Table II. Atomic and Thermal Parameters for $[PtCl(en)(PBu_3)][PtCl(ien)(PBu_3)]Cl_2{\cdot}CH_3COCH_3$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Pt	−0.04332 (3)	0.09764 (5)	0.11925 (3)	0.0815[a]
Cl	−0.1632 (3)	0.0469 (5)	0.0831 (2)	0.1183[a]
P	−0.0864 (3)	0.0660 (4)	0.2048 (2)	0.1011[a]
N(1)	0.0679 (6)	0.1249 (9)	0.1480 (5)	0.079 (3)
N(2)	0.0049 (7)	0.130 (1)	0.0423 (5)	0.085 (3)
C(1)	−0.0206 (9)	0.183 (1)	−0.0028 (7)	0.098 (5)
C(2)	−0.102 (1)	0.232 (2)	−0.0029 (8)	0.118 (6)
C(3)	0.026 (1)	0.198 (1)	−0.0540 (7)	0.105 (5)
C(4)	0.1176 (9)	0.154 (1)	0.0999 (6)	0.090 (4)
C(5)	0.0864 (9)	0.095 (1)	0.0476 (7)	0.094 (5)
C(11)	−0.0128 (8)	0.088 (1)	0.2613 (6)	0.104 (5)
C(12)	−0.043 (1)	0.059 (2)	0.3200 (7)	0.134 (7)
C(13)	0.022 (1)	0.084 (2)	0.3637 (8)	0.141 (7)
C(14)	−0.001 (2)	0.048 (3)	0.4235 (9)	0.20 (1)
C(21)	−0.1228 (9)	−0.078 (1)	0.2139 (8)	0.116 (6)
C(22)	−0.0553 (9)	−0.158 (1)	0.2119 (9)	0.126 (6)
C(23)	−0.084 (1)	−0.278 (2)	0.212 (1)	0.172 (9)
C(24)	−0.013 (2)	−0.354 (2)	0.208 (1)	0.21 (1)
C(31)	−0.168 (1)	0.155 (2)	0.221 (1)	0.157 (8)
C(32)	−0.148 (2)	0.276 (2)	0.209 (2)	0.26 (2)
C(33)	−0.216 (2)	0.327 (3)	0.176 (2)	0.35 (2)
C(34)	−0.198 (3)	0.448 (3)	0.164 (2)	0.34 (3)
Pt′	0.32487 (4)	0.14951 (5)	0.17590 (3)	0.0812[a]
Cl′	0.3689 (4)	0.3154 (4)	0.1445 (3)	0.1382[a]
P′	0.3727 (3)	0.0599 (5)	0.1032 (2)	0.1223[a]
N′(1)	0.2830 (6)	0.010 (1)	0.2143 (5)	0.080 (3)
N′(2)	0.2810 (7)	0.230 (1)	0.2459 (5)	0.091 (4)
C′(4)	0.235 (1)	0.047 (2)	0.2611 (8)	0.118 (6)
C′(5)	0.269 (1)	0.143 (1)	0.2893 (7)	0.101 (5)
C′(11)	0.326 (1)	−0.074 (1)	0.0908 (8)	0.143 (7)
C′(12)	0.352 (1)	−0.131 (2)	0.0362 (9)	0.164 (9)
C′(13)	0.315 (2)	−0.248 (2)	0.035 (1)	0.19 (1)
C′(14)	0.334 (2)	−0.304 (3)	−0.022 (1)	0.26 (2)
C′(21)	0.474 (1)	0.005 (2)	0.120 (1)	0.19 (1)
C′(22)	0.530 (2)	0.099 (3)	0.132 (2)	0.35 (3)
C′(23)	0.615 (2)	0.058 (4)	0.133 (2)	0.35 (2)
C′(24)	0.622 (2)	−0.051 (4)	0.165 (2)	0.30 (2)
C′(31)	0.382 (1)	0.137 (2)	0.0381 (8)	0.175 (9)
C′(32)	0.302 (1)	0.172 (2)	0.0165 (9)	0.151 (8)
C′(33)	0.319 (2)	0.248 (3)	−0.034 (1)	0.28 (2)
C′(34)	0.246 (2)	0.285 (4)	−0.064 (2)	0.29 (2)
Cl(2)	0.3587 (2)	0.3849 (3)	0.3436 (2)	0.0976[a]
Cl(3)	0.1077 (3)	0.3271 (4)	0.2322 (2)	0.1094[a]
O	0.091 (1)	0.409 (2)	0.014 (1)	0.27 (1)
C(6)	0.097 (1)	0.457 (3)	0.060 (1)	0.25 (2)
C(7)	0.178 (2)	0.483 (3)	0.083 (1)	0.25 (2)
C(8)	0.027 (2)	0.469 (3)	0.094 (1)	0.27 (2)

[a] Equivalent *U* values.

Table III. Selected Distances (Å) and Angles (deg) for $[PtCl(en)(PBu_3)][PtCl(ien)(PBu_3)]Cl_2{\cdot}CH_3COCH_3$

Pt–Cl	2.315 (4)	Pt′–Cl′	2.286 (5)
Pt–P	2.226 (5)	Pt′–P′	2.229 (5)
Pt–N(1)	2.06 (1)	Pt′–N′(1)	2.07 (1)
Pt–N(2)	2.08 (1)	Pt′–N′(2)	2.10 (1)
C(1)–N(2)	1.31 (2)		
P–Pt–Cl	87.8 (2)	P′–Pt′–Cl′	92.0 (2)
N(1)–Pt–Cl	173.2 (3)	N′(1)–Pt′–Cl′	172.5 (4)
N(1)–Pt–P(1)	94.2 (3)	N′(1)–Pt′–P′	95.3 (4)
N(2)–Pt–Cl	96.6 (3)	N′(2)–Pt′–Cl′	89.2 (4)
N(2)–Pt–P(1)	175.7 (3)	N′(2)–Pt′–P′	178.4 (4)
N(2)–Pt–N(1)	81.5 (5)	N′(1)–Pt′–N′(2)	83.5 (5)
Pt–N(2)–C(5)	107.0 (9)	C(2)–C(1)–N(2)	118.4 (15)
Pt–N(2)–C(1)	132.2 (11)	C(3)–C(1)–N(2)	123.0 (14)
C(1)–N(2)–C(5)	120.2 (13)	C(3)–C(1)–C(2)	118.7 (15)

shows, in addition, a strong peak at 1649 cm^{-1}, identified with the C=N stretching.[8]

Imines form stable metal complexes only if the imino group is involved in a chelate ring.[9,10] It has been argued that the basic strength of the C=N bond is too low to permit the formation of stable complexes by simple coordination.[9a] Our finding of equal bond lengths for Pt–N(amine) and Pt–N(imine) in chemically equivalent environments suggests that the reactivity of imine metal complexes is not due to an inherent weakness of the M–N(imine) bond but rather to the susceptibility of the coordinated C=N group to nucleophilic attack.

Acknowledgment. We thank Prof. J. C. Chottard for helpful discussions. J.K. wishes to acknowledge financial support from the Ligue Nationale Française Contre le Cancer.

Registry No. **1**, 15282-39-0; **2**(**3**)·CH_3COCH_3, 115704-90-0; en, 107-15-3; CH_3COCH_3, 67-64-1.

Supplementary Material Available: Tables SI–SIII, listing anisotropic thermal parameters, additional bond distances and angles, and least-squares planes for **2**(**3**)·CH_3COCH_3 (3 pages); Table SIV, listing observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(8) Sandorfy, C. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: New York, 1970; pp 1–60.

(9) (a) Smith, J. W. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: New York, 1970; pp 235–253. (b) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83–214.

(10) Recently, the synthesis of some stable platinum(II) complexes involving monodentate aromatic imine ligands has been reported.[11]

(11) Cross, R. J.; Davidson, M. F.; Rocamora, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1147–1157.

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Synthesis and Characterization of a New Type of Heteropolyanion: Pentamolybdobis(*n*-propylarsonate), Having Two Types of Crystals under the Same pH Conditions in the Same Solution

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Received January 22, 1988

We wish to report the synthesis and structure of a new type of heteropolyanion, $[(RAs)_2Mo_5O_{21}]^{4-}$. Although salts of the anions $[(RP)_2Mo_5O_{21}]^{4-}$ and $[(RAs)_2Mo_6O_{24}]^{4-}$ have been synthesized and characterized since 1975,[1-3] no arsenic complexes analogous to $[(RP)_2Mo_5O_{21}]^{4-}$ have been reported. After the X-ray crystal structure investigation of the two organophosphonate complexes $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]{\cdot}5H_2O$ and $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]{\cdot}5H_2O$, Stalick and Quicksall accounted for the inability to isolate the corresponding As_2Mo_5 ions. They said that the larger covalent radius of arsenic (1.22 vs 1.10 Å for phosphorus) might sterically inhibit the formation of heteropolyanions of this type with molybdenum.[4] In this paper, it is clearly demonstrated that $(RAs)_2Mo_5$ polyanions can be formed in spite of earlier speculations about molecular dimensions.

Experimental Section

As part of a program to explore organic derivatives of heteropoly complexes, we have been able to prepare colorless crystals of both $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_5O_{21}]{\cdot}2H_2O$ and $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_6O_{24}]$ on mixing aqueous solutions of Na_2MoO_4 and $n\text{-}C_3H_7AsO(OH)_2$ (2:1 molar ratio) at pH 4–5 and boiling. These heteropolyanions are highly soluble in water. Tests for cations show that sodium, potassium, cesium, tetramethylammonium, tetraethylammonium, calcium, barium, and magnesium salts are very soluble, but the guanidinium salts can be easily precipitated and separated. After several recrystallizations, we found that two different types of crystals, which can

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† Department of Chemistry.

‡ Center of Analysis and Measurement.

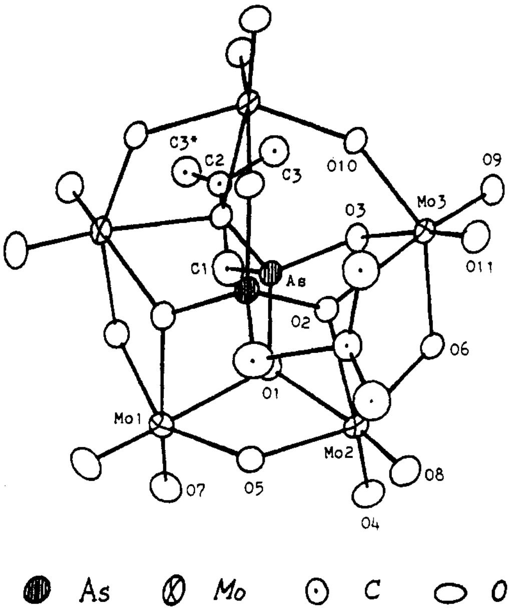

Figure 1. Structure and atomic numbering of the anion of A, $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$.

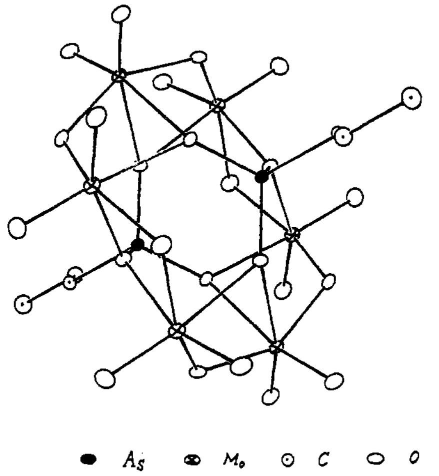

Figure 2. Structure of the anion of B, $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$.

Table I. Atomic Coordinates and Thermal Parameters with Esd's in Parentheses

	x	y	z	B_{eq},[a] Å^2	occ
Mo(1)	0.000	0.02322 (2)	0.250	2.50 (1)	1
Mo(2)	0.25318 (4)	0.09477 (1)	0.31743 (3)	2.234 (7)	1
Mo(3)	0.17437 (3)	0.20999 (1)	0.26967 (3)	1.808 (7)	1
As	0.03434 (4)	0.12824 (2)	0.10658 (3)	1.886 (8)	1
O(1)	0.1104 (3)	0.0839 (1)	0.1757 (2)	2.34 (6)	1
O(2)	0.0987 (3)	0.1424 (1)	0.3394 (2)	2.11 (6)	1
O(3)	0.1219 (3)	0.1776 (1)	0.1149 (2)	2.28 (6)	1
O(4)	0.3543 (3)	0.0606 (1)	0.2564 (3)	3.54 (8)	1
O(5)	−0.1322 (3)	0.0453 (1)	0.1507 (2)	2.65 (6)	1
O(6)	0.2960 (3)	0.1571 (1)	0.2669 (2)	2.23 (6)	1
O(7)	−0.0794 (4)	−0.0145 (1)	0.3214 (3)	3.83 (8)	1
O(8)	0.3260 (3)	0.0983 (1)	0.4383 (3)	3.25 (7)	1
O(9)	0.2457 (3)	0.2522 (1)	0.2025 (2)	2.67 (7)	1
O(10)	0.000	0.2294 (2)	0.250	2.23 (8)	1
O(11)	0.2168 (3)	0.2280 (1)	0.3914 (2)	2.74 (7)	1
O(12)	0.385 (1)	0.0681 (4)	0.6504 (9)	10.0 (3)	0.64
O(12*)	0.449 (2)	0.0992 (8)	0.644 (2)	9.8 (5)	0.36
N(1)	0.5342 (4)	0.1791 (2)	0.3838 (3)	3.11 (9)	1
N(2)	0.6858 (4)	0.1982 (2)	0.5136 (3)	3.6 (1)	1
N(3)	0.4749 (4)	0.2124 (2)	0.5307 (4)	4.7 (1)	1
N(4)	0.5919 (6)	0.0633 (2)	0.4516 (5)	6.0 (1)	1
N(5)	0.7679 (5)	0.0159 (2)	0.4882 (4)	5.2 (1)	1
N(6)	0.6423 (7)	0.0345 (2)	0.6132 (4)	6.5 (2)	1
C(1)	−0.0079 (6)	0.1073 (2)	−0.0310 (4)	3.8 (1)	1
C(2)	−0.0971 (9)	0.1467 (3)	−0.0931 (7)	5.5 (2)	0.78
C(2*)	−0.012 (3)	0.139 (1)	−0.110 (2)	5.2 (6)	0.22
C(3)	−0.045 (2)	0.1844 (6)	−0.116 (1)	8.0 (4)	0.61
C(3*)	−0.148 (2)	0.136 (1)	−0.188 (2)	8.4 (6)	0.39
C(4)	0.5656 (5)	0.1967 (2)	0.4753 (4)	2.9 (1)	1
C(5)	0.6676 (6)	0.0379 (2)	0.5173 (5)	4.4 (1)	1

[a] $B_{eq} = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

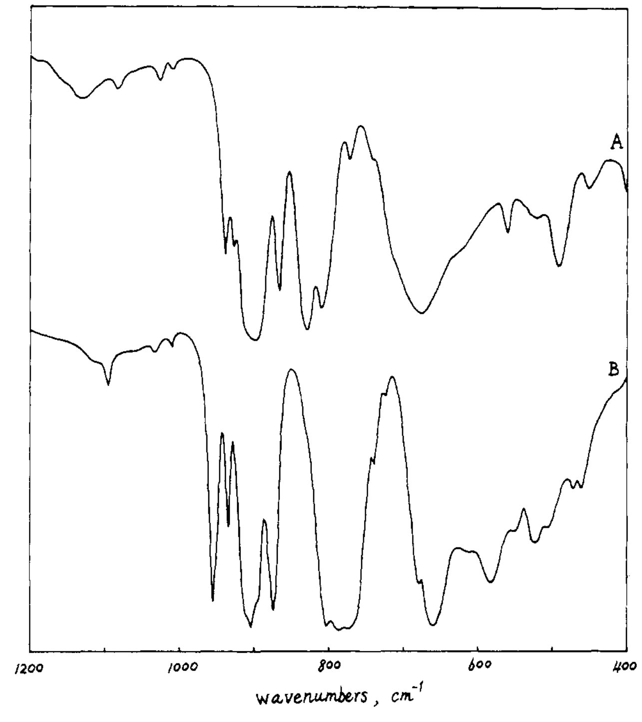

Figure 3. Infrared spectra of compounds A and B.

be easily separated mechanically, are formed under the same pH conditions in the same vessel. Elemental analyses, IR spectra, and single-crystal X-ray diffraction studies revealed that they are two distinct guanidinium salts of the organic derivatives containing different numbers of ring molybdenum atoms.

$(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_5O_{21}]\cdot 2H_2O$ (A) crystallized as monoclinic blocks with the following crystal data: space group $C2/c$, $Z = 4$, $a = 10.653$ (2) Å, $b = 27.966$ (2) Å, $c = 13.277$ (2) Å, $\beta = 96.19$ (1)°. $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_6O_{24}]$ (B) crystallized as large orthorhombic blocks with the following cell dimensions: space group $Cmca$, $Z = 4$, $a = 13.938$ (1) Å, $b = 16.350$ (2) Å, $c = 16.173$ (2) Å. X-ray intensity data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The positions of all Mo and As atoms were found by direct methods. The positions of the non-H atoms were revealed by different Fourier syntheses. The structure was refined by full-matrix least-squares methods, and the final R factors based on 3017 and 2355 observable reflections were 0.025 and 0.047 for compounds A and B, respectively. The anion of A is similar to $[(CH_3P)_2Mo_5O_{21}]^{4-}$ and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ reported by Stalick and Quicksall[4] (see Figure 1). Different from its phosphorus congener, the anion of A possesses 2-fold axis symmetry. It consists of a ring of five MoO_6 octahedra (four edge-shared and one corner-shared) capped on either side by two $n\text{-}C_3H_7As$ groups. The asymmetric unit of the structure contains half a $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$ anion and two $CN_3H_6^+$ cations. Disorder of water molecules and two carbon atoms of the n-propyl group appeared when sequence difference Fourier syntheses were employed to locate the light atoms. Details of the structure for compound A will appear in another publication.[5] The atom positional parameters are listed in Table I. The anion of B is similar to $[(CH_3As)_2Mo_6O_{24}]^{4-}$, reported by Kwak[3] (see Figure 2). Two n-propylarsenic "handles" are

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(1) Kwak, W.; Pope, M. T.; Scully, T. F. *J. Am. Chem. Soc.* **1975**, *97*, 5735.
(2) Pope, M. T.; Quicksall, C. O.; Kwak, W.; Rajkovic, L. M.; Stalick, J. K.; Barkigia, K. M.; Scully, T. F. *J. Less-Common Met.* **1977**, *54*, 129.
(3) Kwak, W.; Rajkovic, L. M.; Stalick, J. K.; Pope, M. T.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 2778.
(4) Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 1577.
(5) Wang, M.; Zheng, P. J.; Liu, B. Y.; Ku, Y. T. *Acta Crystallogr., Sect. C*, in press.

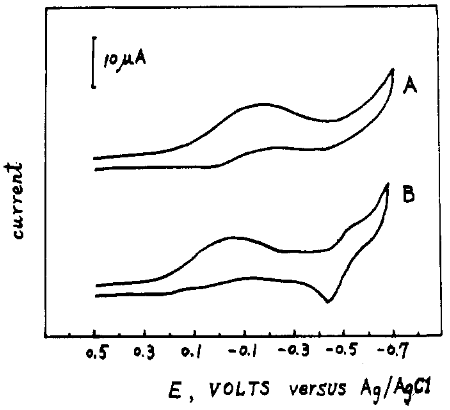

Figure 4. Cyclic voltammograms of 1.43 and 1.22 mM solutions of compounds A and B in 1 M KNO_3 (scan initiated at 0.5 V versus Ag/AgCl in negative direction at 50 mV/s; platinum electrode, area 2.5 mm^2).

attached on either side to a ring of six edge-shared MoO_6 octahedra. It is very interesting that the anion of B has a C_{2h} symmetry,[6] much higher than that of the known hexamolybdobis(methylarsonate) $[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}]\cdot 6H_2O$[3]. Six carbon, two arsenic, and four oxygen atoms are located on the same plane as shown in Figure 2. Details of the structure for compound B can be found in ref 6.

Anal. Calcd for $C_{10}H_{42}N_{12}As_2Mo_5O_{23}$ (compound A): C, 9.04; H, 3.19; N, 12.66; As, 11.28; Mo, 36.12. Found: C, 9.16; H, 3.06; N, 12.80; As, 10.52; Mo, 36.42. Calcd for $C_{10}H_{38}N_{12}As_2Mo_6O_{24}$ (compound B): C, 8.36; H, 2.67; N, 11.71; As, 10.44; Mo, 40.09. Found: C, 8.39; H, 2.61; N, 11.84; As, 9.51; Mo, 41.11.

These two anions have quite different infrared spectra below 1000 cm^{-1} (see Figure 3). The most interesting region is around 760 cm^{-1}, near which the anion of B has a strong absorption while the anion of A has a minimum absorption. The ultraviolet spectra of these two compounds are similar and have no distinguished features.

The thermogravimetry (TG) curves show the thermal decomposition temperature of compound A is 277 °C whereas that of compound B is 300 °C. Compound A lost its two molecules of crystallized water (2.6% of its weight; calculated 2.7%) when heated to 277 °C. Between 277 and 333 °C, it lost 23% of its weight (calculated 22.9%) because of the decomposition of the guanidinium salt. This is an endothermic process. When heated from 330 to 550 °C, it lost its organoarsenic groups (19.6% of its weight; calculated 20.2%). Compound B had no loss of weight below 300 °C. It lost 23.9% of its weight (calculated 23.4%) when heated from 300 to 380 °C. This is also an endothermic decomposition of the guanidinium salt. Between 380 and 450 °C, it lost its organoarsenic groups (16.4% of its weight; calculated 16.4%) and released a great deal of heat. Both final products were MoO_3. Although compound B is more thermostable than compound A, the latter is a rather stable crystal that remains transparent for a long time in the presence of oxygen and moisture.

The cyclic voltammograms (platinum electrode, supporting electrolyte 1 M KNO_3, scan rate 50 mV/s) show that compound A has no redox behavior from −0.7 to +0.5 V but compound B has an almost reversible redox procedure (see Figure 4). It can be found for compound B that at several different scan rates, v, the values of peak potentials are independent of v. The anodic peak potential remains −0.44 V, while the cathodic peak potential remains −0.51 V. Furthermore, as described by the Randles–Sevcik equation, the magnitudes of the peak currents not only increase as $v^{1/2}$ but are directly proportional to the concentrations of compound B as well. It can be seen that this is an almost reversible redox behavior. The formal reduction potential $E°$ is about −0.47 V, and the number of electrons transferred, n, is 1. Although these important parameters of a cyclic voltammogram can be estimated well, it is to be further investigated why compound A has no redox behavior whereas compound B has and which atoms in compound B are responsible for this one-electron transference.

Table II. Distances (Å) between Two Corresponding Oxygen Atoms in the Oxygen Triangle That Accommodates the "Organic Handle" for the $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$, $[(RP)_2Mo_5O_{21}]^{4-}$, and $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$ Anions

	O–O dist		
atoms	$[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$	$[(RP)_2Mo_5O_{21}]^{4-\,a}$	$[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-\,b}$
O(1′)–O(2)	2.75	2.53, 2.54, 2.56	2.82
O(2)–O(3′)	2.68	2.48, 2.52, 2.49	2.80
O(3′)–O(1′)	2.75	2.50, 2.51, 2.56	2.82
av	2.73	2.52	2.81

[a] See ref 4. The first two entries in each row are for anions I and I′, respectively, two crystallographically independent, essentially identical $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions. The third entry in each row is for anion II, $[(NH_3C_2H_4P)_2Mo_5H_{21}]^{2-}$. [b] See ref 5.

n-Propylarsonic acid was purchased from E. Merck. IR measurement was made on a Nicolet FTIR-5DX instrument (KBr pellets). UV spectra were obtained on a Hitachi-557 instrument. Thermogravity curves were obtained on a LCT-2 analyzer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240-C analyzer. Arsenic and molybdenum analyses were performed by the ICP method on a Jarrell-Ash 2000 ICP instrument. The selected wavelengths are λ = 202.3 nm for Mo and λ = 228.8 nm for As.

Discussion

The infrared spectra of compounds A and B are very similar above 1200 cm^{-1} in the N—H, C—H, C=N stretching region. Both of them have very strong absorption peaks near 3400 and 1640 cm^{-1}. However, their different ring structures have a great influence on their IR spectra below 1000 cm^{-1}. The wavenumbers 936, 925, and 895 cm^{-1} in compound A and 953, 933, and 905 cm^{-1} in compound B have been assigned to the molybdenum–oxygen(terminal) stretching frequences. These wavenumbers are located within the 900–950-cm^{-1} region. The differences between them are rather small because the bond lengths of Mo–O_t are all around 1.707 Å in both compounds A and B. The wavenumbers 864, 826, and 806 cm^{-1} in compound A and 873, 801, and 786 cm^{-1} in compound B have been assigned to the arsenic–oxygen stretching frequences. Structural determinations show[5,6] that the As–O bond lengths are 1.75, 1.709, and 1.75 Å in the Mo_6O_{18} ring and 1.696, 1.703, and 1.664 Å in the Mo_5O_{15} ring. The arsenic tetrahedra in compound A must be compressed in order to fit the small Mo_5O_{15} ring. The hypsochromic shifts of absorption peaks in compound A are 20–25 cm^{-1}. This is why compound B has a strong absorption near 760 cm^{-1} while compound A has a minimum absorption. The wavenumbers 673 and 558 cm^{-1} in compound A and 681, 659, and 581 cm^{-1} in compound B have been assigned to the molybdenum–oxygen(bridging) stretching frequences. Structural data show[5,6] that the Mo–O_b bond lengths are 1.924, 1.939, 1.969, 1.970, and 1.926 Å in the Mo_5O_{15} ring and 1.905, 1.910, and 1.943 Å in the Mo_6O_{18} ring. In order to accommodate the larger arsenic atoms, the Mo_5O_{15} ring must be enlarged, especially four of the Mo–O_b bond lengths. The bathochromic shifts of absorption peaks in compound A are 23 cm^{-1}.

In order to determine the effect of the larger arsenic atom on the geometry of the anions, we have compared bond lengths and angles of $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$ with those of $[(RP)_2Mo_5O_{21}]^{4-}$ reported by Stalick and Quicksall.[4] Because the two anions possess different symmetry and different atomic numbering, the corresponding molybdenum, phosphorus, arsenic, and oxygen atoms in each anion have been numbered respectively for clarity as shown in Figure 5.

First, on one side of the ring, the oxygen triangle O(1′)O(2)-O(3′), which accommodates the "organic handle", is quite different in the $(RP)_2Mo_5$, $(RAs)_2Mo_5$, and $(RAs)_2Mo_6$ anions (see Figure 6 and Table II). The average O–O distances are 2.52, 2.73, and 2.81 Å, respectively. It is easily understood that the corresponding oxygen triangle in the $(RAs)_2Mo_6$ anion is the largest one, because it is connected to the Mo_6O_{18} ring. However, the oxygen triangle in the $(RAs)_2Mo_5$ anion is much larger than that in the $(RP)_2Mo_5$ anion, although both triangles are connected to quite similar Mo_5O_{15} rings. In a sense, this triangle can represent the coordination space for phosphorus or arsenic tetrahedra. It can be concluded that this coordination space in the $(RAs)_2Mo_5$ anion must be much larger than that in the $(RP)_2Mo_5$ anion and close to that in the $(RAs)_2Mo_6$ anion. On the other side of the ring

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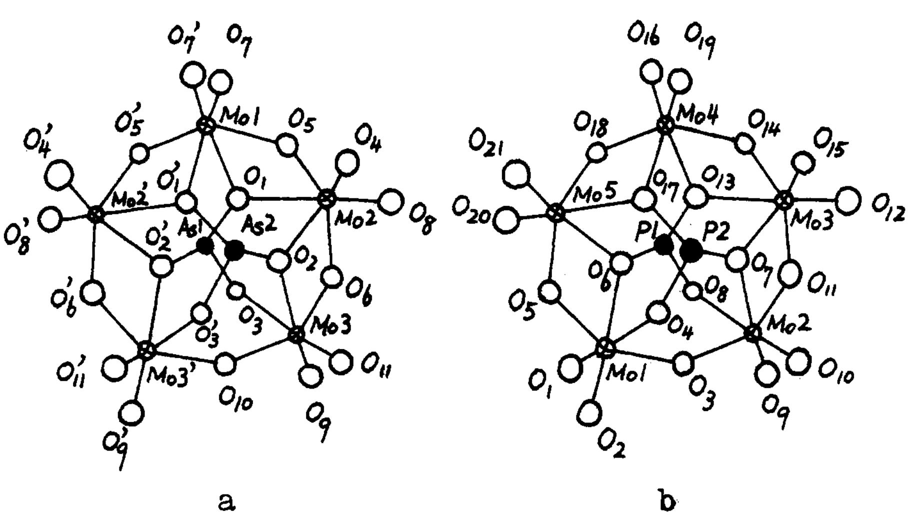
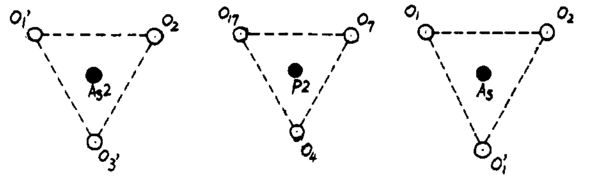
(6) Wang, M.; Zheng, P. J.; Liu, B. Y.; Ku, Y. T. *Acta Phys.-Chim. Sin.* **1987**, *3*, 485.



a b

Figure 5. Stereoscopic view and atomic numbering of the $[(RX)_2Mo_5O_{21}]^{4-}$ anions: (a) X = As; (b) X = P.



a b c

Figure 6. Corresponding oxygen triangles that accommodate the "organic handle" in (a) $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$, (b) $[(RP)_2Mo_5O_{21}]^{4-}$,[4] and (c) $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$.[6]

Table III. Individual and Average Distances (Å) between Corresponding Molybdenum and Bridge Oxygen Atoms in both $[(RAs)_2Mo_5O_{21}]^{4-}$ and $[(RP)_2Mo_5O_{21}]^{4-}$ Anions

	Mo–O$_b$ dist	
atoms	$[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$	$[(RP)_2Mo_5O_{21}]^{4-a}$
Mo(3′)–O(10)	1.926	1.912, 1.926, 1.927
O(10)–Mo(3)	1.926	1.921, 1.923, 1.903
Mo(3)–O(6)	1.970	1.921, 1.925, 1.924
O(6)–Mo(2)	1.939	1.912, 1.946, 1.929
Mo(2)–O(5)	1.969	1.940, 1.948, 1.918
O(5)–Mo(1)	1.924	1.912, 1.924, 1.895
Mo(1)–O(5′)	1.924	1.938, 1.909, 1.889
O(5′)–Mo(2′)	1.969	1.934, 1.948, 1.956
Mo(2′)–O(6′)	1.939	1.928, 1.937, 1.950
O(6′)–Mo(3′)	1.970	1.930, 1.920, 1.921
range	1.924–1.970	1.889–1.956
av	1.946	1.926

[a] See footnote *a* of Table II.

the situation is quite similar. The average O–O distances in the oxygen triangle O(3)O(2′)O(1) are 2.52, 2.73, and 2.81 Å, respectively.

Second, apart from the two oxygen triangles (six oxygen atoms altogether), let us compare the size of the Mo_5O_{15} rings in both $[(RAs)_2Mo_5O_{21}]^{4-}$ and $[(RP)_2Mo_5O_{21}]^{4-}$ anions. As shown in Figure 5, the dimensions of the rings are mainly determined by 10 bond lengths between five molybdenum atoms and five bridge oxygen atoms. Table III lists the 10 individual Mo–O$_b$ distances in two Mo_5O_{15} rings. In the former, the Mo–O$_b$ bond lengths range from 1.924 to 1.970 Å, the average being 1.946 Å, while in the latter the Mo–O$_b$ bond lengths range from 1.889 to 1.956 Å, the average being 1.926 Å. It is noticed that Mo(2)–O(5), Mo(3)–O(6), Mo(2′)–O(5′), and Mo(3′)–O(6′) are especially long, reaching 1.969, 1.970, 1.969, and 1.970 Å, respectively. It is obvious that the Mo_5O_{15} ring in the $[(RAs)_2Mo_5O_{21}]^{4-}$ anion is markedly larger than that in the $[(RP)_2Mo_5O_{21}]^{4-}$ anion. In view of the fact that the larger Mo_5O_{15} ring can be formed to accommodate the larger arsenic atom, the MoO_6 octahedra must be further distorted in order to lower the energy of the whole system.

Table IV. Selected Bond Angles (deg) about As for the $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$, $[(RP)_2Mo_5O_{21}]^{4-}$, and $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$ Anions

	angles about As		
atoms	$[(n\text{-}C_3H_7As)_2\text{-}Mo_5O_{21}]^{4-}$	$[(RP)_2Mo_5O_{21}]^{4-a}$	$[(n\text{-}C_3H_7As)_2\text{-}Mo_6O_{24}]^{4-b}$
O(1′)–As(2)–O(2)	108.2	110.7, 110.8, 111.3	109.0
O(1′)–As(2)–O(3′)	109.8	110.1, 111.0, 113.5	111.0
O(2)–As(2)–O(3′)	105.4	109.3, 109.8, 108.5	110.0
av	107.8	110.6	110.4

[a] See footnote *a* of Table II. [b] See ref 5.

Third, the Mo_5O_{15} ring also has an effect on the organoarsenic tetrahedra. Table IV lists corresponding O–As–O angles for $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$, $[(RP)_2Mo_5O_{21}]^{4-}$, and $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$ anions. A comparison of the bond angles O–As–O in compound A with those in compound B shows that the mean bond angle of compound A is less than the angle of the regular tetrahedron (109°28′), while the mean bond angle of compound B is larger than the regular value. Also in the $(RP)_2Mo_5$ and $(CH_3As)_2Mo_6$ anions, the average bond angles O–P–O and O–As–O are 110.6 and 111.1°, respectively. Both are larger than the regular value. Thus, the tetrahedral $n\text{-}C_3H_7AsO_3$ group in compound A has been distorted. Now we can see the effect of the larger arsenic atom on the Mo_5O_{15} ring and vice versa: on one hand, the Mo_5O_{15} ring has been enlarged to accommodate two larger arsenic groups, and on the other hand, the organoarsenic groups have been slightly compressed to fit in the Mo_5O_{15} ring.

It appears that a new stable system is formed by further distortion of the MoO_6 octahedra and slightly compressed organoarsenic tetrahedra. In previous views it was stated that while phosphorus atoms always prefer the $(RP)_2Mo_5$ structure, the larger arsenic atoms always prefer the $(RAs)_2Mo_6$ structure. Now it is possible to synthesize $(RAs)_2Mo_5$ type complexes under certain conditions. We have tested the reaction of Na_2MoO_4 with $n\text{-}C_3H_7AsO(OH)_2$ at the normal molar ratio (Mo/As = 3) many times. In this case, only the $(RAs)_2Mo_6$ compound has been obtained. Knowledge of the structure of the new system $(RAs)_2Mo_5$ should help us to understand why both compounds A and B can be obtained in the same vessel. We hope that some other compounds belonging to the $[(RAs)_2Mo_5O_{21}]^{4-}$ type will soon be synthesized and characterized.

Registry No. $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_5O_{21}]\cdot 2H_2O$, 109827-04-5; $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_4O_{26}]$, 112065-68-6; Na_2MoO_4, 7631-95-0; $n\text{-}C_3H_7AsO(OH)_2$, 107-34-6.

Supplementary Material Available: Tables of thermal parameters and bond angles and distances associated with the torsional angles for compound A (4 pages); a table of calculated and observed structure factors for compound A (15 pages). Ordering information is given on any current masthead page. Data for compound B can be found in ref 6.