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Rational syntheses, characterization, crystal structure, and replacement reactions of coordinated water molecules of $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ (M = Cd, Co, Cu, Fe, Mn, Ni or Zn)†

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Rational, high-yield, and isomerically pure syntheses of $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ (M = Cd, Co, Cu, Fe, Mn, Ni or Zn) have been achieved. The products were well characterized by means of IR, UV-vis, CV, ^{183}W NMR, TG-DSC, and elemental analyses. The properties have been studied. The results allow a number of conclusions to be drawn. (i) The B-type tri(tungsten)vacant form of B-$[AsW_9O_{34}]^{9-}$ is a key structural requirement for formation of the dimetal(2+)-substituted dimers $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$. (ii) The structures of the compounds $K_{10}[Mn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 18H_2O$ and $K_8Na_2[Cu_4(H_2O)_2(AsW_9O_{34})_2]\cdot 32H_2O$ have been solved, and are similar to that of the zinc derivative, comprising a rhomb-like M_4O_{16} group encapsulated between two fragments of the trivacant Keggin polyanion $[AsW_9O_{34}]^{9-}$. (iii) The crystal structures of the arsenic series have been compared with those of the phosphorus-series. Jahn–Teller distortions of the CuO_6 groups and the absence of Jahn–Teller distortions in the MO_6 octahedra for M = Mn and Zn are predicted. (iv) Two water molecules are coordinated to two metal atoms. $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, SO_3^{2-}, SCN^-, *etc.* can replace the coordinated water giving characteristic colors in aqueous solutions, while in organic solvents the coordinated water molecules are lost, leaving unshared coordination positions that can be occupied by organic ligands such as pyridine, lactic acid, and acetone to restore the octahedral coordination of M^{II}. (v) The crystal morphologies of $[Co_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ anion are dependent on different organic ligands, which substitute the two coordinated waters after phase transfer.

Introduction

Heteropoly tungstoarsenates containing transition metals have revealed several series of compounds after 40 years' research, for example the series 1:11 $[AsW_{11}M(H_2O)O_{39}]^{n-}$,[1,2] 2:17 $[As_2W_{17}M(H_2O)O_{61}]^{n-}$,[3,4] 2:19 $[As_2W_{19}M_2(H_2O)_2O_{67}]^{n-}$,[5] 2:20 $[As_2W_{20}M(H_2O)_2O_{68}]^{n-}$,[6] 2:22 $[As_2W_{22}LnO_{78}]^{n-}$,[7] 4:34 $[As_4W_{34}LnO_{122}]^{n-}$,[8] 4:40 $[LnAs_4W_{40}M_2(H_2O)_2O_{140}]^{n-}$,[9] *etc.*, and their properties such as catalytic activity,[10] magnetism[11] and antivirus activity[12] have also been studied. Recently we have prepared heteropoly compounds of the series of 4:30 $[As_4W_{30}M_4(H_2O)_2O_{112}]^{16-}$ (M = Cd, Cu, Co, Mn, Ni or Zn) and discussed the replacement of the coordinated water molecules. We have obtained the significant results that these molecules could be substituted either in aqueous solution or in organic solvents.[13] We explored novel sandwich-type complexes, $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ (M = Cd, Co, Cu, Fe, Mn, Ni or Zn), of tetranuclear clusters from the B-$[AsW_9O_{34}]^{9-}$ anion, aimed at adding new members to this family and extending the application field of heteropoly tungstoarsenates and confirmed the replacement of coordinated water molecules in aqueous solution and organic solvents.

In 1973, Tourne *et al.* obtained the trivacant heteropoly ligand $[AsW_9O_{33}]^{9-}$ containing As^{III} by acidifying a solution of As_2O_3 and Na_2WO_4.[14] The compounds $[As_2W_{18}M_3(H_2O)_2O_{66}]^{n-}$ (M = Cu or Fe) have been synthesized[15] and the copper one structurally characterized.[16] However, there has been little research on the trivacant anion $[AsW_9O_{34}]^{9-}$ containing As^V. Since the trivacant anion $[PW_9O_{34}]^{9-}$ containing P^V was reported in 1973, this area has been continuously investigated. $[P_2W_{18}M_3(H_2O)_2O_{68}]^{n-}$ (M = Ce^{IV}, Cu^{II}, Co^{II}, Fe^{III}, Mn^{II}, Ni^{II}, Pd^{II}, Sn^{II} or Zn^{II})[17] can be made from A-$[PW_9O_{34}]^{9-}$,[18] while $[P_2W_{18}M_4(H_2O)_2O_{68}]^{n-}$ (M = Co^{II}, Cu^{II}, Fe^{III}, Mn^{II}, Ni^{II} or Zn^{II})[19] can be made from B-$[PW_9O_{34}]^{9-}$.[20] The investigations included not only various kinds of crystal structures, but also their properties, such as magnetism,[21] catalytic activity[10,20,22] and anti-AIDS activity,[12] *etc.* The arsenic species generally parallels the phosphorus species, and further, the As atom, larger than P, has easily changeable As^{III}/As^V oxidation states, so the former not only gives new information on structure but also has more excellent properties than the phosphorus species.

In 1986 Evans *et al.* isolated $K_{10}[As_2W_{18}Zn_4(H_2O)_2O_{68}]$ from prolonged reaction of an 11:1:2:9 mixture of HNO_3–Na_2HAsO_4–$ZnSO_4$–Na_2WO_4 at 90–100 °C and determined its crystal structure by X-ray diffraction (Fig. 1).[23] The compound made by this method has a low yield with a by-product. When this method was used to synthesize $K_{10}[P_2W_{18}Co_4(H_2O)_2O_{68}]$, $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ was obtained simultaneously.[24] So Finke *et al.* considered that $K_{10}[P_2W_{18}M_4(H_2O)_2O_{68}]$ when rationally synthesized from B-$[PW_9O_{34}]^{9-}$ would guarantee the purity and increase the yield.[25] In this paper the following aspects are reported in detail: (i) lacunary anion B-$[AsW_9O_{34}]^{9-}$, prepared by acidifying a solution of H_3AsO_4 and Na_2WO_4 and drying for 1–2 h at 140 °C; (ii) pure

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† Electronic supplementary information (ESI) available: preparative details, CV data, colours, electronic spectra, packing diagrams, crystal morphologies. See http://www.rsc.org/suppdata/dt/b0/b006804g/

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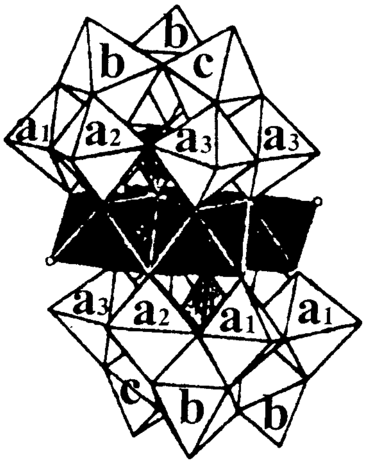

Fig. 1 Polyhedral representation of $M_4As_2W_{18}$.

sandwich-type polyoxometalates (POMs), $[M_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$, with high yield; (iii) structural characterizations of $K_{10}[Mn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 18H_2O$ and $K_8Na_2[Cu_4(H_2O)_2(AsW_9O_{34})_2]\cdot 32H_2O$, showing that Jahn–Teller distortions of the M_4O_{16} cluster are absent in the former and present in the latter; (iv) the unequivocal identity of the ligands at the tetrameric clusters M_4O_{16} (studies of ligand replacement reactions in POMs, especially in the arsenic series, are rare, but are important for oxidation catalysis); (v) the crystal morphology of $[Co_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ anion obtained from a benzene solution after phase transfer observed under a polarizing microscope. Research on the magnetic characterization of $M_4As_2W_{18}$ clusters to compare them with the phosphorus analogs is underway.[21]

Experimental

Materials and general methods

Tetraheptylammonium bromide (tHA)Br and benzene used were of super-pure grade and other reagents used were of analytical grade. Benzene was distilled prior to use and then dried with sodium and stored. Distilled water was used for all syntheses. 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, electronic absorption spectra on a Beckman DU-640 spectrometer. The cyclic voltammograms 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. The glassy carbon electrode was polished with 1.0 µm 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-Elmer TG-7, DSC-7 thermal analyzer.

Preparations

B-$Na_8[HAsW_9O_{34}]\cdot 11H_2O$ ("B-AsW_9"). First 30.0 g of $Na_2WO_4\cdot 2H_2O$ were dissolved in 37 mL of distilled water with stirring. Then 0.8 mL of H_3AsO_4, followed by 5 mL of glacial acetic acid, was added. After a few seconds the solution became cloudy and after about 1 min a heavy white precipitate had formed. The solid was collected on a sintered-glass frit and dried under aspiration until easily manipulated. This product is suggested to be predominantly A-$Na_8[HAsW_9O_{34}]$.[25] Fig. 2(a) shows the infrared spectrum of this product. When the aspirated solid was first dried at room temperature for 24 h or longer and then at 140 °C for about 6 h the final product (labeled with the Δ symbol as suggested by Knoth *et al.*[26]) gave the spectrum shown in Fig. 2(c). Drying the aspirated solid for only 1–2 h at 140 °C gave a product with an intermediate spectrum as shown in Fig. 2(b). This partially thermolyzed $[AsW_9O_{34}]^{9-}$ was successfully used in a number of preparations which gave good yields of $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ presumably due to the 100 °C recrystallization step (see Results and discussion). Yields of $Na_8[HAsW_9O_{34}]$ in all cases were about 25 g (83%) after drying. The dried solid is very hygroscopic, and after equilibration at ambient atmospheric humidity for 2–3 days, TGA finds 11 H_2O (7.54% H_2O found; 7.45% calculated for $Na_8[HAsW_9O_{34}]\cdot 11H_2O$).

Co^{2+} Titration of $Na_8[HAsW_9O_{34}]$. Four separate solutions containing Co^{2+} were prepared by dissolving 0.0547 (0.188), 0.1094 (0.376), 0.1636 (0.564), and 0.2188 g (0.752 mmol) of $Co(NO_3)_2\cdot 6H_2O$ each in 20.0 mL of water. To each solution was added 0.5000 g of $[AsW_9O_{34}]^{9-}$ (0.188 mmol; dried at 140 °C for 1–2 h at 1 atm), which was dissolved with heating, if necessary. An aliquot from each solution was used to obtain the visible spectrum, monitoring the absorbance at 568 nm. Background absorbance due to excess of Co^{2+} past the 2.0 equivalents point was accounted for by directly subtracting the absorbance observed for the excess amounts of Co^{2+} (1 and 2 equivalents) in a 20.0 mL volume of water alone. This experiment was reproducible with a given sample of $[AsW_9O_{34}]^{9-}$ but gave variable results depending upon the exact sample used and how it was dried.

$K_aNa_{10-a}[As_2W_{18}M_4(H_2O)_2O_{68}]\cdot xH_2O$, $M_4As_2W_{18}$ (M = Cd, Co, Cu, Fe, Mn, Ni or Zn). In a typical procedure the chloride or nitrate of the transition metal (1.5 mmol) was dissolved in 15 mL of water. To this solution was added with stirring 2.0 g (0.75 mmol) of solid $Na_8[HAsW_9O_{34}]$ (1 atm, 140 °C, 1–2 h), heated until nearly homogeneous and then filtered hot by gravity filtration through paper. An excess of solid KCl (4.5 g) was added to the clear filtrate, resulting in immediate precipitation. After the mixture was cooled to room temperature this solid was collected on a sintered-glass frit and dried under aspiration. The slightly damp solid was redissolved in about 5–10 mL of hot water and allowed to recrystallize overnight at 5 °C. A crystalline solid was collected and dried at 80 °C under vacuum for 2 h (for experimental details of the preparation, yield, color of the products and the results of elemental analyses, see the Electronic Supplementary Information).

Phase transfer and replacement reactions of coordinated water molecules of the $M_4As_2W_{18}$ anions

(i) Phase transfer. Transfer of the heteropolyanion $[M_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ (M = Cd^{II}, Co^{II}, Cu^{II}, Fe^{II}, Mn^{II}, Ni^{II} or Zn^{II}) into non-polar organic solvents was carried out by previously described procedures:[27] 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 dried either by passing N_2 gas through it for several hours or by evaporation.

(ii) Replacement reactions. The solid (0.1 g) obtained above was dissolved in anhydrous benzene (5 mL). An organic ligand, such as pyridine, acetonitrile, acetone, chloroform, pyrrole or lactic acid was added in stoichiometric amount. Electronic and IR spectra were recorded so as to determine the dehydration of the heteropolyanions and the substitution of the organic ligands for the coordinated water.

Replacement reactions of water molecules coordinated to the $M_4As_2W_{18}$ anion in aqueous solutions

This experiment was performed as follows. An aqueous solution of $M_4As_2W_{18}$ 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 addition of KCl to the resulting solution a precipitate was isolated. The replacement of coordinated water molecules with selected ligands was observed through changes in color and in the electronic spectra of the corresponding solutions.[2,28] The products were identified by elemental analyses and IR spectra.

$K_{16}[Cu_4(L^1)_2(AsW_9O_{34})_2]$, $Cu_4As_2W_{18}$–L^1 ($L^1 = [Fe(CN)_6]^{3-}$). A 10 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_2W_{18}$ was mixed with 1 mL of a hot aqueous solution containing 0.30 g of $K_3Fe(CN)_6$, then heated for 0.5 h. A yellow precipitate (0.48 g) was isolated from the solution by 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 : Fe : W = 16.0 : 4.1 : 1.8 : 18.3, consistent with the formula. IR (KBr, cm^{-1}): 2101 (ν(CN)), 957, 887, 818 and 730.

$K_{18}[Cu_4(L^2)_2(AsW_9O_{34})_2]$, $Cu_4As_2W_{18}$–L^2 ($L^2 = [Fe(CN)_6]^{4-}$). A 10 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_2W_{18}$ was mixed with 1 mL of a hot aqueous solution containing 0.38 g of $K_4Fe(CN)_6$, and then heated for 0.5 h. A dark red precipitate (0.52 g) was isolated from the solution by the addition of 0.3 g of KCl after cooling to room temperature and dried at 80 °C under vacuum for *ca.* 0.5 h. Elemental analyses gave a ratio K : Cu : Fe : W = 18.0 : 4.1 : 1.8 : 18.5, consistent with the formula. IR (KBr, cm^{-1}): 2098 (ν(CN)), 942, 880, 842 and 741.

$K_{10}[Cu_4(L^3)_2(AsW_9O_{34})_2]$, $Cu_4As_2W_{18}$–L^3 ($L^3 = C_2H_8N_2$). A 10 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_2W_{18}$ was mixed with 2 drops of liquid $C_2H_8N_2$ and the solution changed from green to violet. The resulting solution was then heated for 0.5 h. A violet precipitate (0.51 g) was isolated by addition of 0.1 g KCl after cooling 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 = 10.0 : 4.1 : 3.8 : 3.7 : 18.2, consistent with the formula. IR (KBr, cm^{-1}): 1041 (ν(C–N)), 1642 ($\delta(NH_2)$), 949, 881, 815 and 755.

$K_{14}[Cu_4(L^4)_2(AsW_9O_{34})_2]$, $Cu_4As_2W_{18}$–L^4 ($L^4 = SO_3^{2-}$). A 10 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_2W_{18}$ was mixed with 1 mL of a hot aqueous solution containing 0.90 g of $Na_2SO_3·7H_2O$, and then heated for 0.5 h. A white precipitate (0.34 g) was isolated upon addition of 0.5 g KCl after cooling to room temperature and dried at 80 °C under vacuum for *ca.* 0.5 h. Elemental analyses gave a ratio K : Cu : S : W = 14.0 : 3.9 : 1.8 : 18.3, consistent with the formula. IR (KBr, cm^{-1}): 1124 ($\nu(SO_3^{2-})$), 946, 883, 825 and 728.

$K_{12}[Cu_4(L^5)_2(AsW_9O_{34})_2]$, $Cu_4As_2W_{18}$–L^5 ($L^5 = SCN^-$). A 10 mL volume of a hot aqueous solution containing 1.0 g of $Cu_4As_2W_{18}$ was mixed with 1 mL of a hot aqueous solution containing 0.40 g of KSCN, and then heated for 0.5 h. A pale pink precipitate (0.35 g) was isolated upon addition of 0.5 g of KCl after cooling to room temperature and dried at 80 °C under vacuum for *ca.* 0.5 h. Elemental analyses gave a ratio K : Mn : S : W = 12.0 : 3.8 : 1.9 : 17.7, consistent with the formula. IR (KBr, cm^{1}): 2070 ($\nu(SCN^-)$), 958, 880, 819 and 730.

The results of the replacement reaction for other complexes are given in the Electronic Supplementary Information.

Crystal morphologies of $Co_4As_2W_{18}$ occupied by some organic ligands

The solid obtained by 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.[29]

X-Ray crystallography

Crystals of $K_{10}[Mn_4(H_2O)_2(AsW_9O_{34})_2]·18H_2O$ **I** and $K_8Na_2[Cu_4(H_2O)_2(AsW_9O_{34})_2]·32H_2O$ **II** were mounted on glass fiber capillaries in a Siemens P4 four-circle diffractometer equipped with graphite monochromated Mo-Kα radiation. An ω-scan mode at variable speeds was used. The reflection statistics indicated that the crystal lattices were centrosymmetric. A semi-empirical absorption correction from ψ scans was applied. The structure was solved by the direct method (SHELXTL PC)[30a] and refined by the full-matrix least-squares method on F^2 (SHELX 93).[30b] Anisotropic thermal parameters were applied to all atoms except for K^+ and Na^+ and water molecules of crystallization to which isotropic thermal parameters were applied. Disorder due to thermal motion was observed in some of the K^+ and Na^+ cations and water molecules. Crystal parameters are summarized in Table 1.

CCDC reference numbers 152291 and 152573.

See http://www.rsc.org/suppdata/dt/b0/b006804g/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses

B-$Na_8[HAsW_9O_{34}]·11H_2O$. One of the most crucial observations from this work is the finding that only thermolyzed $Na_8[HAsW_9O_{34}]$ gives high yields of $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ products. The exact conditions of temperature, pressure, and time are important (as discussed in detail in the Experimental section); assurance that the initially precipitated by $Na_8[HAsW_9O_{34}]$ is fully converted into B-$Na_8[HAsW_9O_{34}]$ is most easily monitored by IR spectroscopy (Fig. 2). The form of the AsW_9 is important as illustrated in Fig. 3, which is a titration curve showing a sharp break point at 2.0 equivalents of Co^{2+} per equivalent of B-AsW_9 due to the formation of $[As_2W_{18}Co_4(H_2O)_2O_{68}]^{10-}$. The spectral titration is, of course, a valuable way to find optimum conditions leading to a product wanted for heated AsW_9 (but not unheated AsW_9).

$[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$. The reaction of AsW_9 (1 atm, 140 °C, 1–2 h) with 2 equivalents of M^{2+} in water according to eqn. (1), followed by isolation as the potassium or sodium

$$2B\text{-}[AsW_9O_{34}]^{9-} + 4M^{2+} + 2H_2O \longrightarrow [AsW_9M_2(H_2O)O_{34}]_2^{10-} \quad (1)$$

salt and recrystallization from hot water, results in good yields of the crystalline complexes. The elemental analysis is consistent with the titration results, indicating disubstitution of AsW_9, and determines an empirical formula of $(K_{5-n}Na_nAsW_9M_2(H_2O)O_{34}·mH_2O)_x$. Molecular weight determinations, IR spectra, and ^{183}W NMR spectra ($M = Cu^{2+}$) were used to establish that the reactions are indeed rational syntheses of the products.

Crystal structures of compounds I and II

Compounds **I** and **II** are isostructural. Only the crystal structure of **I** is shown in Fig. 4, which gives an ORTEP[31] drawing of the asymmetric unit. Fig. 5 is a ball-and-stick representation of the central $Mn_4(H_2O)_2O_{14}$ unit. Table 2 provides distances

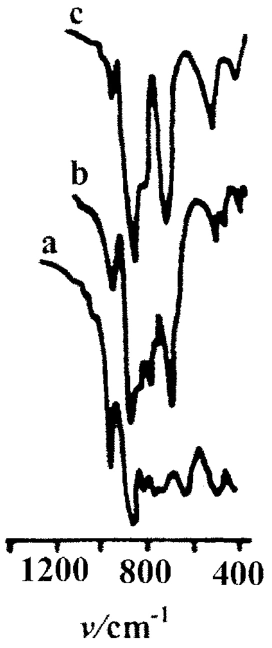

Fig. 2 Infrared spectra of the effect of heat treatments on $[AsW_9O_{34}]^{9-}$; (a) freshly prepared AsW_9 allowed to air-dry at room temperature, (b) fresh solid completely dried at 140 °C for 1–2 h. The changes associated with this drying process are characterized by the appearance of new bands at 890 cm^{-1} while other bands only change in intensity. Prolonged heating (>15 h) at 140 °C causes no further change in spectrum (b). However, if fresh AsW_9 is first air-dried (24–48 h) and then dried at 140 °C for about 6 h the IR bands at 890 cm^{-1} increase in intensity at the expense of the 850 cm^{-1} band as shown in (c). Spectrum (b) seems to be an intermediate case between (a) and (c).

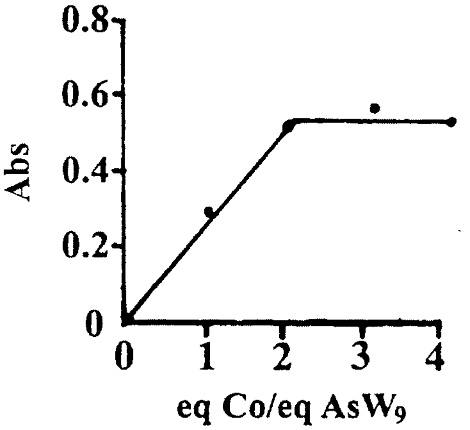

Fig. 3 Co^{2+} titration in water of $[AsW_9O_{34}]^{9-}$ (heated at 140 °C, 1–2 h) monitored by visible spectroscopy at 570 nm. The solid line indicates the idealized curve of this $[AsW_9O_{34}]^{9-}$ sample-dependent experiment (see the Experimental section). The curve suggests that most, but not all, of the Δ-$[AsW_9O_{34}]^{9-}$ is B-type $[AsW_9O_{34}]^{9-}$.

between heavy atoms in the compounds. The crystal structure of **II** and bond lengths and angles are given in the Electronic Supplementary Information.

The two anions have the general structure proposed earlier for the phosphorus analogues by Weakley *et al.*[19a] and subsequently characterized by Finke,[19b,c] Weakley,[19d,e] Gomez-Garcia,[20a] Pope,[20b] and Hill[20c] and their co-workers. It consists of two B-type trivacant Keggin[32] units, $[AsW_9O_{34}]^{9-}$, linked by an M_4 unit in a centrosymmetric arrangement (C_{2h} symmetry). A $[XW_9O_{34}]^{9-}$ moiety is derived from the removal of three WO_6 octahedra from the parent α-Keggin structure, $[XW_{12}O_{40}]^{3-}$. Removing three edge-sharing WO_6 octahedra (one edge-sharing W_3O_{13} triad) results in a B-type $[XW_9O_{34}]^{9-}$,[16,19] while removing three corner-sharing WO_6 octahedra from three separate W_3O_{13} triads results in an A-type $[XW_9O_{34}]^{9-}$.[18] The A- and B-$[XW_9O_{34}]^{9-}$ moieties coordinate to the central transition metal ions to form a sandwich polyoxoanion in different ways, giving rise to structurally distinct complexes.[17] B-$[XW_9O_{34}]^{9-}$ provides seven oxygen donor atoms (one from the central XO_4 group and one each from the six W atoms) that are capable of coordinating the central tetrameric metal unit. In contrast, A-$[XW_9O_{34}]^{9-}$ provides six donor oxygen atoms (one each from the six W atoms) that generally coordinate a central trimeric metal unit. In our cases, two B-$[AsW_9O_{34}]^{9-}$ moieties are bonded to the central M_4 unit. The four M atoms form a plane placed around the crystallographic inversion center situated at the midpoint of the M(1)···M (1A) vector. One of the four oxygen atoms in AsO_4 links to three M atoms on each side of the plane, resulting in a central unit of four edge-sharing MO_6 octahedra which form a regular rhomb-like cluster.

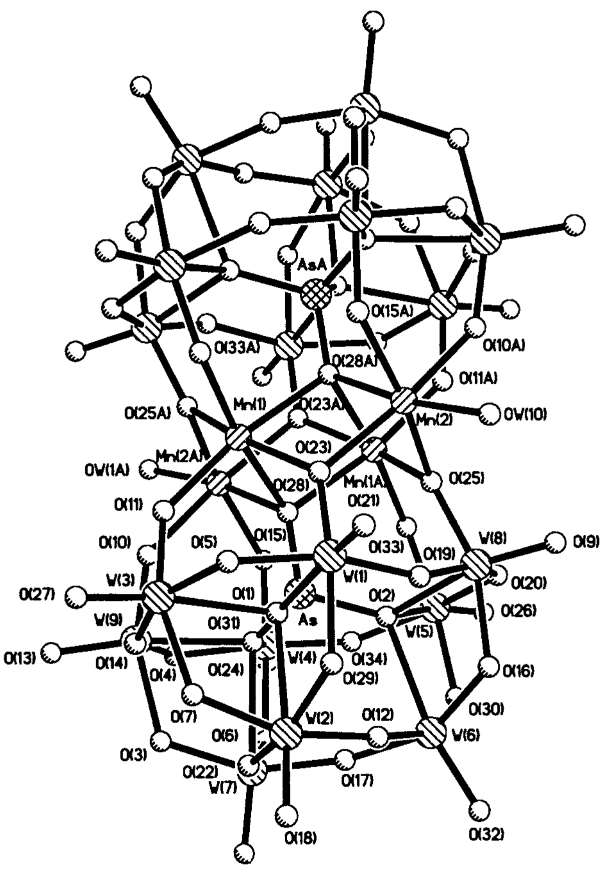

Fig. 4 ORTEP drawing of the centrosymmetric unit of compound **I**.

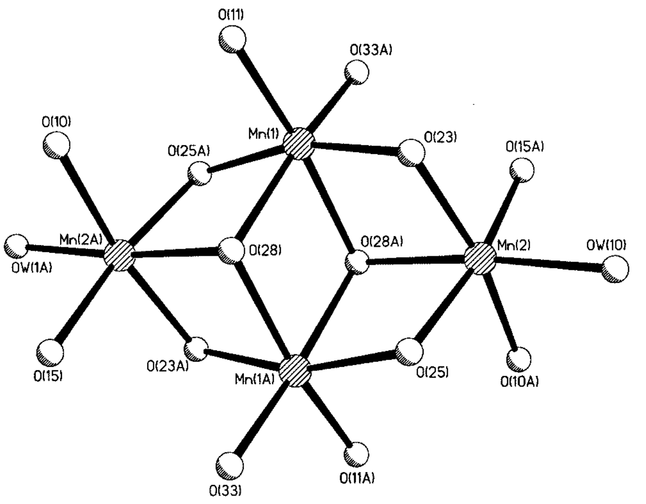

Fig. 5 Structure of the central $Mn_4(H_2O)_2O_{14}$ unit in compound **I**.

Table 1 Crystallographic data for $K_{10}[Mn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 18H_2O$ **I** and $K_8Na_2[Cu_4(H_2O)_2(AsW_9O_{34})_2]\cdot 32H_2O$ **II**

Formula	$H_{40}As_2K_{10}Mn_4O_{88}W_{18}$	$H_{68}As_2K_8Cu_4Na_2O_{102}W_{18}$
M	5518.22	57722.62
Crystal system	Monoclinic	Triclinic
Space group	$P\bar{2}_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	12.375(3)	11.858(2)
b/Å	21.356(4)	12.525(3)
c/Å	15.887(3)	17.107(3)
α/°		82.82(3)
β/°	92.11(3)	71.26(3)
γ/°		81.79(3)
U/Å^3	4196(2)	2372.9(8)
Z	2	1
T/K	293(2)	293(2)
λ/Å	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)
μ/mm^{-1}	26.536	23.766
Independent reflections	5833 ($R_{int} = 0.0613$)	6580 ($R_{int} = 0.0629$)
R_1 [$I > 2\sigma(I)$]	0.0767	0.0723
$wR2$	0.1909	0.1804

Table 2 Distance (Å) between heavy atoms for $K_aNa_{10-a}[M_4(H_2O)_2(XW_9O_{34})_2]\cdot xH_2O$ [X = P or As, M = Co, Mn or Cu]

	M–M		X–M		M–O	M–W				Ref.
M = Cu	Cu(1)–Cu(2A)	3.263	P–Cu(1)	3.211	1.90–2.05	Cu(1)–W(4)	3.750	Cu(1)–W(9)	3.491	19(*d*)
X = P	Cu(1)–C(2)	3.246	P–Cu(1A)	3.205	equatorial	Cu(2)–W(4)	3.423	Cu(2)–W(5)	3.423	
	Cu(1)–Cu(1A)	3.087	P–Cu(2)	3.525	2.34–2.55	Cu(1A)–W(5)	3.769	Cu(1A)–W(6)	3.484	
					axial	Cu(2A)–W(7)	3.501	Cu(2A)–W(8)	3.500	
M = Co	Co(1)–Co(2A)	3.192	P–Co(1)	3.300	1.99–2.24	Co(1)–W(6)	3.547	Co(1)–W(8)	3.590	23
X = P	Co(1)–Co(2)	3.164	P–Co(1A)	3.302	equatorial	Co(2)–W(8)	3.499	Co(2)–W(9)	3.494	
	Co(1)–Co(1A)	3.305	P–Co(2)	3.264	1.98–2.17	Co(1A)–W(7)	3.551	Co(1A)–W(9)	3.593	
					axial	Co(2A)–W(4)	3.569	Co(2A)–W(5)	3.581	
M = Mn	Mn(1)–Mn(2A)	3.290	P–Mn(1)	3.412	2.05–2.32	Mn(1)–W(6)	3.580	Mn(1)–W(8)	3.649	20(*a*)
X = P	Mn(1)–Mn(2)	3.294	P–Mn(1A)	3.404	equatorial	Mn(2)–W(5)	3.539	Mn(1A)–W(7)	3.597	
	Mn(1)–Mn(1A)	3.447	P–Mn(2)	3.373	2.03–2.34	Mn(1A)–W(9)	3.626	Mn(2A)–W(8)	3.560	
					axial	Mn(2A)–W(9)	3.558			
M = Co	Co(1)–Co(2A)	3.224	As–Co(1)	3.354	2.01–2.20	Co(1)–W(6)	3.563	Co(1)–W(8)	3.642	19(*e*)
X = As	Co(1)–Co(2)	3.220	As–Co(1A)	3.345	equatorial	Co(2)–W(8)	3.515	Co(2)–W(9)	3.513	
	Co(1)–Co(1A)	3.384	As–Co(2A)	3.323	2.02–2.19	Co(1A)–W(7)	3.575	Co(1A)–W(9)	3.617	
					axial	Co(2A)–W(4)	3.615	Co(2A)–W(5)	3.625	
M = Mn	Mn(1A)–Mn(2)	3.248	As–Mn(1)	3.422	2.07–2.29	Mn(1)–W(3)	3.609	Mn(1)–W(1)	3.662	This work
X = As	Mn(1)–Mn(2)	3.243	As–Mn(1A)	3.425	equatorial	Mn(2)–W(1)	3.546	Mn(2)–W(8)	3.547	
	Mn(1)–Mn(1A)	3.455	As–Mn(2)	3.428	2.06–2.27	Mn(1A)–W(5)	3.589	Mn(1A)–W(8)	3.685	
					axial	Mn(2A)–W(4)	3.675	Mn(2A)–W(9)	3.680	
M = Cu	Cu(1A)–Cu(2)	3.310	As–Cu(1)	3.249	1.95–2.03	Cu(1)–W(2)	3.840	Cu(1)–W(8)	3.517	This work
X = As	Cu(1)–Cu(2)	3.265	As–Cu(1A)	3.253	equatorial	Cu(2)–W(5)	3.552	Cu(2)–W(7)	3.544	
	Cu(1)–Cu(1A)	3.183	As–Cu(2)	3.570	2.33–2.49	Cu(1A)–W(1)	3.530	Cu(1A)–W(9)	3.804	
					axial	Cu(2A)–W(2)	3.461	Cu(2A)–W(9)	3.465	

Atoms M(1) and M(2) have different coordination environments. In the manganese case, Mn(1) is bonded to three oxygen atoms [O(11), O(23), and O(28)] on each B-$[AsW_9O_{34}]^{9-}$, Mn(2) to one water [OW(10)], two oxygen atoms [O(23) and O(25)] of B-$[AsW_9O_{34}]^{9-}$ on one side of the central Mn_4 plane and three oxygen atoms [O(10A), O(15A) and O(28A)] on the other side. In the copper case, Cu(1) is also bonded to three oxygen atoms [O(5), O(19), and O(24)] on each B-$[AsW_9O_{34}]^{9-}$, but Cu(2) is bonded to one water [OW(8)], three oxygen atoms [O(5), O(28) and O(30)] of B-$[AsW_9O_{34}]^{9-}$ on one side of the central Cu_4 plane, and two oxygen atoms [O(15A) and O(24A)] on the other side.

However, the Jahn–Teller distortion of the MO_6 groups is different in the two complexes. The distortion of the CuO_6 groups is apparent: the axial distances (2.33–2.49, mean 2.42 Å) are significantly larger than the equatorial ones (1.95–2.03, mean 1.99 Å). This is also present in the recently characterized analogous Wells–Dawson sandwich complex $[Cu_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$.[13] The manganese(II) derivative shows an absence of the Jahn–Teller effect in the MnO_6 octahedra: the axial distances range from 2.07 to 2.29 Å (mean 2.17 Å) and the equatorial ones range from 2.06 to 2.27 Å (mean 2.17 Å). This feature, also observed in the $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ series,[19] shows the ability of the trivacant polyoxotungstate fragments to accommodate different transition metals presenting, or not, structural distortions.

A second difference between the two complexes is with the geometry of the three metal atoms from the M_4O_{16} cluster capping the trivacant fragment $[AsW_9O_{34}]^{9-}$. In the copper derivative the copper atoms are asymmetrically placed with respect to the normal through As to the cluster plane. This situation can easily be seen from the three different As–Cu distances (3.249, 3.570, and 3.253 Å). On the contrary, in the manganese derivative, the three metal atoms that cap the trivacant fragment are symmetrically placed with respect to the As atom and, consequently, the three As–Mn distances are almost equal within experimental error, 3.422, 3.425, and 3.428 Å, confirming, thus, that the Jahn–Teller distortion in the Cu_4O_{16} cluster is responsible for this unsymmetrical arrangement of the As atom.

Another difference between the two complexes is that the displacements of the W atoms from the mean plane in the six W belt are bigger in the copper than in the manganese complex. The shifts of W atoms toward the metallic cluster are 0.0094–0.0177 Å and those away from the cluster are 0.0215–0.0226 Å for the copper complex, while they are 0.0024–0.0163 and

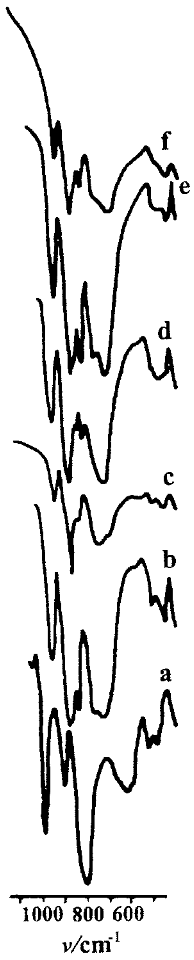

Fig. 6 Infrared spectra of (a) AsW_{12}, (b) $Mn_4As_2W_{18}$, (c) $Co_4As_2W_{18}$, (d) $Cu_4As_2W_{18}$, (e) $Cd_4As_2W_{18}$ and (f) $Zn_4As_2W_{18}$. 2% Samples, in KBr pellets.

0.0016–0.0156 Å, respectively, for the manganese complex. It seems clear that these displacements are due to the presence of the central M_4O_{16} cluster and, consequently, they are bigger in the copper compound as a result of the Jahn–Teller distortions.

In the rhombic M_4O_{16} clusters the side lengths are respectively 3.318 and 3.328 Å with a shortest diagonal of 3.530 Å in compound **I**, 3.265 and 3.309 Å with a shortest diagonal of 3.183 Å in **II**.

All the *trans*-directed bonds along the cluster axial direction, $Mn–O–W_{belt}–O–W_{cap}$, in compound **I** have less pronounced bond length alternations (average distances: 2.13, 1.84, 1.97 and 1.90 Å) than those in **II** (average distances: 2.09, 1.76, 1.99 and 1.89 Å). These observations confirm that the deviations are produced by the change in the valence sums when replacing three W^{VI} of one cap by three M^{II}, as suggested by Weakley and Finke.[19d]

Comparing the arsenic with the phosphorus analogs, some apparent differences can also be found (see Table 2): (i) the biggest change in the skeletal distances in going from P to As is in the $M(1)\cdots M(1A)$ distances (a diagonal of the rhombic M_4O_{16} cluster); $M(1)\cdots M(1A)$ distances are about 0.1 Å shorter in the former than in the latter (see Table 2). There also exist smaller increases (about 0.05 Å) in some $M\cdots W$ and $X\cdots W$ distances in the arsenic analogs than in the phosphorus analogs. (ii) The differences between the longest and the shortest $X\cdots Mn$ distances is smaller in the arsenic analogs. The same is true for the X–O distances. These tendencies are presumably due to the bigger atomic radius of As than that of P.

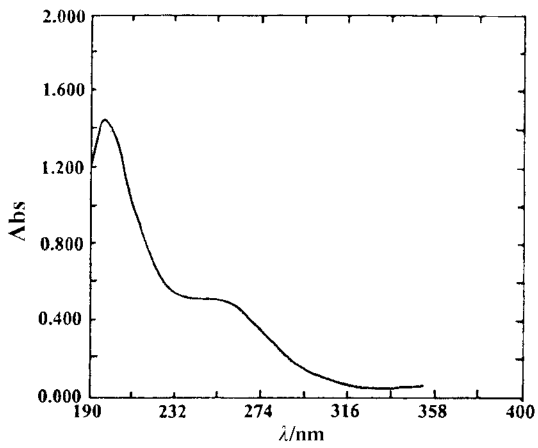

Fig. 7 UV spectrum of $Co_4As_2W_{18}$.

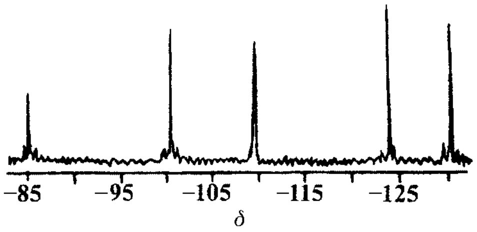

Fig. 8 ^{183}W NMR spectra of $Cu_4As_2W_{18}$.

Physical properties

IR spectra. IR spectra of $M_4As_2W_{18}$ compared with those of $[AsW_{12}O_{40}]^{3-}$ and $[AsW_9O_{34}]^{9-}$ are shown in Figs. 2 and 6. The following points can be made: (i) all of the characteristic vibrational frequencies decrease compared with those of $[AsW_{12}O_{40}]^{3-}$, which is attributed to the increase of the negative charges of the anions;[33] (ii) the asymmetry stretching vibration of $W–O_c–W$ in $[AsW_{12}O_{40}]^{3-}$ is split into 3 peaks when the anion degrades into a trivacant anion $[AsW_9O_{34}]^{9-}$, but into 2 peaks when the corresponding sandwich species are formed; (iii) the vibrational frequency of the As–O bonds overlaps that of $W–O_b$ bonds; (iv) the spectra for the $M_4As_2W_{18}$ series are similar to each other.

UV spectra. All of the UV spectra of the $M_4As_2W_{18}$ series have two absorption bands. The lower energy band at *ca.* 50761 cm^{-1} is attributed to charge transfer $O_d \rightarrow W$, and the higher energy band at *ca.* 39526 cm^{-1} to $(O_c/O_b) \rightarrow W$, indicating their similar electronic structures.[34] The UV spectrum of $Co_4As_2W_{18}$, as an example, is shown in Fig. 7.

CV. The CV of $M_4As_2W_{18}$ was performed in an $MeCO_2H–NaO_2CMe$ buffer solution (pH 4.0), and the data are listed in the Electronic Supplementary Information. The redox reaction of $M_4As_2W_{18}$ is two-step and pseudoreversible. In comparison, the α-$[AsW_{12}O_{40}]^{3-}$ anion is reduced in five steps, all of which are pseudoreversible. The trivacant anion α-$[AsW_9O_{34}]^{9-}$ is formed in a one-step reduction which is pseudo-reversible.

^{183}W NMR. Fig. 8 shows the ^{183}W NMR spectrum of compound **II** in D_2O which confirms its structure. Five resonances at δ −85.3, −100.1, −109.2, −123.6, and −130.2 were observed at room temperature (referenced to Na_2WO_4). These and the dimeric molecular formula require a C_{2h} symmetry structure as shown in Fig. 1 with the five symmetry-distinct types of tungsten atoms labeled a_1, a_2, a_3, b, and c.[26]

TG-DSC. TG-DSC data show a weight loss at 598 °C corresponding to the release of two coordinated water molecules from the $[Mn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ anion.

Table 3 Electronic spectral data of the products isolated from the replacement reactions of the coordinated water molecules in aqueous solutions [cm^{-1} (ε^{a}/M^{-1} cm^{-1})]^{a}

Heteropoly-anion	Ligand					
	$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	SCN^-	$C_2H_8N_2$	SO_3^{2-}	H_2O
$Cu_4As_2W_{18}$	22883(156)	20534(142)	19302(171)	18282(162)	—	11834(150)
$Fe_4As_2W_{18}$	14706(278)	14185(315)	23641(232)	17953(71)	continual	21739(218)
$Co_4As_2W_{18}$	23641(468) 18149(20)	23529(240) 14065(66)	20040(21)	continual	17731(15)	17606(57)
$Ni_4As_2W_{18}$	24272(327) 17483(23)	12392(146)	—	—	—	12563(41) 23256(79)

[a] Electronic spectra determined for the K^+ salt; absorption coefficients in parentheses.

Table 4 Electronic spectral data for $M_4As_2W_{18}$ containing 0.1 M (tHA)Br in benzene [cm^{-1} (ε/M^{-1} cm^{-1})]^{a}

Conditions	$Cu_4As_2W_{18}$	$Ni_4As_2W_{18}$	$Co_4As_2W_{18}$
Water	11834(150)	12563(41) 23256(79)	17606(57)
Before loss of water	13115(138)	11558(38) 21769(68)	17483(54)
After loss of water	13138(136)	11495(40) 20699(66)	16921(70)
Pyridine	11868(142)	11948(39) 22857(75)	17699(68)
Lactic acid	12245(147)	12493(42) 23128(80)	17380(58)
Acetone	12639(147)	12903(45) 22958(76)	17422(64)
Acetonitrile	12179(143)	12225(49) 23012(72)	17361(54)
Chloroform	11960(140)	12451(43) 22955(68)	17452(42)
Pyrrole	11979(158)	12706(49) 23225(73)	17513(80)

[a] Absorption coefficients.

Replacement reactions of the coordinated water molecules by other ligands in aqueous solution

The experimental results show that, even in 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 those of the products isolated from aqueous solutions containing only corresponding simple transition metal complexes and ligands are listed in the Electronic Supplementary Information. In most cases the two types of products differ in their colors. Table 3 gives the electronic spectral data 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 $M_4As_2W_{18}$–$L^{1,2}$ and for $M_4As_2W_{18}$–L^5, ν(C–N) at *ca.* 1040 cm^{-1} and $\delta(NH_2)$ at *ca.* 1640 cm^{-1} for $M_4As_2W_{18}$–L^3 and $\nu(SO_3^{2-})$ at *ca.* 1120 cm^{-1} for $M_4As_2W_{18}$–L^4 were observed, indicating that the ligands indeed participated in the replacement reactions.[2,28]

Phase transfer and loss of the coordinated water molecules

Aqueous solutions of heteropolyanions containing transition metals usually display specific colors. After phase transfer followed by loss of the coordinated water molecules the color of the solution changes to some extent.[35] The colors of the solutions before and after loss of the coordinated water molecules are given in the Electronic Supplementary Information.

Table 4 presents the electronic spectral data which show that the coordinated water molecules of the heteropolyanions are lost upon phase transfer, as either the position or the intensity of the peaks was noticeably changed. In most cases, addition of a selected organic ligand, such as pyridine, lactic acid, acetone, acetonitrile, chloroform or pyrrole, to the dehydrated benzene solution restored the original spectrum. We therefore deduce that the spectral changes are due to loss of the coordinated water molecules and their replacement by such organic ligands.[13,27,36–38] Electronic spectra are given in the Electronic Supplementary Information.

In the IR spectra of the sample of $Co_4As_2W_{18}$ with pyridine or lactic acid, isolated from benzene, ν(N=C) at *ca.* 1650 or ν(C=O) at *ca.* 1780 cm^{-1} appeared respectively in addition to the characteristic vibration peaks of the $Co_4As_2W_{18}$ anion, indicating that the replacement of the coordinated water molecules by pyridine or lactic acid had indeed taken place.

Crystal morphologies of $Co_4As_2W_{18}$ occupied by some organic ligands

The crystal morphologies of $[Co_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ after phase transfer, occupied by pyridine, pyrrole, lactic acid, acetone, acetonitrile, or chloroform as described in the Experimental section, are shown in the Electronic Supplementary Information. The different morphologies are probably due to the presence of different organic ligands in the anions. We expect this method (see Fig. 5 in the Electronic Supplementary Information) to be useful to identify isostructural polyoxoanions containing different organic ligands.

Conclusion

The main conclusions are as follows: (1) Seven new compounds in the series $[M_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ (M = Cd^{II}, Co^{II}, Cu^{II}, Fe^{II}, Mn^{II} Ni^{II} or Zn^{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 $K_{10}[Mn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 18H_2O$ and $K_8Na_2[Cu_4(H_2O)_2(AsW_9O_{34})_2]\cdot 32H_2O$ and shows that it closely resembles that of the related $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion. (3) The structure of **I** differs from that of **II**, in that the $Mn_4O_{14}(H_2O)_2$ unit in **I** shows no Jahn–Teller distortion. The deviations of the W atoms from their mean plane are smaller in **I** than in **II**. (4) The biggest change in the skeletal distances in going from the phosphorus analogs to the As is in M(1)···M(1A) distances and smaller changes occur in some M···W and X···W distances. These tendencies are presumably due to the bigger atomic radius of As than that of P. (5) In organic solvents, and even in aqueous solutions, selected ligands can replace the coordinated water to form characteristically colored anions. (6) Crystal morphologies, formed in a benzene solution and observed under a polarizing microscope, of $Co_4As_2W_{18}$ containing different organic ligands were different, probably depending on the presence of the different organic ligands. We expect to identify isostructural polyoxoanions containing different organic ligands by this method. However, further structural studies are needed, namely the crystal structure of the $[AsW_9O_{34}]^{9-}$ anion itself.

Acknowledgements

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