Crystal Structure and Replacement Reaction of Coordinated Water Molecules of the Heteropoly Compounds of Sandwich-Type Tungstoarsenates

Li-Hua Bi,[†] En-Bo Wang,*[,†,‡] Jun Peng,[†] Ru-Dan Huang,[†] Lin Xu,[†] and Chang-Wen Hu[†]

Department of Chemistry, Northeast Normal University, 130024 Changchun, P. R. China, and
State Key Laboratory of Coordination Chemistry, Nanjing University, 210093 Nanjing, P. R. China

Received May 24, 1999

Six new heteropoly compounds in the $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ series (M = Cu^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}), previously unknown, were synthesized and characterized by means of IR, UV−vis, CV, ^{183}W NMR, TG-DSC, and elemental analyses. The synthetic method used in preparing this type of heteropoly compounds was different from that in preparing the corresponding tungstophosphates in that the starting materials were transition metal chlorides in 1.5 times the stoichiometric amount and the required pH value is lower than 2. The crystal structure of $Na_{16}[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]\cdot 47H_2O$ was solved in *triclinic*, $P\bar{1}$ symmetry, with $a = 12.721(3)$ Å, $b = 24.516(5)$ Å, $c = 26.450(5)$ Å, $\alpha = 89.90(3)°$, $\beta = 77.32(3)°$, $\gamma = 89.96(3)°$, $V = 8048(3)$ Å^3, $Z = 2$, and $R = 0.0966$. This anion is isostructural with the previously reported $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$, having a rhombic tetrameric cluster Cu_4O_{16} sandwiched by two trivacant Dawson−Wells anions $[As_2W_{15}O_{56}]^{12-}$. The range of the bond lengths of the equatorial Cu−O bonds is 1.83−2.05 Å, while that of the axial Cu−O bonds is 2.30−2.39 Å. The distortion of the Cu_4O_{16} cluster is smaller in the As species than in the P species. Two copper atoms in the Cu_4O_{16} cluster are coordinated by water molecules. The replacement reactions of the coordinated water molecules of this series of heteropoly compounds in aqueous solutions and in selected organic solvents are also reported here for the first time. The results show that $[Fe (CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $H_2NCH_2CH_2NH_2$, etc., can replace the coordinated water to form its characteristic color in aqueous solutions, while in organic solvents the coordinated water molecules are lost, leaving unshared coordination positions that can be occupied by some organic ligands such as pyridine, lactic acid, and acetone to restore the octahedral coordination of M^{2+}. The crystallographic morphologies of this series of heteropolyanions after phase transfer are dependent on different transition metal ions present in the central M_4O_{16} clusters although the anions are isostructural with each other.

Introduction

In 1970, Baker and Figgis[1] established a new fundamental class of heteropoly compounds formulated $[(Y^{y-})\ M^{m+}O_5X^{x+}O_4\text{-}(W\text{ or }Mo)_{11}O_{30}]^{(12-m-x+y)-}$ and indicated that a great variety of ligands can function as Y. In 1984, Pope first showed these polyoxometalate compounds (POMs) extract into nonpolar organic solvents for stoichiometric reactions.[2] In 1986, Hill first showed catalysis by these complexes.[3] This opened up the phase transfer, nonaqueous chemistry of heteropolyanions.[1−8] In our previous studies on phase transfer, ligand replacement reactions in substituted polyoxomolybdates, including 9-, 11-, and 17-series, were carried out by not only small inorganic molecules but also organic ligands such as pyridine, lactic acid, acetone, phenol, etc., obtaining significant results concerning nonlinear optical properties and liquid-crystal behaviors of the studied polyoxometalates in phase transfer systems.[9−16] Previous investigations of replacement reactions focused mainly on the substitution of coordinated water attached to the surface of heteropolyanions. The sandwich-type heteropolyanions have two coordinated water molecules attached to the central tetrameric cluster M_4O_{16}, the replacement of which by other ligands is also interesting. To our knowledge, investigations of this aspect are rare.[2,4] In this paper we report the replacements of the coordinated water molecules, as well as the syntheses and

---

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

[†] Northeast Normal University.

[‡] Nanjing University.

(1) Baker, L. C. M.; Figgis, J. S. *J. Am. Chem. Soc*. **1970**, *92*, 3794−3797.

(2) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737−2738.

(3) (a) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc*. **1986**, *108*, 536−538. (b) Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528−3529.

(4) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc*., *Dalton Trans*. **1989**, 1483−1489.

(5) Piepgrass, K.; Pope, M. T. *J. Am. Chem. Soc*. **1989**, *111*, 753−754.

(6) Katsoulis, D. E.; Tausch, V. S.; Pope, M. T. *Inorg. Chem*. **1987**, *26*, 215−217.

(7) Harmalker, S. P.; Pope, M. T. *J. Inorg. Biochem.* **1986**, *28*, 85−89.

(8) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209−7221.

(9) (a) Huang, R. D.; Fei, B. L.; Wang, E. B.; Li, B. T. *Chem. J. Chin. Univ.* **1998**, *19*, 1721−1723. (b) Huang, R. D.; Fei, B. L.; Wang, E. B.; Peng, J. *Chem. Res. Chin. Univ.* **1998**, *14*, 335−336.

(10) Wang, E. B.; Zhou, Y. S. *Transition Met. Chem.* **1996**, *21*, 447−450.

(11) Zhou, Y. S.; Wang, E. B.; Peng, J. *Polyhedron* **1999**, *18*, 1419−1423.

(12) Peng, J.; Wang, E. B.; Zhou, Y. S. *J. Chem. Soc., Dalton Trans.* **1998**, 3865−3869.

(13) Wang, E. B.; Liu, X.; Wang, Z. P. *Chem. J. Chin. Univ.* **1994**, *15*, 1285−1287.

(14) Zhang, S. Y.; Huang, R. D.; Wang, E. B. *J. Chem. Res. Chin. Univ.* **1996**, *12*, 397−400.

(15) Huang, R. D.; Qiao, Z. P.; Wang, E. B. *Chem. J. Chin. Univ.* **1991**, *20*, 32−35.

(16) Wang, E. B.; Hu, C. W.; Xu, L. *Introduction to polyoxometalate chemistry*; Chemical Industry Press: Beijing, 1998.

(17) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, U. *J. Am. Chem. Soc.* **1981**, *103*, 1587−1589.

(18) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006−1008.

10.1021/ic990596v CCC: $19.00

structural characterization of $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ (denoted $M_4As_4W_{30}$, M = Cu^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}), previously unknown.

Analogous heteropolyanions with P as the heteroatom were previously reported by Finke,[17−20] Droege,[17−19] Weakley, [20,21] and Pope[22] and used in other applications later by Gomez-Garcia,[23] Hill,[24] and Neumann[25] et al. This type of heteropoly compound has many interesting properties,[26] such as magnetic properties,[27−29] catalytic activity,[24,30−35] anti-AIDS activity,[36] etc. On the basis of the recognition that the As species generally parallel the P species and, further, the As atom, larger than the P atom, has easily changeable As^{III}/As^{V} oxidation states, we explore novel sandwich-type complexes of $M_4As_4W_{30}$, aimed at adding new members to this family and extending the applications of polyoxometalates. This paper covers pure, isolated As-centered sandwich-type polyoxometalates of the Dawson−Wells class with full synthetic and characterization details; the structural characterization of one of the members, $Na_{16}[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]\cdot 47H_2O$, which shows a smaller distortion of the central cluster Cu_4O_{16} for the As species than that for the P species; the unequivocal identity of the ligands at the tetrameric clusters M_4O_{16} (the studies of ligand replacement reactions in POMs, especially in the As series, are rare, but these are important for oxidation catalysis); and crystallographic morphologies, formed from a benzene solution and observed under a polarizing microscope, of $M_4As_4W_{30}$ containing tetra-*n*-heptylammonium bromide ((tHA)Br). Research of the magnetic characterizations of the As species to compare with those of the P analogs is underway.[23]

Experimental Section

Materials and General Methods. The tetraheptylammonium bromide and benzene used were of superpure grade, and other reagents used were of analytical grade. Benzene was distilled prior to use and then dried with sodium and stored for usage. Distilled water was used for all syntheses. The elemental analyses were completed by means of an ICP-AES analyzer. The IR spectra (2% sample, in KBr pellets) were recorded on an Alpha Centaurt FT/IR spectrometer. The electronic absorption spectra were measured on a Beckman DU-640 spectrometer. The cyclic voltammograms (CV) were obtained on a CH Instrument (model 600V) analyzer. A typical three-electrode cell having a glassy carbon working electrode, a platinum counter electrode, and a silver/silver chloride reference electrode was used for the voltammetry experiments. The glassy carbon electrode was polished with 1.0 and 0.3 μm Al_2O_3 powders in turn and then washed ultrasonically. ^{183}W NMR spectra were recorded on a Unity-400 NMR system with 10-mm sample tubes and Na_2WO_4 saturated in D_2O as the external standard at room temperature. The crystallographic morphologies were observed by means of an OPTON polarizing microscope equipped with a heating plate and a microscopic photography instrument. TG-DSC measurements were carried out on a Perkin-Elemer TG-7, DSC-7 thermal analyzer.

α-$K_6As_2W_{18}O_{62}\cdot 14H_2O$, As_2W_{18}-K. This preparation was done according to literature.[37−39] To 300 mL of a solution containing 220 g of $Na_2WO_4\cdot 2H_2O$ was slowly added 150 mL of concentrated arsenic acid (11 M), followed by 100 mL of 4 M hydrochloric acid. The solution was heated for 4 h and then cooled to room temperature. A 100 g amount of ammonium chloride was added in two steps, 50 g in each step to isolate isomers: the first addition gave the precipitate A (38 g, 20%) that was filtered off; the second addition gave the main precipitate B that was almost a pure α-isomer (114 g, 63%). The precipitate B was dissolved in 200 mL of water and left for 1 day at 5 °C. The resulting precipitate was dissolved in water and treated with 32 g of solid potassium chloride, and then the new precipitate formed was isolated and recrystallized from 125 mL of hot water. Anal. Calcd (found) for α-$K_6As_2W_{18}O_{62}\cdot 14H_2O$: K, 4.75 (4.78); W, 67.01 (66.82); As, 3.04 (3.02); H_2O, 5.10 (5.13).

α-$Na_{12}As_2W_{15}O_{56}\cdot 21H_2O$, As_2W_{15}-Na. This preparation was done according to the literature.[19,38] The salt α-$K_6As_2W_{18}O_{62}\cdot 14H_2O$ (50 g) was dissolved in 180 mL of H_2O under mild heat. After the solution was cooled to room temperature, 45 g of $NaClO_4$ was added and a white precipitate of $KClO_4$ was formed immediately. The mixture was stirred for 1 h, and then $KClO_4$ was removed by filtration. A solution of 1 M Na_2CO_3 was added dropwise to the filtrate. At pH 8.5 a white precipitate formed. More Na_2CO_3 was added to maintain the solution at pH 9 for 1 h. The solid $Na_{12}As_2W_{15}O_{56}$ was collected and washed with a saturated NaCl solution, 95% ethanol, and diethyl ether, respectively. The solid was dried in a desiccator over concentrated H_2SO_4 for 2 days. The yield was 39.6 g (79.2%). Anal. Calcd (found) for $Na_{12}As_2W_{15}O_{56}\cdot 21H_2O$: Na, 6.19 (6.21); W, 61.90 (62.32); As, 3.36 (3.28); H_2O, 8.48 (8.54).

$Na_{16}[M_4(H_2O)_2(As_2W_{15}O_{56})_2]$, $M_4As_4W_{30}$-Na. $Na_{16}[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (1). $CuCl_2\cdot 2H_2O$ (0.57 g, 3.36 mmol) was dissolved in 50 mL of a 1 M NaCl solution; solid $Na_{12}As_2W_{15}O_{56}$ (5.0 g, 1.12 mmol) was then added and dissolved by heating and stirring. A 1.2 mL volume of 6 M HCl was added dropwise to the solution, the color of which turned from pale-blue to pale-green. The resulting clear green solution was cooled at 5 °C overnight, from which pale-green crystals were then collected. The product was dried at 80 °C under vacuum for ca. 0.5 h. The yield was 4.22 g (84.4%). Anal. Calcd (found) for $Na_8As_2W_{15}Cu_2(H_2O)O_{56}$: Na, 4.46 (4.38); As, 3.63 (3.53); W, 66.69 (66.48); Cu, 3.08 (3.02); H_2O not specifically determined.

$Na_{16}[Mn_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (2). The preparation procedure was the same as the preparation of $Cu_4As_4W_{30}$-Na described above except that $MnCl_2\cdot 4H_2O$ (0.7 g) was used. The yield was 4.45 g (89%) of

---

(19) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886−3896.

(20) Finke, R.; Weakley, T. J. R. *J. Chem. Crystallogr*. **1994**, *24*, 123−125.

(21) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem*. **1990**, *29*, 1235−1241.

(22) Kim, K. C.; Pope, M. T. *J. Am. Chem. Soc.* **1999**, *121*, 8512−8517.

(23) (a) Gomez-Garcia, C. J.; Borras-Almenar, J. J.; Coronado, E.; Ouahab, L. *Inorg. Chem*. **1994**, *33*, 4016−4022. (b) Clemente-Juan, J. M.; Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J. *Inorg. Chem*. **1999**, *38*, 55−63.

(24) (a) Hill, C. L.;Prosser-Mclartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407−455. (b) Zhang, X.; Chen, Q.; Duncan, D. C.; Campana, C. F.; Hill, C. L. *Inorg. Chem*. **1997**, *36*, 4208−4215. (c) Rhule, J. T.; Hill, C. L.; Judd, D. A. *Chem. Rev*. **1998**, *98*, 327−357.

(25) Neumann, R. *Prog. Inorg. Chem*. **1998**, *47*, 317−370.

(26) (a) Pope, M. T.; Müller, A., Eds. *Polyoxometalates: from Platonic Solids to Anti-retroviral Activity*; Kluwer: Dordrecht, The Netherlands, 1994. (b) Hill, C. L. *Chem. Rev*. **1998**, *98*(1).

(27) (a) Gomez-Garcia, C. J.; Casan-Pastor, N.; Coronado, E.; Baker, L. C. W.; Pourroy, G. *J. Appl. Phys*. **1990**, *67*, 5995−5997. (b) Gomez-Garcia, C. J.; Coronado, E.; Borras-Almenar, J. J. *Inorg. Chem*. **1992**, *31*, 1667−1673. (c) Gomez-Garcia, C. J.; Coronado, E.; Gomez-Romero, P.; Casan-Pastor, N. *Inorg. Chem*. **1993**, *32*, 3378−3381.

(28) Casan-Pastor, N.; Bas, J.; Coronado, E.; Pourroy, G.; Baker, L. C. W. *J. Am. Chem. Soc*. **1992**, *114*, 10380−10383.

(29) Gomez-Garcia, C. J.; Coronado, E.; Borras-Almenar, J. J.; Aebersold, M.; Gudel, H. U.; Mutka, H. *Physica B* **1992**, *180−181*, 238−240.

(30) Zhang, X.; Chen, Q.; Duncan, D. C.; Lachicotte, R. J.; Hill, C. L. *Inorg. Chem*. **1997**, *36*, 4381−4386.

(31) Xu, L.; Sun, Y. Q.; Wang, E. B.; Shen, E. H. *Inorg. Chem. Commun*. **1998**, *1*, 382−385.

(32) Khenkin, A. M.; Hill, C. L. *Mendeleev Commun*. **1993**, 140−141.

(33) (a) Neumann, R.; Gara, M. *J. Am. Chem. Soc*. **1994**, *116*, 5509−5510. (b) Neumann, R.; Gara, M. *J. Am. Chem. Soc*. **1995**, *117*, 5066−5074. (c) Neumann, R.; Khenkin, A. M. *Inorg. Chem*. **1995**, *34*, 5753−5760.

(34) Peng, J.; Zhou, Y. S.; Wang, E. B.; Xing, Y. *J. Mol. Struct*. **1998**, *444*, 213−219.

(35) (a) Hu, C. W.; He, Q. L.; Zhang, Y. H.; Wang, E. B. *Catal. Today* **1996**, *30*, 141−143. (b) Hu, C. W.; Hashimoto, M.; Okuhara, T. *J. Catal*. **1993**, *143*, 437−439. (c) Hu, C. W.; He, Q. L.; Wang, E. B. *J. Chem. Soc., Chem. Commun*. **1996**, *2*, 121−124.

(36) Judd, D. A.; Schinazi, R. F.; Hill, C. L. *Antiviral Chem. Chemother*. **1994**, *5*, 410−414.

(37) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem*. **1984**, *23*, 1478−1482.

(38) Contant, R.; Thouvenot, R. *Can. J. Chem*. **1991**, *69*, 1498−1506.

(39) Contant, R.; Thouvenot, R. *Inorg. Chim. Acta* **1993**, *212*, 41−50.

orange-yellow crystals. Anal. Calcd (found) for $Na_8As_2W_{15}Mn_2(H_2O)O_{56}$: Na, 4.22 (4.09); As, 3.44 (3.47); W, 63.09 (63.23); Mn, 2.52 (2.48); H_2O not specifically determined.

$Na_{16}[Co_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (3). The preparation procedure was the same as the preparation of $Cu_4As_4W_{30}$-Na described above except that $CoCl_2{\cdot}6H_2O$ (0.8 g) was used. The yield was 4.34 g (86%) of a green-brown powder. Anal. Calcd (found) for $Na_8As_2W_{15}Co_2(H_2O)O_{56}$: Na, 4.47 (4.27); As, 3.64 (3.48); W, 66.83 (66.65); Co, 2.86 (2.57); H_2O not specifically determined.

$Na_{16}[Ni_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (4). The preparation procedure was the same as the preparation of $Cu_4As_4W_{30}$-Na described above except that $NiCl_2{\cdot}6H_2O$ (0.8 g) was used. The yield was 3.87 g (77%) of green crystals. Anal. Calcd (found) for $Na_8As_2W_{15}Ni_2(H_2O)O_{56}$: Na, 4.47 (4.35); As, 3.64 (3.50); W, 66.84 (66.58); Ni, 2.85 (2.80); H_2O not specifically determined.

$Na_{16}[Zn_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (5). The preparation procedure was the same as the preparation of $Cu_4As_4W_{30}$-Na described above except that $ZnCl_2$ (0.5 g) was used. The yield was 4.45 g (89%) of white crystals. Anal. Calcd (found) for $Na_8As_2W_{15}Zn_2(H_2O)O_{56}$: Na, 4.45 (4.25); As, 3.63 (3.48); W, 66.63 (66.42); Zn, 3.16 (3.02); H_2O not specifically determined.

$Na_{16}[Cd_4(H_2O)_2(As_2W_{15}O_{56})_2]$ (6). The preparation procedure was the same as the preparation of $Cu_4As_4W_{30}$-Na described above except that $CdCl_2$ (0.4 g) was used. The yield was 3.95 g (79%) of white crystals. Anal. Calcd (found) for $Na_8As_2W_{15}Cd_2(H_2O)O_{56}$: Na, 4.35 (4.18); As, 3.55 (3.33); W, 65.14 (64.95); Cd, 5.32 (5.18); H_2O not specifically determined.

Phase Transfer and Replacement Reaction of Coordinated Water Molecules for the $M_4As_4W_{30}$ Anion. (i) Phase Transfer. Transferring the heteropolyanion $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ (M = Cu^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}) into nonpolar organic solvents was carried out by using previously described procedures:[2] 5 mL of an aqueous solution of the anion (ca. 0.01 M) was mixed with an equal volume of a benzene solution containing (tHA)Br in an amount equivalent to the polyanion's charge. The anions were then extracted into the benzene solution. The solution was then dried either by passing N_2 gas through the solution for several hours or by evaporation.

(ii) Replacement Reaction of Coordinated Water Molecules for the $M_4As_4W_{30}$ Anion. The solid (0.1 g) obtained above was then dissolved in anhydrous benzene (5 mL). To the benzene solution was added an organic ligand, such as pyridine, acetonitrile, acetone, chloroform, or lactic acid, in a stoichiometric amount. Electronic spectra and IR spectra were recorded so as to determine the dehydration of the heteropolyanions and the substitution of such organic ligands for the coordinated water.

Replacement Reaction of the Water Molecules Coordinated to the $M_4As_4W_{30}$ Anion in Aqueous Solutions. This experiment was performed as follows. An aqueous solution of $M_4As_4W_{30}$-Na was mixed with an aqueous solution of $[Fe\ (CN)_6]^{3-}$, $[Fe\ (CN)_6]^{4-}$, $C_2H_8N_2$ (ethylenediamine), SO_3^{2-}, or SCN^-. By the addition of KCl to the resulting solution, a precipitate was isolated. The replacement of coordinated water molecules with selected organic ligands was observed by changes in color and changes in the electronic spectra of the corresponding solutions.[1] The products were identified by elemental analyses and IR spectra.

$K_{22}[Cu_4(L_1)_2(As_2W_{15}O_{56})_2]$, $Cu_4As_4W_{30}$-L_1 (L_1 = $[Fe(CN)_6]^{3-}$). An 8 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_4W_{30}$-Na was mixed with 1 mL of a hot aqueous solution containing 0.08 g of $K_3Fe(CN)_6$; the resulting solution was then heated for 0.5 h. A yellow precipitate (0.56 g) was isolated from the solution with the addition of 0.1 g of KCl after cooling it to room temperature and dried at 80 °C under vacuum for ca. 0.5 h. Elemental analyses gave a ratio K:Cu:Fe:W = 22.0:3.8:1.8:30.5 that was consistent with the formula. IR (KBr, cm^{-1}): 2115 (ν(CN)), 942, 871, 818, 717.

$K_{22}[Mn_4(L_1)_2(As_2W_{15}O_{56})_2]$, $Mn_4As_4W_{30}$-L_1. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_1 described above except that $Mn_4As_4W_{30}$-Na was used and the product was a yellow powder (0.52 g). Elemental analyses gave a ratio K:Mn:Fe:W = 22.0:4.0:2.1:30.3 that was consistent with the formula. IR (KBr, cm^{-1}): 2117 (ν(CN)), 942, 872, 818, 716.

$K_{22}[Co_4(L_1)_2(As_2W_{15}O_{56})_2]$, $Co_4As_4W_{30}$-L_1. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_1 described above except that $Co_4As_4W_{30}$-Na was used and the product was a purple powder (0.43 g). Elemental analyses gave a ratio K:Co:Fe:W = 22.0:4.2:1.9:30.4 that was consistent with the formula. IR (KBr, cm^{-1}): 2118 (ν(CN)), 943, 869, 823, 723.

$K_{22}[Ni_4(L_1)_2(As_2W_{15}O_{56})_2]$, $Ni_4As_4W_{30}$-L_1. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_1 described above except that $Ni_4As_4W_{30}$-Na was used and the product was a yellow-green powder (0.61 g). Elemental analyses gave a ratio K:Ni:Fe:W = 22.0:3.8:2.0:30.7 that was consistent with the formula. IR (KBr, cm^{-1}): 2114 (ν(CN)), 941, 869, 819, 722.

$K_{24}[Cu_4(L_2)_2(As_2W_{15}O_{56})_2]$, $Cu_4As_4W_{30}$-L_2 (L_2 = $[Fe(CN)_6]^{4-}$). An 8 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_4W_{30}$-Na was mixed with 1 mL of a hot aqueous solution containing 0.08 g of $K_4Fe(CN)_6$; the resulting solution was then heated for 0.5 h. A dark-red precipitate (0.62 g) was isolated from the solution with the addition of 0.1 g of KCl after cooling it to room temperature and dried at 80 °C under vacuum for ca. 0.5 h. Elemental analyses gave a ratio K:Cu:Fe:W = 24.0:3.8:1.9:30.3 that was consistent with the formula. IR (KBr, cm^{-1}): 2092 (ν(CN)), 940, 876, 815, 723.

$K_{24}[Mn_4(L_2)_2(As_2W_{15}O_{56})_2]$, $Mn_4As_4W_{30}$-L_2. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_2 described above except that $Mn_4As_4W_{30}$-Na was used and the product was a yellow-green powder (0.58 g). Elemental analyses gave a ratio K:Mn:Fe:W = 24.0:4.1:1.9:29.7 that was consistent with the formula. IR (KBr, cm^{-1}): 2092 (ν(CN)), 940, 873, 819, 719.

$K_{24}[Co_4(L_2)_2(As_2W_{15}O_{56})_2]$, $Co_4As_4W_{30}$-L_2. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_2 described above except that $Co_4As_4W_{30}$-Na was used and the product was a dark-green powder (0.48 g). Elemental analyses gave a ratio K:Co:Fe:W = 24.0:4.1:2.0:30.2 that was consistent with the formula. IR (KBr, cm^{-1}): 2090 (ν(CN)), 942, 871, 821, 725.

$K_{24}[Ni_4(L_2)_2(As_2W_{15}O_{56})_2]$, $Ni_4As_4W_{30}$-L_2. The preparation procedure was the same as that for $Cu_4As_4W_{30}$-L_2 described above except that $Ni_4As_4W_{30}$-Na was used and the product was a yellow powder (0.65 g). Elemental analyses gave a ratio K:Co:Ni:W = 24.0:3.8:1.7:30.2 that was consistent with the formula. IR (KBr, cm^{-1}): 2089 (ν(CN)), 943, 873, 830, 732.

$K_{16}[Cu_4(L_3)_2(As_2W_{15}O_{56})_2]$, $Cu_4As_4W_{30}$-L_3 (L_3 = $C_2H_8N_2$). An 8 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_4W_{30}$-Na was mixed with 2 drops of liquid $C_2H_8N_2$, and the solution changed its color from green to violet. The resulting solution was then heated for 0.5 h. A violet precipitate (0.48 g) was isolated from the solution with the addition of 0.1 g of KCl after cooling it to room temperature and dried at 80 °C under vacuum for ca. 0.5 h. Elemental analyses gave a ratio K:Cu:C:N:W = 16.0:3.9:4.1:4.3:30.3 that was consistent with the formula. IR (KBr, cm^{-1}): 1041 (ν(C−N)), 1642 ($\delta(NH_2)$), 939, 878, 812, 721.

$K_{16}[Ni_4(L_3)_2(As_2W_{15}O_{56})_2]$, $Ni_4As_4W_{30}$-L_3. The preparation procedure was the same as that of $Cu_4As_4W_{30}$-L_3 described above except that $Ni_4As_4W_{30}$-Na was used and the product was a yellow powder (0.54 g). Elemental analyses gave a ratio K:Ni:C:N:W = 16.0:3.7:3.9:4.0:30.2 that was consistent with the formula. IR (KBr, cm^{-1}): 1042 (ν(C−N)), 1643 ($\delta(NH_2)$), 938, 872, 822, 725.

$K_{20}[Cu_4(L_4)_2(As_2W_{15}O_{56})_2]$, $Cu_4As_4W_{30}$-L_4 (L_4 = SO_3^{2-}). An 8 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_4W_{30}$-Na was mixed with 1 mL of a hot aqueous solution containing 0.06 g of $Na_2SO_3{\cdot}7H_2O$; the resulting solution was then heated for 0.5 h. A pale-green precipitate (0.49 g) was isolated from the solution with the addition of 0.3 g of KCl after cooling it to room temperature and dried at 80 °C under vacuum for ca. 0.5 h. Elemental analyses gave a ratio K:Cu:S:W = 20.0:3.7:2.0:30.5 that was consistent with the formula. IR (KBr, cm^{-1}): 1120 ($\nu(SO_3^{2-})$), 941, 875, 820, 718.

$K_{20}[Mn_4(L_4)_2(As_2W_{15}O_{56})_2]$, $Mn_4As_4W_{30}$-L_4. The preparation procedure was the same as that of $Cu_4As_4W_{30}$-L_4 described above except that $Mn_4As_4W_{30}$-Na was used and the product was a red powder (0.55 g). Elemental analyses gave a ratio K:Mn:S:W = 20.0:4.1:2.3:29.8 that was consistent with the formula. IR (KBr, cm^{-1}): 1123 ($\nu(SO_3^{2-})$), 943, 873, 818, 719.

$K_{20}[Co_4(L_4)_2(As_2W_{15}O_{56})_2]$, $Co_4As_4W_{30}$-L_4. The preparation procedure was the same as that of $Cu_4As_4W_{30}$-L_4 described above except that $Co_4As_4W_{30}$-Na was used and the product was a purple powder (0.49 g). Elemental analyses gave a ratio K:Co:S:W = 20.0:4.3:1.8:29.7 that was consistent with the formula. IR (KBr, cm^{-1}): 1123 ($\nu(SO_3^{2-})$), 940, 878, 825, 725.

$K_{20}[Ni_4(L_4)_2(As_2W_{15}O_{56})_2]$, $Ni_4As_4W_{30}$-L_4. The preparation procedure was the same as that of $Cu_4As_4W_{30}$-L_4 described above except that $Ni_4As_4W_{30}$-Na was used and the product was a pale-green powder (0.56 g). Elemental analyses gave a ratio K:Ni:S:W = 20.0:3.6:2.0:30.3 that was consistent with the formula. IR (KBr, cm^{-1}): 1125 ($\nu(SO_3^{2-})$), 943, 870, 828, 728.

$K_{18}[Mn_4(L_5)_2(As_2W_{15}O_{56})_2]$, $Mn_4As_4W_{30}$-L_5 (L_5 = SCN^-). An 8 mL volume of a hot aqueous solution containing 1.0 g of $Mn_4As_4W_{30}$-Na was mixed with 1 mL of a hot aqueous solution containing 0.03 g of KSCN; the resulting solution was then heated for 0.5 h. A yellowish precipitate (0.55 g) was isolated from the solution with the addition of 0.1 g of KCl after cooling it to room temperature and dried at 80 °C under vacuum for ca. 0.5 h. Elemental analyses gave a ratio K:Mn:S:W = 18.0:3.8:1.9:29.7 that was consistent with the formula. IR (KBr, cm^{-1}): 2076 ($\nu(SCN^-)$), 942, 869, 823, 722.

$K_{18}[Co_4(L_5)_2(As_2W_{15}O_{56})_2]$, $Co_4As_4W_{30}$-L_5. The preparation procedure was the same as that of $Mn_4As_4W_{30}$-L_5 described above except that $Co_4As_4W_{30}$-Na was used and the product was a white powder (0.42 g). Elemental analyses gave a ratio K:Co:S:W = 18.0:4.2:2.3:29.7 that was consistent with the formula. IR (KBr, cm^{-1}): 2077 ($\nu(SCN^-)$), 940, 869, 820, 722.

$K_{18}[Ni_4(L_5)_2(As_2W_{15}O_{56})_2]$, $Ni_4As_4W_{30}$-L_5. The preparation procedure was the same as that of $Mn_4As_4W_{30}$-L_5 described above except that $Ni_4As_4W_{30}$-Na was used and the product was a white powder (0.51 g). Elemental analyses gave a ratio K:Ni:S:W = 18.0:3.9:1.7:30.2 that was consistent with the formula. IR (KBr, cm^{-1}): 2078 ($\nu(SCN^-)$), 939, 868, 829, 718.

Crystallographic Morphologies of $M_4As_4W_{30}$. The solid obtained from the phase transfer described earlier was dissolved in anhydrous benzene. The sample crystallized from the benzene solution was put between glass plates that had been washed with concentrated nitric acid, deionized water, and acetone, respectively. The morphologies were observed under a polarizing microscope.[40]

X-ray Crystallography. A hexagonal green crystal of **1** with approximate dimensions of 0.52 mm × 0.42 mm × 0.38 mm was mounted on a glass fiber capillary which was put on a Siemens P4 four-circle diffractometer equipped with graphite monochromatic Mo Kα radiation (λ = 0.710 73 Å). A total of 20 958 (17 317 independent, R_{int} = 0.0545) reflections were collected at 293 K in the range 1.58 < θ < 21.09° using an ω-scan mode at variable speeds (5−30°/min). The reflection statistics indicated that the crystal lattice was centrosymmetric. A semiempirical absorption correction from ψ-scans was applied. The structure was solved by direct methods (SHELXTL-93)[41] and refined by the full-matrix least-squares method on F^2. Anisotropic temperature factors were applied to all atoms (W, Cu, As, O) in **1**, and isotropic temperature factors were applied to the sodium cations and water molecules of crystallization. Disorder due to thermal motion was observed in some of the sodium cations and water molecules. Structure solution and refinement based on 15 816 reflections with $I > 2\sigma(I)$ and on 1196 parameters gave R1 (wR2) = 0.0966 (0.2306) {$R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$}. Crystal data, details of the intensity measurements, and data processing parameters are summarized in Table 1.

Results and Discussion

Syntheses. Tetrameric sandwich-type polyoxoanions of **1**−**6** formulated $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ were prepared in high yields and in high purity. In this procedure, several important factors were noted: (i) $Na_2WO_4 \cdot 2H_2O$ was mixed with arsenic acid, and the mixture was refluxed. Then NH_4Cl was added in two steps. The precipitate obtained from the first addition of NH_4Cl was a β-isomer, while the precipitate isolated from the second addition of NH_4Cl to the filtrate was an α-isomer. KCl was added to the α-isomer solution which was left to grow X-ray-quality crystals of α-$K_6As_2W_{18}O_{62}$. The pH value of the solution was controlled at 9 for 1 h during degradation. α-$Na_{12}As_2W_{15}O_{56}$ with a high yield was obtained. (ii) All of the transition metal salts used were chlorides. (iii) The molecular ratio of M to α-$Na_{12}As_2W_{15}O_{56}$ is 1.5:1. (iv) Reasonable pH value and temperature were applied to avoid the formation of insoluble intermediates.

Table 1. Crystallographic Data for $Na_{16}[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2] \cdot 47H_2O$ (**1**)

formula	$H_{98}As_4Cu_4Na_{16}O_{161}W_{30}$	fw	9111.96
a, Å	12.721(3)	space group	$P\bar{1}$
b, Å	24.516(5)	T, K	293(2)
c, Å	26.450(5)	λ, Å	0.710 73 (Mo Kα)
α, deg	89.90(3)	ρ_{calc}, Mg/m^3	3.760
β, deg	77.32(3)	μ, cm^{-1}	228.33
γ, deg	89.96(3)	R_1 [$I > 2\sigma(I)$]^a	0.0966
V, Å^3	8048(3)	wR_2^{a}	0.2306
Z	2		

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

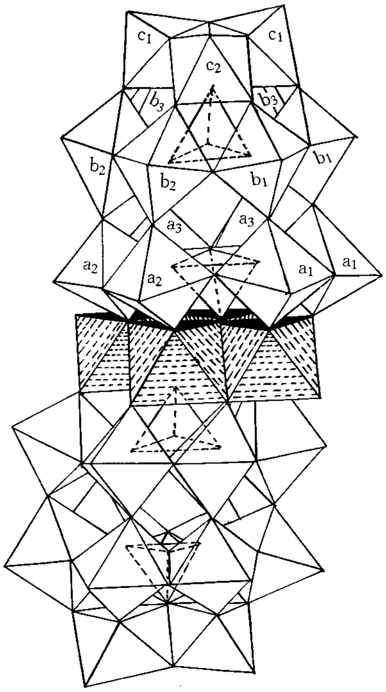

Figure 1. Polyhedral representation of **1**.

Crystal Structure of $Na_{16}[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2] \cdot 47H_2O$ (1). The crystal structure of **1** is shown in Figures 1−4. Figure 1 shows the structure in polyhedral notation, Figure 2 gives an ORTEP drawing of the asymmetric unit in **1**, Figure 3 illustrates a ball-and-stick representation of the central $Cu_4O_{14}(H_2O)_2$ unit, and Figure 4 exhibits a general view of the $[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ anion. Table 2 provides key distances and angles.

The $[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ anion has the general structure proposed earlier for the $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{n-}$ series and confirmed by Weakley,[21] Finke,[19] Gomez-Garcia,[23a] Hill,[24b] and co-workers for the Cu^{II}, Zn^{II}, Mn^{II}, Ni^{II}, and Fe^{III} derivatives (see Figures 2 and 4): two α-$As_2W_{15}O_{56}^{12-}$ units each share seven oxygen atoms, including an oxygen atom on As(2), with a central set of four edge-sharing CuO_6 octahedra.

---

[40] Zhou, Q. F.; Wang, X. J. *Liquid Crystals Superpolymer*; Science Press: Beijing, 1994.

[41] *SHELXTL PC*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

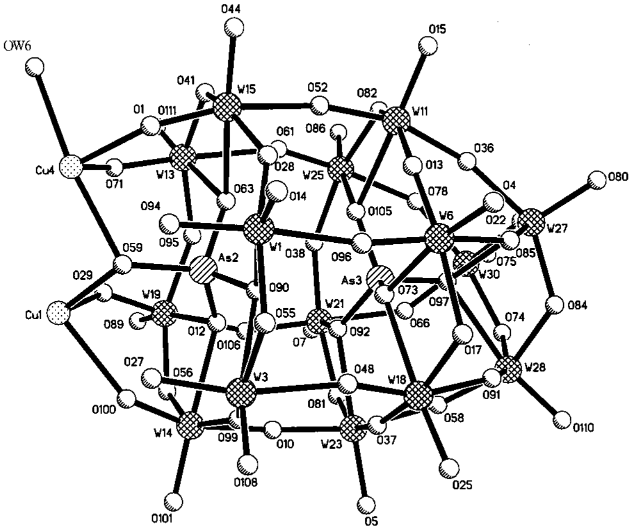

Figure 2. ORTEP drawing of the asymmetric unit of **1**.

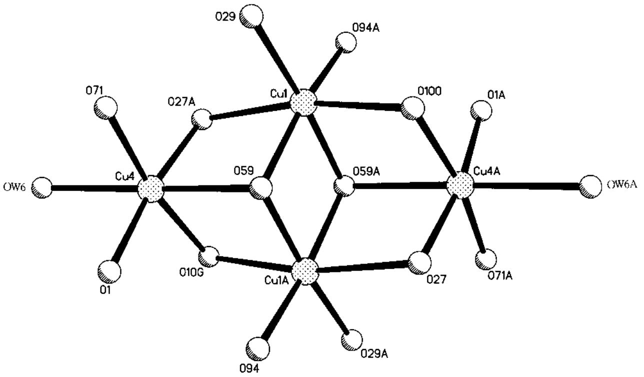

Figure 3. Structure of the central tetrameric unit $Cu_4(H_2O)_2O_{14}$ in **1**.

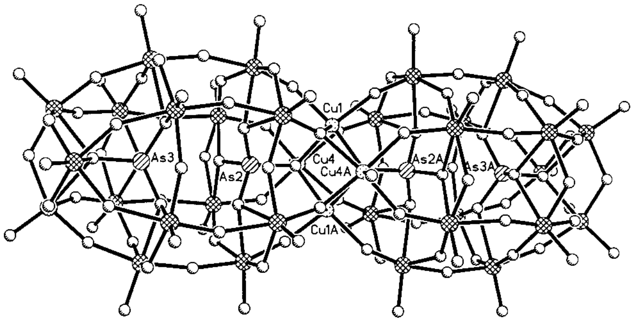

Figure 4. General view of **1**.

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

W(1)−O(14)	1.71(4)	Cu(1)−O(59A)	1.98(4)
W(1)−O(94)	1.77(5)	Cu(1)−O(29)	2.02(4)
W(1)−O(55)	1.89(5)	Cu(1)−O(100)	2.31(3)
W(1)−O(28)	1.90(4)	Cu(1)−O(94A)	1.92(5)
W(1)−O(96)	2.02(4)	Cu(1)−O(59)	1.98(3)
W(1)−O(90)	2.27(4)	Cu(1)−O(27A)	2.38(5)
W(2)−O(40)	1.72(4)	Cu(4)−O(1)	1.94(3)
W(2)−O(67)	1.89(4)	Cu(4)−OW6	2.30(5)
W(2)−O(62)	2.04(3)	Cu(4)−O(71)	1.93(4)
W(2)−O(88)	1.84(4)	Cu(4)−O(100)#3	2.01(3)
W(2)−O(109)	1.95(4)	Cu(4)−O(59)	2.35(4)
W(2)−O(50)	2.24(5)	Cu(1)···(19)	3.52(3)
As(1)−O(50)	1.71(4)	As(2)···Cu(1)	3.268
As(1)−O(46)	1.72(4)	As(2)···Cu(4)	3.536
As(1)−O(8)	1.69(3)	As(2)···Cu(1A)	3.233
As(1)−O(49)	1.72(4)	Cu(4)···Cu(1A)	3.180
Cu(1)···Cu(4)	3.196	Cu(1)···Cu(1A)	3.080
Cu(4)···Cu(4A)	5.582	Cu(4)−O(27)#3	1.94(5)
W(1)···W(6)	3.809	Cu(1)···W(14)	3.781
W(1)···W(3)	3.358	Cu(4)···W(15)	3.525
W(1)···W(15)	3.672	Cu(4)···W(13)	3.526
W(3)···W(14)	3.649	Cu(1A)···W(1)	3.501
W(3)···W(18)	3.807	Cu(4A)···W(3)	3.446

O(75)−W(30)−O(78)	101(3)	O(59)−As(2)−O(63)	109(2)
O(75)−W(30)−O(97)	171(2)	Cu(1)···Cu(4)···Cu(1A)	57.8
O(7)−W(21)−O(106)	97(2)	Cu(4)···Cu(1)···Cu(4A)	122.2
O(7)−W(21)−O(92)	168(2)	Cu(4)···Cu(1)···Cu(1A)	60.9
O(97)−As(3)−O(92)	107(2)	W(27)···W(28)···W(30)	60.2
Cu(4A)···Cu(1)···Cu(1A)	61.4	W(27)···W(30)···W(28)	59.6
Cu(4)···As(2)···Cu(1A)	55.8	W(28)···W(27)···W(30)	59.6
W(27)···As(3)···W(28)	57.2	W(15)···As(2)···W(1)	63.5
W(28)···As(3)···W(30)	57.1	W(13)···As(2)···W(15)	56.5

The polyanion **1** has C_{2h} symmetry and approximate axial [As(3)···As(2) direction] and equatorial dimensions of 20.737 and 10.411 Å, respectively. The four Cu atoms lie in the same plane and form a regular rhomblike cluster with sides of 3.196 and 3.180 Å, a short and long diagonal of 3.080 and 5.582 Å, and angles between Cu atoms of 57.8 and 122.2° (Figure 3). Each of the seven vertices on both faces of the rhombus, which are all occupied by oxo groups, is corner-shared with two α-$[As_2W_{15}O_{56}]^{12-}$ units, leaving the remaining one vertex on each side of the inversion center located at the midpoint of the Cu4···Cu4A vector occupied by water molecules (OW6 and OW6A) with a bond (Cu4−OW6) distance of 2.30 Å. The water molecules coordinated to the Cu atoms can be replaced by other ligands described in the Experimental Section.

The α-$As_2W_{15}O_{56}^{12-}$ ligand, originally regarded as $As_2W_{16}O_{59}^{12-}$, results from degradation of α-$As_2W_{18}O_{62}^{6-}$ in an aqueous solution at pH 9.[38] The structure of noncoordinated $As_2W_{15}O_{56}^{12-}$ has not yet been determined but is unlikely to differ in connectivity from the structure adopted in the present complex and previously deduced from the ^{183}W NMR spectrum of the derivative $As_2W_{15}Mo_3O_{62}^{6-}$: namely, the Dawson (α-$As_2W_{18}O_{62}^{6-}$) structure with one end cap of three edge-sharing WO_6 octahedra missing.

The noncoordinated α-$As_2W_{15}O_{56}^{12-}$ ligand is presumed to have 3-fold symmetry, which is lost when it is bonded to Cu. The symmetry loss is implied by the following two points:

(i) The first is the deviations of the belt of six W atoms nearest the Cu atoms from their mean plane. The atoms furthest from, and related by, the approximate mirror plane of the whole anion are displaced toward the Cu atoms [W(1) and W(19), 0.0274 and 0.0270 Å]; the other atoms are displaced away from the Cu atoms [W(3), W(13), W(14), and W(15), 0.0089−0.0176 Å]. Similar displacements occur for the atoms corresponding to W(1, 19) in the other W_6 belt [W(6) and W(21), 0.0245 and 0.027 Å toward the Cu atoms]. The other atoms are displaced away from the Cu atoms [W(11), W(18), W(23), and W(25), 0.007−0.0159 Å]. The distortion of the heavy-atom framework in the anion may serve to accommodate the steric requirements of the Cu atoms.

(ii) The ligand $As_2W_{15}O_{56}^{12-}$ is capped by three of the central CuO_6 groups, which share a vertex of the AsO_4 tetrahedron [As(2)]. The Cu atoms, however, are asymmetrically placed with respect to the normal through As to the Cu_4 plane; this may be seen from the As(2)−Cu(1,4,1A) distances (3.268, 3.536, and 3.233 Å), the longest one of which involves the Cu atom on the local mirror plane of the anion. The Jahn−Teller distortion of the CuO_6 groups is predicted and is accommodated by the tungstoarsenate ligand. Each CuO_6 octahedron exhibits marked axial distances (2.31−2.39 Å, mean value 2.35 Å) which are significantly longer than the equatorial ones (1.89−2.02 Å, mean value 1.95 Å).

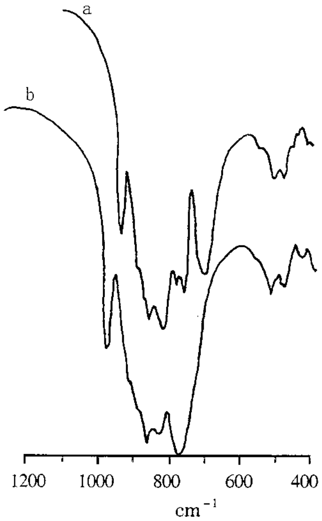

Figure 5. Infrared spectra of $Na_{12}As_2W_{15}O_{56}$ (a) and $K_6As_2W_{18}O_{62}$ (b).

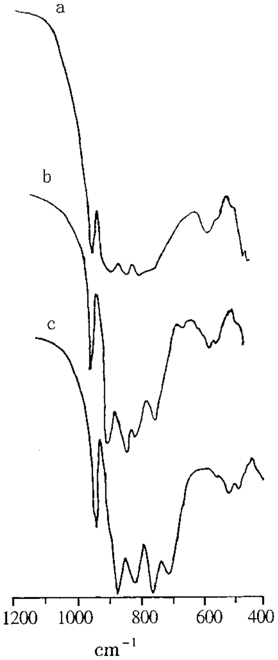

Figure 6. Infrared spectra of $Cu_4As_4W_{30}$-Na (a), $Zn_4As_4W_{30}$-Na (b), and $Mn_4As_4W_{30}$-Na (c) (2% sample, in KBr pellets).

Additionally, we can also note that in the compound both As atoms of the trivacant polyoxotungstate are significantly displaced, in the same sense, from the mean plane of their corresponding W belts: As(3) is displaced 0.0945 Å away from the Cu_4O_{16} cluster, whereas As(2) is displaced 0.1043 Å toward the Cu_4O_{16} cluster. The small difference in the displacement of the As(3) atom is expected since the As(3) atom is very far from the central cluster.

The central Cu atoms, the cap W atoms [W (27), W(28), W(30)], and the two sets of belt W atoms [W(6), W(11), W(18), W(21), W(23), W(25) and W(1), W(3), W(13), W(14), W(15), W(19)] form four least-squares planes with a maximum deviation of 0.0274 Å. They are parallel to each other with a maximum dihedral angle of 0.8°. In comparison, the four least-squares planes in α-$[As_2W_{18}O_{62}]^{6-}$ (two planes each composed of three cap W atoms and two planes each composed of six belt W atoms) have a maximum deviation of 0.041 Å and a maximum dihedral angle of 0.4°.[22−24]

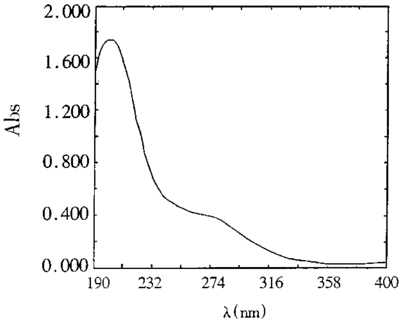

Figure 7. UV spectra of $Cu_4As_4W_{30}$-Na.

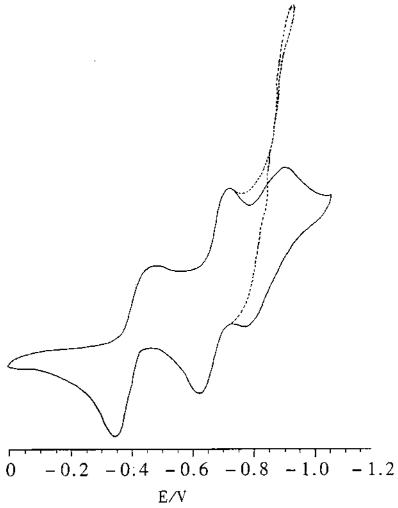

Figure 8. Cyclic voltammogram of 1 mM $Zn_4As_4W_{30}$-Na before (—) and after (···) the addition of 10 mM NO_2^- (pH = 4.0, scan rate = 50 mV·s^{-1}).

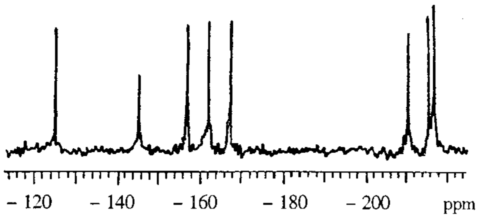

Figure 9. ^{183}W NMR spectra of $Cu_4As_4W_{30}$-Na.

Noteworthily, all the trans-directed bonds along the cluster axial direction, Cu−O−W_{belt}−O−W_{belt}−O−W_{cap}, have pronounced bond length alternations (average distances 2.09, 1.79, 2.04, 1.84, 1.98, and 1.88 Å). This observation confirms that the deviations are produced by the change in the valence sums when replacing three W^{VI} atoms of one cap by three Cu^{II}, as suggested by Weakley and Finke.[21]

The above mentioned structural features are more similar to those for $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ than to those for $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{n-}$ (M = Zn^{II}, Mn^{II}, Fe^{III}). However some differences are also apparent: (i) The $Cu_4O_{14}(H_2O)_2$ unit in **1** shows smaller Jahn−Teller distortion than that in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ (the axial distances 2.31−2.61 Å and mean value 2.45 Å; the equatorial distances 1.89−2.08 Å and mean value 1.95 Å). (ii) The average As(2)−Cu distance in **1** is 3.346 Å, which is longer than the average P(2)−Cu distance in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ (3.273 Å). (iii) The As(2) atom is displaced only 0.1043 Å from the Cu_4O_{16} plane, and the As(3) atom is displaced 0.0945 Å toward the Cu_4O_{16} unit in **1**. In comparison, the P(2) atom is displaced 0.194 Å and P(1) atom is displaced 0.186 Å in the $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ anion.

Table 3. CV Data for $M_4As_4W_{30}$-Na Compounds (V)[a]

heteropolyanions	E_{pa}	E_{pc}	ΔE_p (mV)	heteropolyanions	E_{pa}	E_{pc}	ΔE_p (mV)
α-$As_2W_{18}O_{62}^{6-}$	0.122	0.056	66	$Co_4As_4W_{30}$	−0.310	−0.387	77
	−0.06	−0.123	63		−0.464	−0.602	138
	−0.432	−0.505	73		−0.680	−0.800	120
	−0.669	−0.790	121	$Zn_4As_4W_{30}$	−0.349	−0.480	131
α-$As_2W_{15}O_{56}^{12-}$	−0.317	−0.440	123		−0.626	−0.716	90
	−0.575	−0.705	130		−0.772	−0.901	129
$Cu_4As_4W_{30}$	−0.296	−0.352	56	$Cd_4As_4W_{30}$	−0.313	−0.414	101
	−0.348	−0.417	69		−0.517	−0.583	66
	−0.580	−0.640	60		−0.631	−0.738	107
$Mn_4As_4W_{30}$	−0.300	−0.391	91				
	−0.482	−0.551	69				
	−0.574	−0.714	140				

[a] E_{pa}, oxidation potential; E_{pc}, reduction potential; ΔE_p, the difference between the pair of redox potentials. Condition: pH 4.0 of a buffer solution of HAc−NaAc; 25 °C; glassy carbon working electrode; scan rate 50 mV·s^{-1}; potentials recorded vs Ag/AgCl.

Table 4. Colors and States of the Products Isolated from the Replacement Reactions in Aqueous Solutions[a]

heteropolyanions	ligands				
	$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$C_2H_8N_2$	SO_3^{2-}	SCN^-
$Cu_4As_4W_{30}$	yellow ↓ (brown-yellow)	dark-red ↓ (red-green) ↓	violet ↓ (blue)	pale-green ↓ (yellow ↓)	no reacn (dark ↓)
$Mn_4As_4W_{30}$	yellow ↓ (brown)	yellow-green ↓ (white ↓)	no reacn (yellowish ↓)	red ↓ (no reacn)	yellowish (no reacn)
$Co_4As_4W_{30}$	purple ↓ (dark-red)	dark-green ↓ (green ↓)	no reacn (brown)	purple ↓ (no reacn)	white ↓ (blue)
$Ni_4As_4W_{30}$	yellow-green ↓ (yellow ↓)	yellow ↓ (greenish) ↓	yellow ↓ (blue)	pale-green ↓ (blue ↓)	white ↓ (no reacn)

[a] The colors and states of the products isolated from aqueous solutions, in which only corresponding simple transition metal ions and ligands present, are shown in parentheses.

Table 5. Electronic Spectral Data for the Products Isolated from the Replacement Reactions of the Coordinated Water Molecules in Aqueous Solutions [cm^{-1} (ϵ, M^{-1}·cm^{-1})][a]

heteropoly-anions	ligands			
	$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$C_2H_8N_2$	H_2O
$Cu_4As_4W_{30}$	20 877 (93)	11 933 (98)	17 668 (89)	11 765 (103)
$Mn_4As_4W_{30}$	11 891 (18)	17 301 (38), 12 563 (20)		11 862 (19)
$Co_4As_4W_{30}$	23 641 (15), 16 750 (146)	20 408 (18), 19 231 (32), 17 241 (143)		18 939 (178), 18 282 (176), 17 953 (176)
$Ni_4As_4W_{30}$	17 483 (23), 14 948 (55)	13 459 (62)	21 053 (28), 14 225 (52)	14 388 (38)

[a] Electronic spectra determined for the K$^+$ salt; extinction parameters in parentheses.

Table 6. Colors and Crystallographic Morphologies of $M_4As_4W_{30}$ in Aqueous Solutions (Na Salt) and in Benzene (tHA Salt)

heteropoly anions	aqueous solution		benzene	
	colors	types	colors	types
$Cu_4As_4W_{30}$	green	hexagonal	yellow-green	spherical
$Mn_4As_4W_{30}$	orange	needle	red	needle
$Co_4As_4W_{30}$	green-brown	flakelet	purple	filiform
$Ni_4As_4W_{30}$	pale-green	oil	yellow	fringe
$Zn_4As_4W_{30}$	white	cubic	white	microspherical
$Cd_4As_4W_{30}$	white	powder	pale-yellow	branch

Obviously, the displacement of As atoms is smaller than that of P atoms. (iv) Among the six belt W atoms near the central Cu_4O_{16} group, two W atoms move 0.027−0.0274 Å toward the Cu_4O_{16} plane and four W atoms move 0.0089−0.0176 Å away from it. The deviations of the mean plane of the six belt W atoms are less than those in the $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ series where the corresponding data are 0.034−0.047 and 0.005−0.034 Å, respectively. (v) The four Cu atoms lie in the same plane and form a rhombic cluster with sides of 3.196 and 3.180 Å and a shortest diagonal of 3.305 Å in **1** whereas, with sides of 3.05 and 3.19 Å, a shortest diagonal of 3.22 Å in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$. These differences are due to the larger atomic radius of As (0.335 Å) compared with that of P (0.17 Å).

Physical Properties. IR Spectra. IR spectra for $M_4As_4W_{30}$ compared with those of $As_2W_{18}O_{62}^{6-}$ and $As_2W_{15}O_{56}^{12-}$ are shown in Figures 5 and 6.

The following points can be drawn from the IR spectra: (i) All of the characteristic vibrational frequencies decrease compared with those of $As_2W_{18}O_{62}^{6-}$, which is attributed to the increase of the negative charges of the anions.[38] (ii) The asymmetry stretching vibration of W−O$_c$−W in $As_2W_{18}O_{62}^{6-}$ is split into 3 peaks when the anion degrade into a trivacant-anion $As_2W_{15}O_{56}^{12-}$, but it is split into 2 peaks when the corresponding sandwich species are formed. (iii) The vibrational frequency of As−O bonds overlaps that of W−O$_b$ bonds. (iv) The IR spectra for the $M_4As_4W_{30}$ series are similar to each other.

UV Spectra. All of the UV spectra of the $M_4As_4W_{30}$ series have two absorption bands. The lower energy band at ca. 50 000 cm^{-1} is attributed to the charge transfer of O$_d$ → W, and the higher energy band at ca. 37 000 cm^{-1} is attributed to that of (O$_c$/O$_b$) → W, indicating their similar electronic structures.[42,43] The UV spectrum of **1**, as an example, is shown in Figure 7.

---

(42) Evans, H. T.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1975**, 505−508.

(43) Bi, L. H.; Peng, J.; Chen, Y. G.; Qu, L. Y. *Polyhedron* **1994**, *13*, 2421−2424.

Table 7. Electronic Spectral Data for $M_4As_4W_{30}$ Containing 0.1 M (tHA)Br in Benzene [cm^{-1} (ϵ, $M^{-1}\cdot cm^{-1}$)]^a

	$Cu_4As_4W_{30}$	$Ni_4As_4W_{30}$	$Co_4As_4W_{30}$
H_2O	11 765 (103)	14 388 (38)	18 939 (178), 18 282 (176), 17 953 (176)
	13 003 (88)	14 065 (22)	18 315 (168), 17 007 (182)
pyridine	11 876 (100)	14 948 (29)	20 408 (151), 19 305 (148), 18 450 (146)
lactic acid	12 346 (107)	14 493 (32)	20 790 (160), 19 608 (158), 17 637 (161)
acetone	12 821 (97)	14 903 (35)	19 231 (170), 18 518 (154)
acetonitrile	12 019 (93)	14 225 (29)	20 833 (141), 20 576 (142), 19 305 (145)
chloroform	11 990 (96)	14 451 (33)	19 194 (153), 18 282 (150), 17 036 (148)
phenol	12 077 (108)	14 706 (39)	20 408 (168), 18 382 (162), 17 361 (156)

^{a} Extinction parameter in parentheses.

CV. The CV of $M_4As_4W_{40}$ was determined in an HAc−NaAc buffer solution (pH = 4.0), and the data are listed in Table 3. From Table 3 it can be seen that the redox reaction of $M_4As_4W_{30}$ is three-step pseudoreversible. In comparison, the α-$As_2W_{18}O_{62}^{6-}$ anion is reduced in four steps.[38,44−46] The first three steps of the reduction of $W^{VI} \rightarrow W^{V}$ are reversible, while the fourth step is pseudoreversible. When the trivacant anion α-$As_2W_{15}O_{56}^{12-}$ is formed, four-step reductions become two-step reductions and all of them are pseudoreversible.[38]

Electrocatalytic Reduction of NO_2^-. The electrochemical behavior of $Zn_4As_4W_{30}$ and its electrocatalytic reduction for nitrite in an aqueous solution have also been studied. When scan rates are changed, the reduction peak currents are approximately proportional to the square root of the scan rate up to 500 $mV\cdot s^{-1}$, which indicates that the electrode reaction of $Zn_4As_4W_{30}$ is diffusion-controlled.[47−49] The direct electroreduction of NO_2^- requires a large overpotential.[50−52] Three well-defined redox couples can be observed in solutions of pH 4.0 (Figure 8). By addition of NO_2^-, the cathodic current of the third wave of $Zn_4As_4W_{30}$ is enhanced remarkably, while the corresponding anodic current nearly disappears. The result indicates that the $Zn_4As_4W_{30}$ anion has a good electrocatalytic activity for the NO_2^- reduction.[53−56]

^{183}W NMR. Figure 9 shows the ^{183}W NMR spectrum of **1** in D_2O. The structure of **1** is also confirmed by its ^{183}W NMR spectrum. Eight ^{183}W NMR resonances at −125.6, −146.1, −157.5, −162.4, −167.7, −210.8, −216.1, and −217.0 ppm were observed at room temperature (referenced to Na_2WO_4). Therefore, eight ^{183}W resonances and the dimeric molecular formula require a C_{2h} symmetry dimer structure as shown in Figure 1 with the eight types of tungsten atoms labeled with a_1, a_2, a_3, b_1, b_2, b_3, c_1, and c_2.[19]

TG-DSC. TG-DSC data show weight loss at 620 °C corresponding to the release of two coordinated water molecules from the $[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ anion.

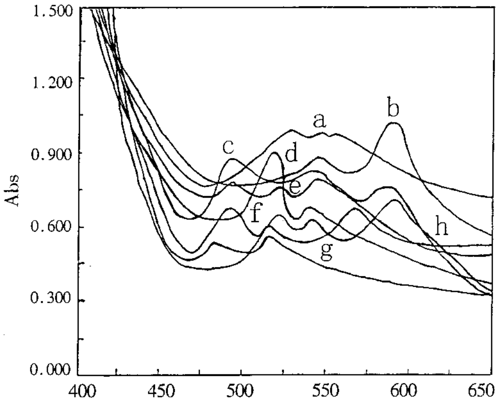

Figure 10. Electronic spectra of $Co_4As_4W_{30}$ in an aqueous solution (a) and in benzene (b), $Co_4As_4W_{30}$−phenol in benzene (c), $Co_4As_4W_{30}$−acetone in benzene (d), $Co_4As_4W_{30}$−lactic acid in benzene (e), $Co_4As_4W_{30}$−pyridine in benzene (f), $Co_4As_4W_{30}$−acetonitrile in benzene (g), and $Co_4As_4W_{30}$−chloroform in benzene (h).

Replacement Reaction of the Coordinated Water Molecules by Other Ligands in an Aqueous Solution. The experimental results show that, even in an aqueous solution, many ligands can replace the coordinated water molecules in the anions. When the replacement reactions take place, the colors, states, and electronic spectra change noticeably. The colors and states of the products isolated from the replacement reactions in aqueous solutions compared with the colors and states of the products isolated from aqueous solutions in which only corresponding simple transition metal ions and ligands present are listed in Table 4. In most cases, the two types of products differ in their colors. Table 5 gives the data of electronic spectra of the replacement reaction systems.

In the IR spectra of the products isolated from the replacement reactions, in addition to the characteristic vibrational peaks of the heteropolyanions, ν(CN) and ν(SCN) at ca. 2100 cm^{-1} for $M_4As_4W_{30}$-$L_{1,\,2}$ and for $M_4As_4W_{30}$-L_5, ν(C−N) at ca. 1040 cm^{-1} and $\delta(NH_2)$ at ca. 1640 cm^{-1} for $M_4As_4W_{30}$-L_3 and $\nu(SO_3^{2-})$ at ca. 1120 cm^{-1} for $M_4As_4W_{30}$-L_4 were observed, indicating that the ligands had indeed participated in the replacement reactions.[1,16]

Phase Transfer and the Loss of the Coordinated Water Molecules. Aqueous solutions of the heteropolyanions containing transition metals usually display specific colors. After a phase transfer followed by the loss of the coordinated water molecules, the color of the solution changes to some extent.[2,4,5] Table 6 lists the colors of the solutions before and after the loss of the coordinated water molecules.

Table 7 and Figure 10 present the electronic spectral data. The electronic spectral data prove that the coordinated water molecules of the heteropolyanions were lost upon phase transfer, as either the position or the intensity of the peaks was noticeably changed after undergoing a phase transfer process. In most cases, addition of a selected organic ligand, such as pyridine, lactic

---

(44) Pope, M. T.; Constantinous, E. P. *Inorg. Chem.* **1967**, *6*, 1147−1152.
(45) Preyssler, C. *Bull. Soc. Chim. Fr.* **1970**, 137−138.
(46) Bourret, P.; Lecuire, J. M.; Gissinger, *J. M. Electrochim. Acta* **1972**, *17*, 2353−2361.
(47) Toth, J. E.; Anson, F. C. *J. Electroanal. Chem.* **1988**, *256*, 361−370.
(48) Southampton Electrochemistry Group. *Instrumental Methods in Electrochemistry*; Ellis Harwood Limited: Chichester, U.K., 1985.
(49) Cheng, L.; Zhang, X, M.; Xi, X. D.; Dong, S. J. *J. Electroanal. Chem.* **1996**, *407*, 97−103.
(50) Dong, S. J.; Xi, X. D.; Tian, M. J. *Electroanal. Chem.* **1995**, *385*, 227−231.
(51) Keita, B.; Nadjo, L. *J. Electroanal. Chem.* **1987**, *227*, 77−98.
(52) Keita, B.; Belhouari, A.; Nadjo, L.; Contant, R. *J. Electroanal. Chem.* **1988**, *247*, 157−172.
(53) Dong, S.; Jin, Z. *J. Chem. Soc., Chem. Commun.* **1987**, 1871−1872.
(54) Xi, X. D.; Wang, G.; Liu, B. F.; Dong, S. *J. Electrochim. Acta* **1995**, *40*, 1025−1029.
(55) Toth, J. E.; Anson, F. C. *J. Am. Chem. Soc.* **1989**, *111*, 2444−2451.
(56) (a) Xi, X. D.; Lin, S. Q.; Wang, E. B.; Dong, S. J. *Chin. J. Anal. Chem.* **1998**, *26*, 719−723. (b) Keit, B.; Belhouari, A.; Nadjo, L.; Contant, R. *J. Electroanal. Chem.* **1995**, *381*, 243−245.

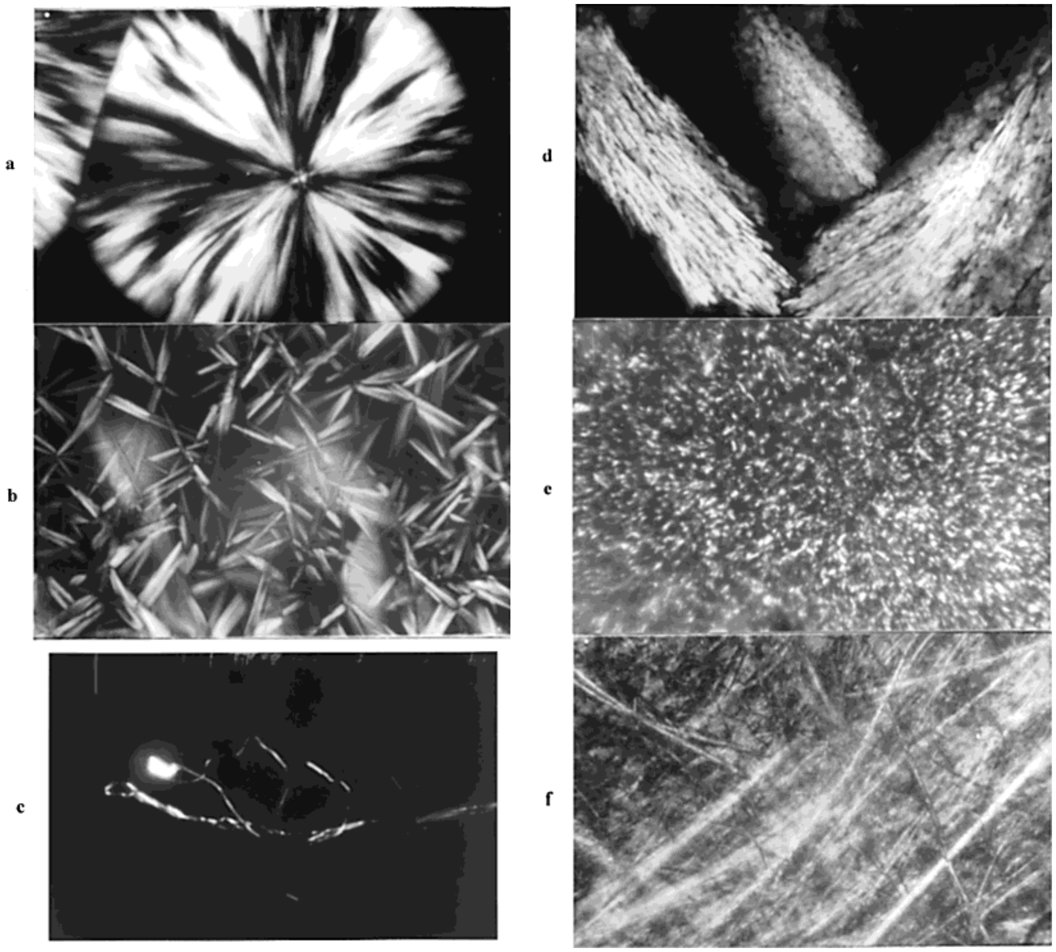

Figure 11. Crystallographic morphologies of $M_4As_4W_{30}$ isolated from benzene solutions: $Cu_4As_4W_{30}$ (a); $Mn_4As_4W_{30}$ (b); $Co_4As_4W_{30}$ (c); $Ni_4As_4W_{30}$ (d); $Zn_4As_4W_{30}$ (e); $Cd_4As_4W_{30}$ (f).

acid, acetone, acetonitrile, chloroform, or phenol, to the dehydrated benzene solution restored the original spectrum. We therefore deduce that the spectral changes are due to the loss of the coordinated water molecules and the replacement by such organic ligands.[2,4−16]

In the IR spectra of the sample of $Cu_4As_4W_{30}$ with pyridine or lactic acid, isolated from benzene, ν(N═C) at ca. 1650 cm^{-1} or ν(C═O) at ca. 1780 cm^{-1} appeared respectively in addition to the characteristic vibration peaks of the $Cu_4As_4W_{30}$ anion, indicating that the replacement reaction of the coordinated water molecules by pyridine or lactic acid indeed took place.

Crystallographic Morphologies of the Heteropoly Compounds. The crystallographic morphologies of the phase transfer products described in the Experimental Section were summarized in Table 6 and shown in Figure 11. Their different morphologies are probably due to the presence of different transition metal ions in the anions. We expect this observation be useful to identify isostructural polyoxometalates.

Conclusions

The main points of the conclusions are as follows: (1) Six new compounds in the series of $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ ($M = Cu^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}$) were synthesized for the first time and characterized by all available physical methods. (2) X-ray single-crystal analysis confirms the structure of the $[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ anion and shows that the structure closely resembles that of the related $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ anion. The $Cu_4O_{14}(H_2O)_2$ unit in **1** shows a smaller Jahn−Teller distortion than that in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$. The deviations of the As and W atoms from their mean plane are smaller in **1** than in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$. These differences are due to the fact that the atomic radius of As is larger than the atomic radius of P. (3) In organic solvents, and even in aqueous solutions, selected ligands can replace the coordinated water to form characteristic-color anions. (4) Crystallographic morphologies, formed from a benzene solution and observed under a polarizing microscope, of $M_4As_4W_{30}$ containing tetra-*n*-heptylammonium bromide ((tHA)Br) were different, probably depending on the presence of different transition metal ions. We expect to identify isostructural polyoxometalates by this method. However, further structural studies are needed, namely, the crystal structures of the $As_2W_{15}O_{56}^{12-}$ anion itself and the $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ anion (e.g. $M = Zn^{II}, Mn^{II}$) in which no distortion is expected for the M_4O_{16} groups.

Acknowledgment. The support of National Natural Science Foundation of China (Grant 29771006) is gratefully acknowledged.

Supporting Information Available: Listings of crystallographic data, atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, and bond lengths and angles, structure drawings with fully labeled atomic numbering, packing diagrams, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990596V