Compounds **2** and **3** are isostructural. Compared with **1**, **2** and **3** exhibit different supramolecular arrays. As shown in Figure 3, **2** consists of one Keggin-type polyoxoanion $[PMo_{12}O_{40}]^{3-}$, one novel trimeric cation $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]^{3+}$, six DMF molecules, and one dissociated acetonitrile molecule. The $[PMo_{12}O_{40}]^{3-}$ polyoxoanion is located at a $\bar{3}$ axis (−1, 0, $^1/_2$) and exhibits a distorted Keggin structure. The central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. The P−O distances range from 1.536(7) to 1.542(12) Å (see Table 3). This structural feature often appears in $XMo_{12}O_{40}^{n-}$ with the α-Keggin structure, which has been explained by several groups.[14,24]

The Mo−O distances can be grouped into three sets: Mo−O_t (terminal) 1.643(7)−1.634(7) Å, Mo−O_c (central) 2.421(10)−2.433(11) Å, and Mo−O_b (bridge) 1.807(7)−2.014(8) Å. In the polyoxoanion of **2**, there are alternating "short" and "long" Mo−O_b−Mo bonds with average distances of 1.814 and 2.014 Å, respectively, owing to small displacements of Mo atoms from the mirror planes of the M_3O_{13} triplets.[6] The Mo−O_b−Mo angles are nearly equal, ranging from 138.1(6)° to 139.8(5)°.

In the trimeric cations of **2** (see Figure 4), Na^+ ions are coordinated to dibenzo-18-crown-6 molecules with Na−O(crown ether) of 2.623(14)−2.829(13) Å. Na^+ ions are nearly located in the plane defined by the crown ether oxygen atoms (0.0504 Å). Furthermore, Na^+ ions are coordinated to two water molecules with Na−OW 2.284(17)−2.47(3) Å and OW(1)−Na−OW(2) 171.0(9)°. The unusual feature here is that three umbrella-like $[Na(DB18C6)(H_2O)_2]^+$ units are linked together by two dissociated water molecules via OW(1)−H···OW(3) hydrogen bonds (2.733 Å) and form a semiopen cagelike supramolecular cation (Figure 4). In previous studies, anions have widely been introduced into the crown ether supramolecular cages as "guests".[25−27] In this case, however, the two water molecules act as the "guests" and are encapsulated in the cagelike crown ether "hosts", which has never been reported.

Outside the supramolecular cage, there exist six DMF molecules, every two of which are distributed above and below the Na^+-coordinated water molecules. The O(13) oxygen atom of every DMF molecule is linked to OW(2A) through a hydrogen bond of 2.964 Å (Table 4). Furthermore, the O(13) oxygen atom connects with C(10A) of the adjacent crown ether molecule via weaker interactions (3.352 Å). Therefore, three adjacent trimeric cations are connected together by six DMF molecules among them. On the basis of these intermolecular forces, an interesting 2-D supramolecular assembly with "honeycomblike" pores (6.67 × 6.67 Å^2) is formed (see Figure 5). The large pores in adjacent organic layers are arranged in a parallel fashion. Interestingly, the $[PMo_{12}O_{40}]^{3-}$ polyoxoanions act as "guests" and are located in the large pores of the 2-D organic assembly "hosts". Scheme 1 illustrates this host−guest supramolecular architecture. It is also noteworthy that the polyoxoanions are not fully encapsulated in the pores but distributed between two organic layers as illustrated in Scheme 2. The thickness of every organic layer is ca. 10.971 Å, while the distance between two layers is about 1.89 Å. This structural feature is somewhat similar to the model of polyoxometalate-pillared compounds previously reported by Hu et al.[10g]

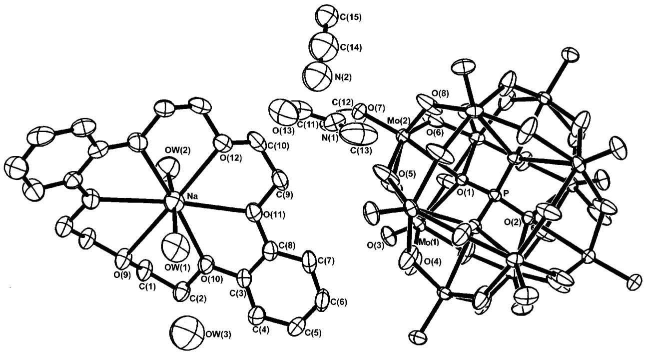


Figure 3. ORTEP drawing of **2** showing the labeling of atoms with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

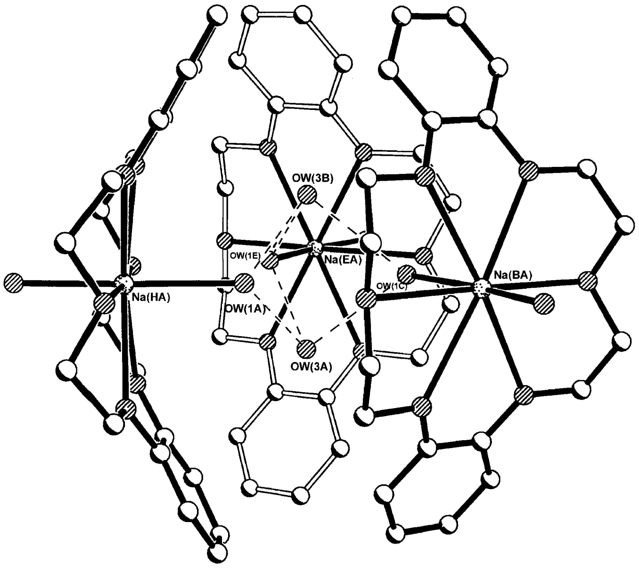


Figure 4. View of the cagelike trimeric cations. Hydrogen atoms are omitted for clarity.

Compound **3** has the same structural feature with **2** and no more description will be provided.

The obvious structural difference between the present compounds **1**, **2**, and **3** and those in our previous reports[17] is the introduction of sodium cations into the cavity of crown ethers. These alkali metal ions can effectively support flexible crown ether molecules via coordinate covalent bonds and make their molecular skeletons more robust so that the resulting umbrella-like crown ether−sodium complex cations act as appropriate building blocks for the construction of novel 3-D or 2-D supramolecular assemblies in the present work. Furthermore, for compounds **1**, **2**, and **3**, the different packing arrangements of crown ether−sodium coordination cations in their structures may originate from the various symmetries and charges of the polyoxoanions ($[Mo_6O_{19}]^{2-}$, O_h symmetry; $[XMo_{12}O_{40}]^{3-}$, T_d symmetry).

FT-IR Spectroscopy. In the IR spectrum of **1**, the characteristic peaks at 790, 897, and 965 cm^{-1} are attributed to the ν(Mo−O_c−Mo), ν(Mo−O_b−Mo), and ν(Mo=O_t) of the $Mo_6O_{19}{}^{2-}$ polyanions, respectively. Bands in the range 2929−1061 cm^{-1} are characteristic of DB18C6 molecules, while the feature band pertaining to the ν(C≡N) of the acetonitrile molecule is overlapped by the C−H and C−O vibration peaks of DB18C6. In the IR spectrum of compound

---

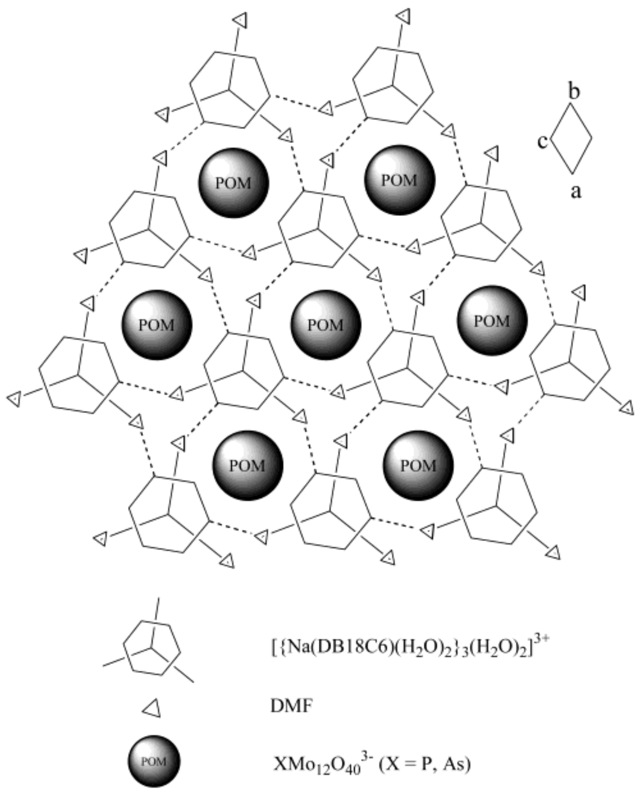
(24) (a) Evans, H. T.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501−505. (b) Attanasio, D.; Bonamico, M.; Fares, V.; Imperatori, P.; Suber, L. *J. Chem. Soc., Dalton Trans.* **1990**, 3221−3228. (c) Maguerès, P. L.; Ouahab, L.; Golhen, S.; Grandjean, D.; Pena, O.; Jegaden, J. C.; Gomez-Garecia, C. J.; Delhaès, P. *Inorg. Chem.* **1994**, *33*, 5180−5187. Fender, N. S.; Kahwa, I. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1729−1730.

(25) Fender, N. S.; Kahwa, I. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1729−1730.

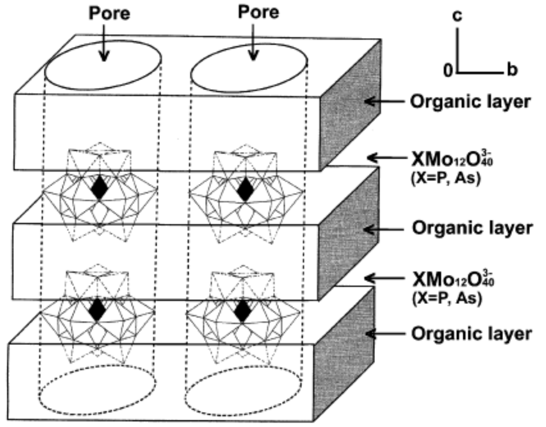
(26) Willems, J. B.; Köckerling, M. *Chem. Commun.* **2001**, 1380−1381.

(27) Fender, N. S.; Fronczek, F. R.; John, V.; Kahwa, I. A.; McPherson, G. L. *Inorg. Chem.* **1997**, *36*, 5539−5547 and references therein.

Scheme 1. Drawing of 2-D Crown Ether Supramolecular "Host" of **2** Encapsulating the Polyoxoanion "Guests"



Scheme 2. Schematic Illustration of the Packing Arrangement of **2** along the *a* Axis



2, the characteristic peaks at 1061, 897, 854, and 794 cm^{-1} are attributed to ν_{as}(P$-$O$_c$), ν_{as}(Mo$=$O$_t$), ν_{as}(Mo$-$O$_b$$-$Mo), and ν_{as}(Mo$-O_c$$-$Mo), respectively, showing that the polyoxoanion has an α-Keggin structure. Bands at 2931−1129 cm^{-1} are characteristic of DB18C6. The strong peak at 1668 cm^{-1} is attributed to the ν(C$=$O) vibration of DMF molecules. The broad peak at 3440 cm^{-1} and bands in the range 1450−1300 cm^{-1} are characteristic of water molecules. The IR spectrum of **3** is analogous to that of **2** except that the characteristic ν_{as}(As$-$O$_c$) peak appears at 966 cm^{-1}.

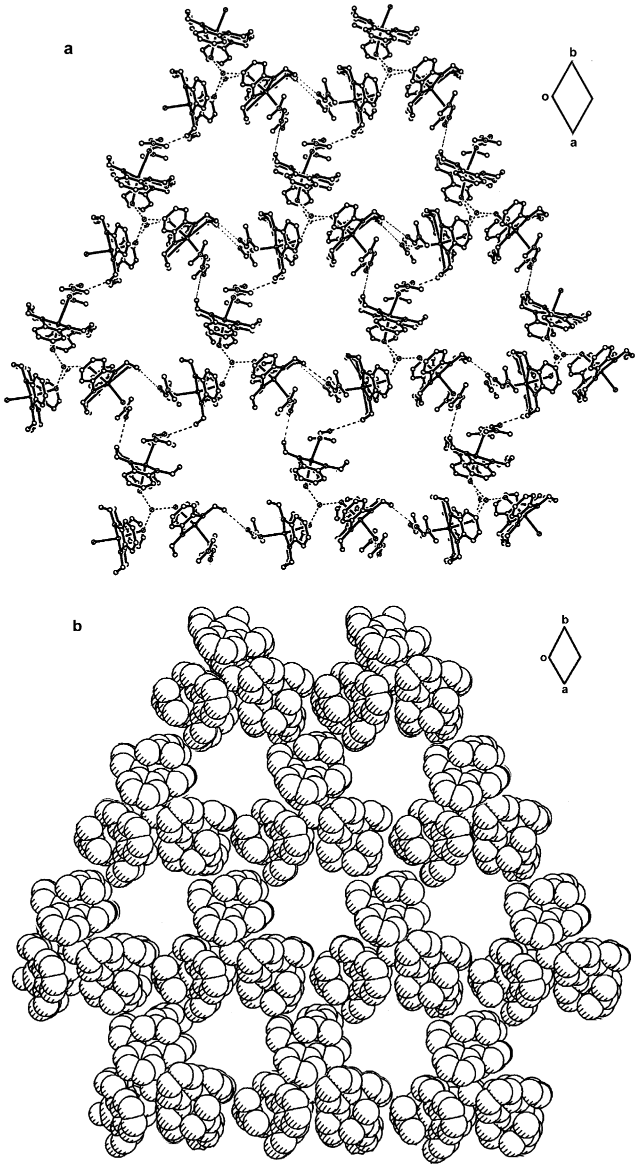


Figure 5. (a) View of the hydrogen-bonded 2-D supramolecular assembly of **2** along the *c* axis. The hydrogen atoms and polyoxoanions are omitted for clarity. (b) Space-filling diagram showing the porous supramolecular assembly of **2** along the *c* axis.

TG Analyses. The TG curve of compound **1** is divided into two stages. The first weight loss is ca. 5.95% in the temperature range 70−150 °C, corresponding to the release of the dissociated acetonitrile and coordinated water molecules. The hydrogen-bonded 3-D architecture of **1** is stable in the temperature range 150−280 °C. The second weight loss of ca. 41.40% from 290 to 500 °C is ascribed to the release of the DB18C6 molecules. The whole weight loss (ca. 47.35%) is in good agreement with the calculated value (46.85%).

The TG curve of compound **2** exhibits four continuous weight loss stages, corresponding to the release of dissociated water, CH$_3$CN, coordinated water, DMF, and DB18C6 molecules, respectively. The whole weight loss (47.62%) is in good agreement with the calculated value (47.41%). The TG curve of compound **3** exhibits similar weight loss stages to those of compound **2**. The whole weight loss (46.69%) is in good agreement with the calculated value (46.79%).

Photochromism. It was found that irradiation of the crystals of **1**, **2**, and **3** by a mercury lamp at room temperature for 1 h induced obvious photochromism of **2** and **3**, except not for **1**. Both crystals of **2** and **3** changed from light-red to

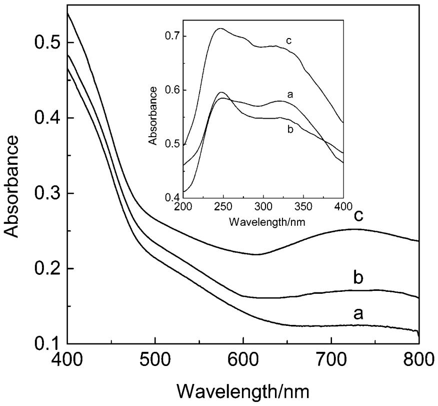


Figure 6. UV−vis spectra of (a) $H_3AsMo_{12}O_{40}\cdot26H_2O$ and compound **3** (b) before irradiation and (c) after irradiation.

deep-brown. The absorption spectra of compound **3** before and after UV irradiation are shown in Figure 6. After UV irradiation, a new absorption band appeared in the visible region, which is assigned to the intervalence charge transfer ($Mo^{5+} \rightarrow Mo^{6+}$) bands of heteropoly anions.[5] These results have also been confirmed by means of EPR analyses. The irradiated samples of **2** and **3** exhibited significant paramagnetic signals, attributed to Mo^{5+} with $g = 1.94$ (see Figure 7). The EPR signals suggest that electron transfer may occur between the organic moieties and the heteropoly anions, which results in the reduction of Mo^{6+} to Mo^{5+}.[5,28] When the irradiation stopped, the crystals could slowly change from dark-brown to red in the dark. It is assumed that the weak intermolecular interactions between the solvent molecules and the polyoxometalate moieties might result in the photosensitive behavior of these compounds, similar to that suggested by Hill et al. for $H_3PMo_{12}O_{40}\cdot6DMA\cdot CH_3CN\cdot0.5H_2O$.[29] A study on the detailed photochromic mechanism is underway.

Conclusions

In summary, the successful syntheses of $[(DB18C6)Na(H_2O)_{1.5}]_2Mo_6O_{19}\cdot CH_3CN$, **1**, and $[\{Na(DB18C6)(H_2O)_2\}_3(H_2O)_2]XMo_{12}O_{40}\cdot6DMF\cdot CH_3CN$ (X = P, **2**, and As, **3**) may provide a matrix for the preparation of novel supramolecular assemblies belonging to the crown ether−polyoxoanions systems. The extended research on the structural chemistry of this system may focus on the replacement of DB18C6 molecules and polyoxoanions (Lindqvist and Keggin) with other crown ethers and a series of POMs. Study in this respect is going on to reveal the synthetic rules and to explore their attractive properties. Furthermore, the 3-D framework of compound **1** exhibits good stability in the temperature range 150−280 °C, suggesting that **1** may have potential applications in solvent absorption and separation. Compounds **2** and **3** exhibit good photochromic properties and may be applied in the field of photosensitive materials.

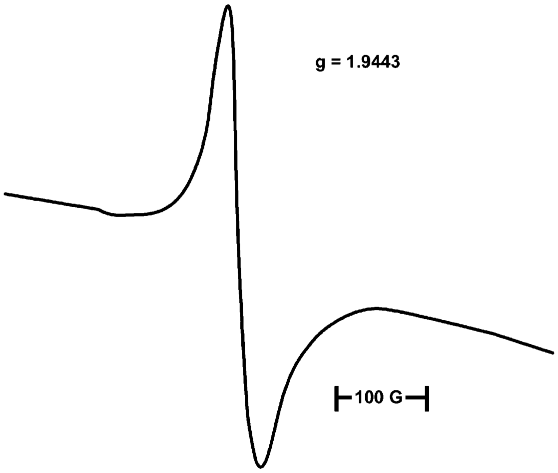


Figure 7. EPR spectrum of compound **3**.

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 the structure determination of compounds **1**−**3**. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026172+

---

(28) Wang E. B.; Xu L.; Hu, C. W. *Chin. Sci. Bull.* **1991**, *20*, 1544.

(29) Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1436−1441.