

Dodecamolybdotetrakis(organoarsonates) and the Structure of a Neutral Zwitterionic Heteropoly Complex¹

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Several salts of the heteropoly molybdoarsonate anions $[(\text{RAs})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$ ($\text{R} = \text{CH}_3$, C_6H_5 , $p\text{-C}_6\text{H}_4\text{NH}_3^+$, $\text{C}_2\text{H}_4\text{OH}$) have been prepared and characterized by spectroscopic techniques. The derivative with $\text{R} = p\text{-C}_6\text{H}_4\text{NH}_3^+$ is stable to at least 250 °C and shows anomalous solubility behavior in mixed solvents. The structure of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 6\text{H}_2\text{O} \cdot 10\text{CH}_3\text{CN}$ (*Fdd*2, $a = 38.916$ (6) Å, $b = 38.972$ (7) Å, $c = 11.901$ (2) Å, $Z = 8$) has been determined by single-crystal X-ray diffraction and refined to final consistency indices R and R_w of 0.069 and 0.062, respectively. The metal oxide portion of the structure is similar to that in $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{46} \cdot 4\text{H}_2\text{O}$ and consists of four groups of three MoO_6 octahedra, which share edges within each group and corners with neighboring groups. The octahedra are bridged by four tetrahedral $p\text{-H}_3^+\text{NC}_6\text{H}_4\text{As}$ groups. The complexes are held together by H_2O molecules, which are presumably hydrogen bonded to the nitrogens of the organic groups, and by CH_3CN molecules, which lie in diagonal rows between the complexes.

Introduction

The incorporation of covalently bound organic groups into the heteropoly framework²⁻⁹ has produced a variety of species such as $[(\text{CH}_3)_2\text{AsMo}_4\text{O}_{15}\text{H}]^{2-}$,³ $[\text{BW}_{11}\text{O}_{39}(\text{C}_4\text{H}_9\text{Sn})]^{6-}$,⁴ $[(\text{C}_6\text{H}_5\text{As})_2\text{W}_6\text{O}_{25}\text{H}]^{5-}$,⁵ $[(\text{C}_6\text{H}_5)_2\text{Fe}(\text{CO})_2\text{Ge}]_2\text{W}_{11}\text{PO}_{40}]^{3-}$,⁶ $\alpha\text{-}[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{PW}_{11}\text{O}_{39})]^{4-}$,^{6,7} $[(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{25}\text{H}_2]^{4-}$,⁸ and $[(\text{NH}_3\text{C}_2\text{H}_4\text{P})_2\text{Mo}_5\text{O}_{21}]^{4-}$.⁹ These anions cover a wide range of stoichiometries and contain a diversified selection of heteroatom and organic groups. As derivatives of metal oxides with surface bound organic groups, these complexes are expected to show properties of both "ionic" metal oxides and covalent organic groups. We present here the synthesis and spectroscopic characterization of a series of organometalates having the general formula $[(\text{RAs})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$. Because the complex $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 6\text{H}_2\text{O} \cdot 10\text{CH}_3\text{CN}$ exhibited the dual ionic-covalent nature, we have determined its structure by X-ray diffraction. Complexes with this stoichiometry were prepared first by Debray¹⁰ and Rosenheim¹¹ and studied later by Contant.¹² An X-ray structure of $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{46} \cdot 4\text{H}_2\text{O}$ has been carried out by Sasaki.¹³ Filowitz and Klemperer have reported the ¹⁷O NMR spectrum of the phenyl derivative.¹⁴

Experimental Section

Preparation of Complexes. Dodecamolybdotetrakis(methylarsonate), ammonium salt, was obtained by slow addition of concentrated HNO_3 (2 mL, 0.03 mol) to a boiling solution of disodium methylarsonate (1.8 g) and ammonium heptamolybdate (5.5 g) in 50 mL of water. White microcrystals of the product were obtained

by partial evaporation of the solvent. These were recrystallized from hot dilute HNO_3 (pH 0.5). Anal. Calcd for $\text{C}_4\text{H}_{28}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{46} \cdot 16\text{H}_2\text{O}$: Mo, 44.17; H₂O, 11.04. Found: Mo, 44.07; H₂O, 10.67. The tetra-*n*-butylammonium (TBA) salt was prepared by addition of a solution of Bu_4NHSO_4 (3.2 g in 50 mL of water) to the hot reaction mixture described above. The precipitated salt was washed with water and recrystallized from acetonitrile. Anal. Calcd for $\text{C}_{68}\text{H}_{156}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{46}$: C, 25.37; H, 4.89; N, 1.74; As, 9.31; Mo, 35.81. Found: C, 25.60; H, 4.91; N, 1.80; As, 9.22; Mo, 36.08. Ammonium and TBA salts of the phenylarsonate derivative were prepared from phenylarsonic acid by an analogous procedure employing a larger volume of solution (300 mL). Both salts are anhydrous. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{46}$: C, 11.22; H, 1.41; N, 2.18; As, 11.67; Mo, 44.86. Found: C, 11.25; H, 1.54; N, 2.04; As, 11.87; Mo, 44.93. Calcd for $\text{C}_{88}\text{H}_{164}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{46}$: C, 30.48; H, 4.77; N, 1.62; As, 8.65; Mo, 33.25. Found: C, 29.24; H, 4.57; N, 1.57; As, 8.48; Mo, 33.17. The *p*-aminophenylarsonate derivative was isolated as a beige precipitate from a boiling solution of *p*-aminophenylarsonic acid (2.5 g) and sodium molybdate (7.3 g) in 300 mL of water that had been slowly acidified to pH 0.5 with concentrated HNO_3 . The product was recrystallized from hot 50% aqueous acetonitrile and afforded efflorescent pink-yellow needles. Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{46} \cdot 11\text{H}_2\text{O}$: C, 10.44; H, 1.83; N, 2.03; As, 10.86; Mo, 41.77; H₂O, 7.18. Found (air-dried material): C, 10.30; H, 2.06; N, 2.11; As, 10.03; Mo, 41.96; H₂O, 7.09. The TBA salt of the 2-hydroxyethylarsonate derivative was precipitated from a hot acidified (pH 0.5) solution of 2.1 g of $\text{HOCH}_2\text{CH}_2\text{AsO}_3\text{H}_2$ and 7.3 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 100 mL of water by addition of Bu_4NHSO_4 (3.2 g in 50 mL). Large colorless but photosensitive and efflorescent crystals were obtained upon recrystallization from hot acetonitrile. Anal. Calcd for $\text{C}_{72}\text{H}_{164}\text{N}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}$: C, 25.89; H, 4.95; N, 1.68; As, 8.98; Mo, 34.52. Found: C, 25.83; H, 4.88; N, 1.80; As, 8.94; Mo, 34.58. Tributylammonium, tetraphenylarsonium, and tetraphenylphosphonium salts of the same anion were isolated by analogous procedures. Ammonium dodecamolybdotetraarsonate, $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{46} \cdot 4\text{H}_2\text{O}$, was prepared by the method of Debray¹⁰ and Sasaki.¹³ The TBA salt was obtained by precipitation from aqueous solution and recrystallization from acetonitrile.

Analyses. Carbon, hydrogen, nitrogen, arsenic, and molybdenum analyses were performed as described previously.^{9a}

Physical Measurements. Spectroscopic and electrochemical measurements were carried out as previously reported.^{9a}

X-ray Structure Determination of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$. Initial batches of pinkish yellow material were found to be amorphous from X-ray photographs. However, material maintained in acetonitrile-water mother liquor appeared crystalline but quickly transformed into pinkish yellow opaque flakes upon removal. Suitable crystals were finally grown from a solution of 9% water and 81% acetonitrile by volume at 25 °C. Since the crystals required the presence of mother liquor, a specimen $0.5 \times 0.3 \times 0.1$ mm was sealed in a Lindemann glass capillary tube with a drop of solution. From Weissenberg photographs of the *h*k0, *h*k1, and *h*k2 layers, the Laue symmetry was determined to be *mmm* and the space group *Fdd*2, No. 43. Since the obvious symmetry was fourfold, the

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Table I. Crystal Data for
 $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$

space group $Fdd2$	$\rho_{\text{calcd}} = 2.27 \text{ g/cm}^3$
$Z = 8$	ρ_{obsd} not measurable
$a = 38.913 (6) \text{ \AA}$	$V = 180.48 \text{ \AA}^3$
$b = 38.972 (7) \text{ \AA}$	$fw = 2817$
$c = 11.901 (2) \text{ \AA}$	$\mu = 32.2 \text{ cm}^{-1}$

^a The standard error in parentheses refers to the last decimal place given in this and successive tables.

space group determination was not straightforward and the only apparent breakdown was a single, seemingly extraneous reflection. In addition, the a and b crystallographic axes were equal within experimental measurement. Throughout the determination, the occurrence of fourfold pseudosymmetry plagued facile solution and refinement.

The same crystal used for Weissenberg photography was mounted on the Picker FACS-I diffractometer. During the month of data collection, the color of the crystal changed from yellow to deep amber. Subsequent Weissenberg photography, however, showed that the crystal had not decomposed. One octant of data was collected to $2\theta_{\text{max}} = 50^\circ$ with use of Mo $K\alpha$ radiation, $\lambda = 0.70930 \text{ \AA}$. Systematically absent reflections $h00$ ($h = 4n + 1$), $0k0$ ($k = 4n + 1$) and $00l$ ($l = 4n + 1$) were not measured. Peaks were scanned from 1° below the $K\alpha_1$ peak to 1° above the $K\alpha_2$ peak at a takeoff angle of 2.0° . The background was measured for 10 s on each side of the peak. Three reflections were monitored after every 100 reflections, and these reflections fluctuated by as much as 10% due to uncontrollable temperature variations. During data collection, the counting chain malfunctioned, which led us to scale the two partial data sets differently. In total, 4437 data were measured and treated as described in our previous paper.^{3b} Of these, 2714 having $I \geq 2\sigma(I)$ were used in the solution and refinement of the structure. A linear absorption coefficient, 29 cm^{-1} , was calculated, but no absorption corrections were applied, since the crystal faces were barely recognizable when data collection was completed.

Cell constants were determined from a least-squares fit of the $+2\theta$ value of 20 reflections having $2\theta \geq 35^\circ$ with use of Mo $K\alpha$ radiation, $\lambda = 0.71070 \text{ \AA}$. An experimental density was measured several times in a mixture of CCl_4 and 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$. Observed values ranged from 1.7 to 2.45 g/cm^3 , presumably due to occlusion of the solvents by the crystals (vide infra). Crystal data are presented in Table I.

Solution and Refinement of the Structure.¹⁵ Since the molecule contains a twofold axis that passes through two corner-sharing octahedra, $1/2 + 1$ of the atoms are crystallographically independent. Initial attempts to solve the structure by the heavy-atom method were unsuccessful since the Patterson map showed one group of three octahedra to be exactly related to the other by a $\bar{4}$ axis. The structure was correctly solved by direct methods using the MULTAN series of programs. A total of 213 reflections were selected for which $E \geq 1.50$; an E map was computed by using the set of signs with the highest figures of merit, and this revealed the positions of the six Mo and two As atoms. The major difference between the correct positions and those calculated from the Patterson map is the lack of exact $\bar{4}$ symmetry between the two groups of Mo atoms. On the basis of the positions of the eight heavy atoms, a structure factor calculation was carried out, in which the atomic scattering factors were taken from standard sources.¹⁶ The values of for the anomalous corrections were also taken from standard tabulations.¹⁷

The structure was refined by least-squares techniques, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w was taken as $1/\sigma_F^2$ and F_o and F_c are the observed and calculated structure factor amplitudes. After exhaustive full-matrix least-squares refinement in which the Mo and As atoms were treated anisotropically, O and solvent isotropically, and the $p\text{-H}_3\text{NC}_6\text{H}_4$ groups as rigid bodies,¹⁸ the final values of R and R_w , where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$, were 0.069 and 0.062, respectively. A

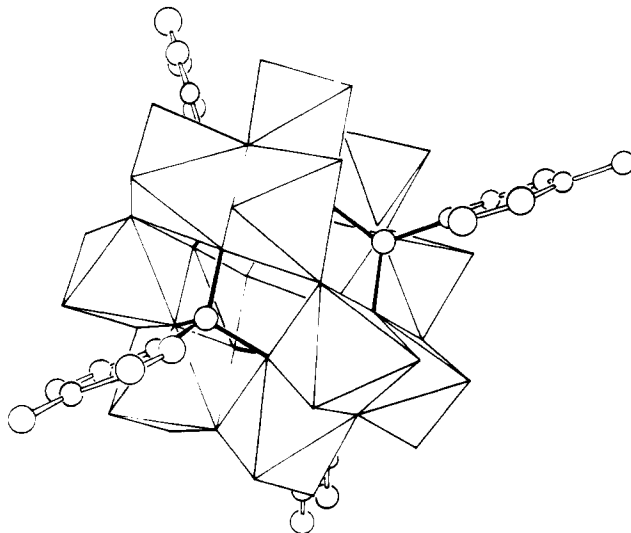
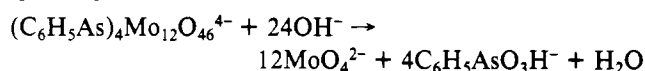


Figure 1. Structure of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 6\text{H}_2\text{O} \cdot 10\text{CH}_3\text{CN}$ as an assemblage of MoO_6 octahedra.

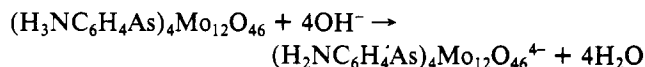
final difference map indicated no density greater than $0.4 \text{ e/\AA}^3$. The final positional and thermal parameters for the nongroup atoms are presented in Table II, while the rigid group parameters are given in Table III. A table of the final values of $|F_o|$ and $|F_c|$ is available as supplementary material.

Results and Discussion

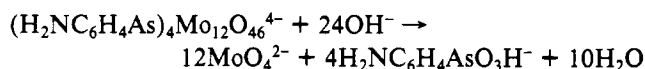
The dodecamolybdates are formed in aqueous solution at pH values less than 1 from stoichiometric mixtures of the appropriate arsonic acid and sodium molybdate. Solutions of the complexes display a UV maximum at $\sim 250 \text{ nm}$ with $\epsilon_{\text{max}} \sim 8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, similar to that observed for $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{4-}$,^{9a} $[(\text{RAS})_2\text{Mo}_6\text{O}_{24}]^{4-}$,¹⁹ $[\text{R}_2\text{AsMo}_4\text{O}_{15}\text{H}]^{2-}$,^{3a,b} and $[\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}]^{4-20}$ anions. A potentiometric titration of $(\text{NH}_4)_4[(\text{C}_6\text{H}_5\text{As})_4\text{Mo}_{12}\text{O}_{46}]$ with sodium hydroxide gives a single end point with 24.19 ± 0.15 mequiv of base corresponding to the reaction



For $[(\text{H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]$, two end points are observed, the first at 3.76 ± 0.15 mequiv of base and the second at 28.09 ± 0.15 mequiv of base in accord with the reactions



and



The existence of the first reaction, $pK = \text{ca. } 3$, confirms the zwitterionic nature of the complex.

IR spectra recorded in KBr matrices show characteristic bands in the $1000\text{--}600\text{-cm}^{-1}$ region for the molybdenum-oxygen and arsenic-oxygen stretching modes. The positions and intensities of these bands are slightly dependent on cation, organic group, and recrystallization medium and are summarized in Table IV. Additional bands are observed for the organic groups and cations, and include $\nu(\text{As-C}_{\text{alkyl}})$, $1265\text{--}1270 \text{ cm}^{-1}$, and $\nu(\text{As-C}_{\text{aryl}})$, $1088\text{--}1093 \text{ cm}^{-1}$.

The NMR spectrum of a saturated solution of $(\text{Bu}_4\text{N})_4[(\text{HOC}_2\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]$ in dichloromethane gives two triplets at 3.12 and 4.37 ppm for the ethyl protons of the organic

(15) Programs used for the structure solution and refinement included local modifications of the ALFF Fourier program by Hubbard, Quicksall, and Jacobson, MULTAN by Main et al., ORFLS by Busing, Levy, and Martin, ORFF2 by Busing and Levy, and ORTEP2 by Johnson.

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Table II. The Final Positional and Thermal Parameters for $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]\cdot 10\text{CH}_3\text{CN}\cdot 6\text{H}_2\text{O}$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.06057 (6)	0.08084 (5)	0.04700	4.0 (2)	2.8 (1)	36 (2)	-0.5 (1)	0.3 (6)	1.1 (5)
Mo(2)	0.00201 (6)	0.00336 (5)	0.0506 (3)	2.9 (2)	4.2 (2)	38 (2)	-0.1 (2)	2.2 (5)	1.2 (5)
Mo(3)	0.04307 (6)	0.02107 (5)	-0.1532 (3)	4.3 (2)	4.2 (2)	23 (2)	-0.6 (2)	0.4 (5)	0.2 (4)
Mo(4)	0.08189 (6)	-0.05976 (5)	0.2765 (2)	3.3 (2)	3.3 (2)	37 (2)	0.5 (1)	-0.1 (5)	1.5 (4)
Mo(5)	-0.00334 (6)	0.10064 (5)	0.2722 (2)	4.1 (2)	2.7 (1)	36 (2)	-0.2 (1)	-0.8 (5)	1.3 (4)
Mo(6)	0.02211 (6)	-0.04219 (5)	0.4767 (3)	4.0 (2)	3.5 (2)	27 (2)	0.1 (2)	-0.8 (5)	1.3 (4)
As(1)	0.05333 (7)	0.02807 (6)	0.3012 (3)	2.5 (2)	2.8 (2)	26 (2)	0.2 (2)	-0.8 (6)	-0.2 (5)
As(2)	0.02707 (7)	-0.05356 (6)	0.0201 (3)	2.9 (2)	2.3 (1)	27 (2)	0.1 (2)	0.9 (6)	0.1 (5)

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
O(1)	0.0150 (4)	0.0483 (3)	-0.005 (1)	1.1 (3)	O(19)	-0.1904 (4)	-0.1192 (4)	0.381 (1)	2.7 (4)
O(2)	0.0792 (4)	0.0405 (4)	-0.046 (1)	1.5 (3)	O(20)	0.0294 (4)	-0.1342 (4)	0.228 (2)	2.7 (4)
O(3)	0.0	0.0	-0.179 (2)	2.5 (5)	O(21)	0.0947 (4)	-0.0992 (4)	0.231 (2)	2.9 (4)
O(4)	0.0711 (4)	-0.0030 (4)	-0.229 (1)	3.2 (4)	O(22)	0.0150 (4)	0.0479 (3)	0.324 (1)	1.6 (3)
O(5)	0.1358 (5)	0.0289 (4)	0.097 (2)	3.2 (4)	O(23)	0.0486 (4)	-0.0142 (3)	0.327 (1)	1.3 (3)
O(6)	0.0992 (4)	0.0947 (4)	0.094 (1)	2.6 (4)	O(24)	0.0394 (4)	0.0575 (4)	-0.229 (2)	3.1 (4)
O(7)	0.0644 (4)	0.0345 (4)	0.165 (1)	1.9 (3)	Aq(1)	0.2202 (7)	0.0251 (7)	0.072 (3)	9.3 (7)
O(8)	0.0318 (4)	0.0986 (4)	0.160 (1)	1.8 (3)	Aq(2)	0.2256 (6)	0.0776 (5)	0.751 (2)	6.5 (6)
O(9)	0.1199 (5)	-0.0191 (4)	-0.057 (2)	3.2 (4)	Aq(3)	0.1546 (7)	0.0334 (6)	0.795 (2)	8.2 (6)
O(10)	0.0490 (4)	-0.0155 (3)	-0.006 (1)	1.5 (3)	C1Ac1	0.093 (1)	0.157 (1)	0.285 (3)	5.6 (8)
O(11)	0.0989 (4)	-0.0307 (4)	0.164 (1)	2.3 (3)	C2Ac1	0.069 (1)	0.183 (1)	0.324 (3)	5.4 (8)
O(12)	0.0345 (4)	-0.0657 (3)	0.155 (1)	1.2 (3)	NAc1	0.050 (1)	0.204 (1)	0.368 (4)	11 (1)
O(13)	0.0	0.0	0.501 (2)	2.4 (5)	C1Ac2	0.011 (1)	0.181 (1)	0.050 (4)	9 (1)
O(14)	-0.0024 (4)	-0.0700 (4)	0.553 (1)	2.7 (4)	C2Ac2	0.026 (2)	0.213 (2)	0.044 (6)	15 (2)
O(15)	0.0414 (4)	-0.0777 (3)	0.367 (1)	1.6 (3)	NAc2	0.039 (2)	0.241 (2)	0.055 (6)	21 (2)
O(16)	0.1097 (5)	-0.0514 (4)	0.385 (2)	3.5 (4)	C1Ac3	0.182 (1)	-0.005 (1)	0.344 (4)	9 (1)
O(17)	0.0587 (4)	-0.0381 (4)	0.554 (2)	2.9 (4)	C2Ac3	0.195 (2)	0.010 (2)	0.445 (6)	14 (2)
O(18)	0.0515 (4)	0.1083 (4)	-0.058 (2)	3.0 (4)					

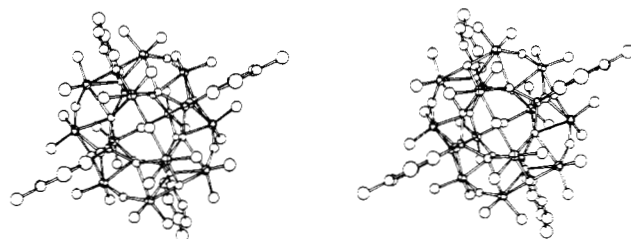
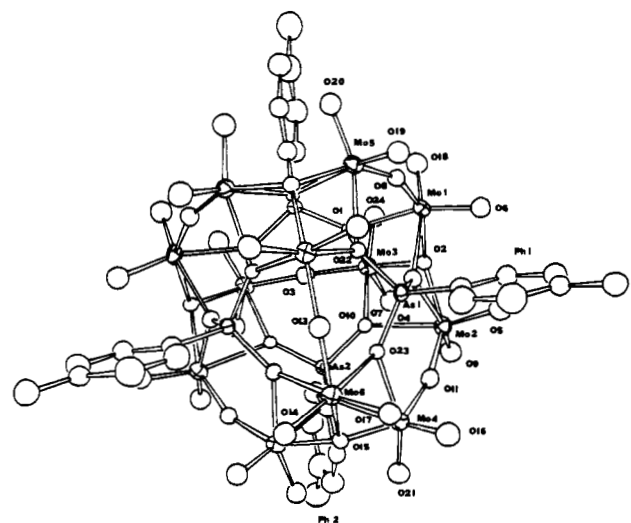
Table III. Rigid-Group Parameters for $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]\cdot 10\text{CH}_3\text{CN}\cdot 6\text{H}_2\text{O}$

atom	x	y	z	B, Å ²
Ph1C1 ^a	0.0863	0.0466	0.3964	2.5 (5)
Ph1C2	0.1164	0.0617	0.3514	2.5 (5)
Ph1C3	0.1422	0.0744	0.4241	2.9 (6)
Ph1C4	0.1382	0.0719	0.5422	2.3 (5)
Ph1C5	0.1081	0.0567	0.5871	4.5 (7)
Ph1C6	0.0823	0.0441	0.5145	3.9 (7)
Ph1N	0.1654	0.0853	0.6190	3.1 (5)
Ph2C1 ^b	0.0434	-0.0886	-0.0769	2.7 (6)
Ph2C2	0.0590	-0.1181	-0.0308	2.6 (6)
Ph2C3	0.0664	-0.1465	-0.1002	3.7 (7)
Ph2C4	0.0583	-0.1456	-0.2163	4.9 (8)
Ph2C5	0.0427	-0.1160	-0.2625	4.2 (7)
Ph2C6	0.0353	-0.0876	-0.1930	3.3 (6)
Ph2N	0.0662	-0.1756	-0.2897	5.2 (6)

^a This atom is the group origin. The group angles are $\phi = 63.8 (4)^\circ$, $\theta = 37.6 (4)^\circ$, and $\rho = 90.8 (7)^\circ$. ^b This atom is the group origin. The group angles are $\phi = 165.4 (5)^\circ$, $\theta = -35.7 (4)^\circ$, and $\rho = 104.0 (7)^\circ$.

groups. These are shifted 0.3 ppm downfield with respect to the triplets in free 2-hydroxyethylarsonic acid at 2.81 and 4.04 ppm. Similar downfield shifts on complexation of the acid were found for the $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{4-9a}$ and $[\text{R}_2\text{AsMo}_4\text{O}_{15}\text{H}]^{2-3b}$ anions.

The X-ray results for $[(p\text{-H}_3\text{NC}_6\text{H}_7\text{As})_4\text{Mo}_{12}\text{O}_{46}]\cdot 10\text{CH}_3\text{CN}\cdot 6\text{H}_2\text{O}$ show that it is composed of four groups of three MoO_6 octahedra that are bridged by four $p\text{-H}_3\text{NC}_6\text{H}_4$ moieties. Within each group, the octahedra share edges, and they share corners between groups as depicted in Figure 1. This determination confirms the hypothesized zwitterionic nature of the complex, since no cations were located. The structure of the metal oxide core is similar to that in $(\text{N-H}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{46}\cdot 4\text{H}_2\text{O}$ and may be viewed as an inverted Keggin structure.²¹ As in the Keggin structure the oxygen atoms form a close-packed arrangement, which in the present case is centered on a missing oxygen atom. The central cavity

**Figure 2.** View of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]\cdot 6\text{H}_2\text{O}\cdot 10\text{CH}_3\text{CN}$ looking down the pseudo-4 axis.**Figure 3.** Atomic numbering scheme for $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]\cdot 6\text{H}_2\text{O}\cdot 10\text{CH}_3\text{CN}$.

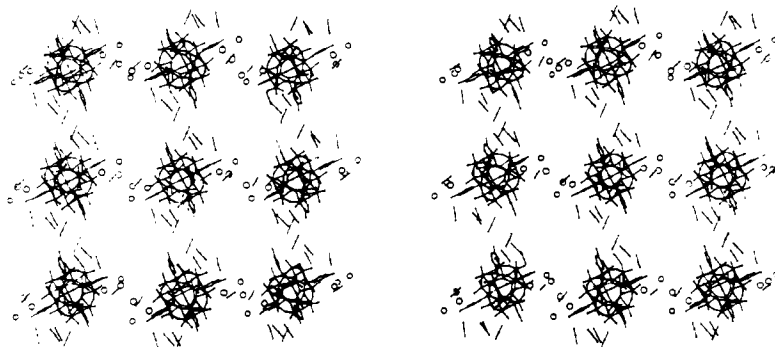
of the structure has a radius of 1.4 Å but appears to be empty in both Sasaki's and our structure.

Except for the $p\text{-H}_3\text{NC}_6\text{H}_4$ groups, the molecule possesses a pseudo-4 axis. A view down this axis is shown in Figure 2, and the atomic numbering scheme is displayed in Figure 3. The presence of this pseudosymmetry prevented the successful solution of the structure by the heavy-atom method.

Table IV. Metal–Oxygen IR Frequencies (cm^{-1}) for $[(\text{RAs})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$ ^a

R							
OH		CH ₃		C ₆ H ₅		CH ₂ CH ₂ OH	C ₆ H ₄ NH ₂
NH ₄ ⁺	[N(C ₄ H ₉) ₄] ⁺	NH ₄ ⁺	[N(C ₄ H ₉) ₄] ⁺	NH ₄ ⁺	[N(C ₄ H ₉) ₄] ⁺	[N(C ₄ H ₉) ₄] ⁺	H ⁺
992 sh	898 m	991 w	989 m	980 sh	978 sh	993 sh	983 sh
					973 s	972 w	
966 m	960 s	964 s	956 s	954 s	950 s	945 s	957 m
938 m	934 s	937 s	935 s	925 s		916 s	930 m
880 s	882 sh		890 vs				
	867 sh	870 vs		870 sh	867 vs		870 s
		860 sh				860 sh	
				840 s	840 sh	840 sh	850 sh
806 sh	814 w		812 w				
	783 w					795 m	
	745 sh		750 w	748 w	742 w	735 sh	
710 sh		685 m	690 w	690 w	687 w		
			640 w			665 m	

^a Abbreviations: s = strong; v = very; b = broad; m = medium; w = weak; sh = shoulder.

Figure 4. Stereoscopic view of the unit cell of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 6\text{H}_2\text{O} \cdot 10\text{CH}_3\text{CN}$.

The metal to oxygen distances, given in Table V, fall into four categories. For the terminal oxygens, O(4), O(5), O(6), O(9), O(14), O(16), O(17), O(18), O(19), O(21), and O(24), the average Mo–O distance is 1.71 Å. The average for the doubly shared oxygens, O(3), O(8), O(11), and O(13), is 1.89 Å. For O(15) and O(12), the mean is 2.05 Å, while for O(1), O(7), O(10), O(12), O(22), and O(23), the average length is 2.30 Å. The corresponding metal to oxygen distances in $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50} \cdot 4\text{H}_2\text{O}$ ¹³ are 1.68, 1.88, 2.03, and 2.29 Å, respectively.

The geometry about the arsenic atom does not deviate significantly from tetrahedral, with a mean bond angle of 109.5°. The As–O bond lengths average 1.70 Å, in agreement with those in $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50} \cdot 4\text{H}_2\text{O}$ ¹³ and also with those in uncoordinated *p*-aminophenylarsonic acid (1.73 Å).²² The average As–C is 1.87 Å in the complex as compared to 1.95 Å in the acid.²²

The bifunctional nature of the complex is clearly indicated in the packing diagram, Figure 4, as both acetonitrile and water molecules crystallize with the molecule. The water molecules tend to agglomerate near the $p\text{-H}_3^+\text{NC}_6\text{H}_4$ groups, presumably to form a hydrogen-bonded network. Distances of the water molecules to the nitrogens of the complex are given in Table VI. The acetonitrile molecules, in diagonal rows between the complexes, remain separate from the water molecules and appear to cement the complex molecules together.

This complex is only the second known example of a neutral zwitterionic heteropoly. The first so characterized is $[(\text{en})_2\text{H}_2\text{CoOPO}_3]_2\text{Mo}_5\text{O}_{15} \cdot 8\text{H}_2\text{O}$ and is totally insoluble as such.²³ In contrast, the molybdoarsonate, perhaps by virtue

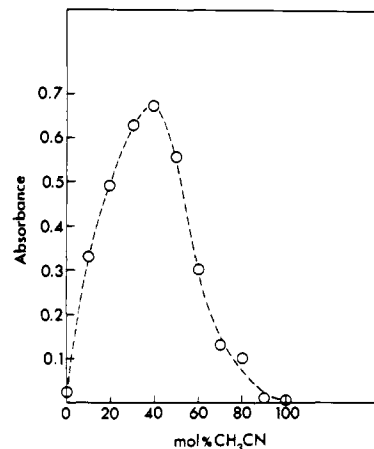


Figure 5. Relative absorbance at 250 nm of saturated solutions of $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]$ in water–acetonitrile mixtures at 25 °C. In separate experiments the extinction coefficient at 250 nm was found to be independent of solvent composition. The maximum shown corresponds to a solubility of 3.53×10^{-2} M.

of its novel octupolar charge distribution, is soluble in both water and acetonitrile to the extent of ca. 10^{-4} M at room temperature. The solubility rises to about 10^{-2} M at 70 °C. A highly unusual cooperative solvation was observed in mixtures of water and acetonitrile as shown in Figure 5. In such mixtures the solubility is increased by up to two orders of magnitude. At 25 °C for example, the maximum solubility (0.035 M) occurs in 40 mol % acetonitrile. Quantitatively similar results were observed with water–methylene chloride, –nitromethane, and –methanol mixtures. This behavior is undoubtedly connected with the existence of both polar and nonpolar domains on the surface of the complex. Selective

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Table V. Selected Distances (Å) for $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$

For Terminal Oxygens			
Mo(1)–O(18)	1.68 (2)	Mo(4)–O(21)	1.71 (2)
Mo(1)–O(6)	1.69 (2)	Mo(4)–O(16)	1.72 (2)
Mo(2)–O(9)	1.70 (2)	Mo(5)–O(19)	1.72 (2)
Mo(2)–O(5)	1.74 (2)	Mo(5)–O(20)	1.74 (2)
Mo(3)–O(24)	1.69 (2)	Mo(6)–O(17)	1.70 (2)
Mo(3)–O(4)	1.70 (2)	Mo(6)–O(14)	1.71 (2)
For Doubly Bridging Oxygens			
Mo(1)–O(8)	1.88 (2)	Mo(4)–O(11)	1.87 (2)
Mo(2)–O(11)	1.90 (2)	Mo(5)–O(8)	1.91 (2)
Mo(3)–O(3)	1.89 (4)	Mo(5)–O(13)	1.88 (4)
For Triply Bridging Oxygens (2 Mo and 1 As)			
Mo(1)–O(1)	2.27 (2)	Mo(4)–O(23)	2.28 (1)
Mo(1)–O(7)	2.30 (2)	Mo(4)–O(12)	2.36 (2)
Mo(2)–O(10)	2.29 (2)	Mo(5)–O(22)	2.26 (1)
Mo(2)–O(7)	2.34 (2)	Mo(5)–O(12)	2.30 (1)
Mo(3)–O(10)	2.27 (1)	Mo(6)–O(22)	2.33 (2)
Mo(3)–O(1)	2.34 (1)	Mo(6)–O(23)	2.33 (1)
For Triply Bridging Oxygens (3 Mo)			
Mo(1)–O(2)	2.05 (2)	Mo(4)–O(15)	2.03 (2)
Mo(2)–O(2)	2.05 (2)	Mo(5)–O(15)	2.07 (2)
Mo(3)–O(2)	2.05 (2)	Mo(6)–O(15)	2.05 (1)
Around Arsenic			
As(1)–O(23)	1.69 (1)	As(2)–O(1)	1.70 (1)
As(1)–O(22)	1.70 (2)	As(2)–O(10)	1.73 (1)
As(1)–O(7)	1.69 (2)	As(2)–O(12)	1.69 (1)
As(1)–Ph1C1	1.85	As(2)–Ph2C1	1.89
For Nonbonded Atoms			
Mo(1)–Mo(2)	3.424 (3)	Mo(3)–As(2)	3.616 (3)
Mo(1)–Mo(3)	3.401 (3)	Mo(4)–Mo(5)	3.447 (4)
Mo(1)–Mo(5)	3.737 (3)	Mo(4)–Mo(6)	3.400 (3)
Mo(1)–As(1)	3.669 (3)	Mo(4)–As(1)	3.611 (3)
Mo(1)–As(2)	3.610 (4)	Mo(4)–As(2)	3.717 (3)
Mo(2)–Mo(3)	3.409 (3)	Mo(5)–Mo(6)	3.413 (3)
Mo(2)–Mo(4)	3.727 (3)	Mo(5)–As(1)	3.603 (3)
Mo(2)–As(1)	3.662 (3)	Mo(5)–As(2)	3.642 (3)
Mo(2)–As(2)	3.662 (3)	Mo(6)–As(1)	3.652 (3)
For Solvent Molecules			
C1Ac1–C2Ac1	1.48 (4)	C2Ac3–NA3	1.25 (7)
C2Ac1–NAc1	1.20 (4)	C1Ac4–C2Ac4	1.43 (7)
C1Ac2–C2Ac2	1.39 (6)	C2Ac4–NAc4	1.14 (4)
C2Ac2–NAc2	1.20 (7)	C1Ac5–C2Ac5	1.41 (6)
C1Ac3–C2Ac3	1.43 (7)	C2Ac5–NAc5	1.24 (5)
For Probable Hydrogen Bonds			
Aq(1)–Ph2N	2.71	Aq(2)–Ph1N	2.82
Aq(2)–Ph2N	2.97 ^a	Aq(2)–Ph1N	2.94
Aq(3)–Ph2N	2.77 ^a		

^a These are related by the symmetry operation $0.25 - x, 0.25 + y, 0.25 + z$.

solvation of these domains by water and acetonitrile is shown by the packing diagram (Figure 4).

In the solid state the zwitterionic complex is stable to 250 °C according to differential scanning calorimetry. The heated material became dark brown or black but showed the same IR absorption bands as the unheated complex and could be recrystallized from hot aqueous acetonitrile to give the original pink-yellow material.

Polyanions with *cis*-dioxo metal groups are not expected to undergo reversible reduction to heteropoly blues.²⁴ Souchay and Contant²⁰ have shown that $\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}^{4-}$ is irreversibly reduced to unstable violet-pink species (four and eight reactions per anion). The four-electron product has been isolated^{20,25} and shown to contain Mo/As = 3/1, but its structure and true formula are not known. Polarograms of $(\text{NH}_4)_4[(\text{C}_6\text{H}_5\text{-}$

Table VI. Selected Angles (Deg) for $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$

Around Mo(1)			
O(1)–Mo(1)–O(7)	77.1 (5)	O(6)–Mo(1)–O(2)	96.2 (7)
O(2)–Mo(1)–O(7)	72.7 (5)	O(6)–Mo(1)–O(8)	100.2 (7)
O(2)–Mo(1)–O(1)	72.7 (5)	O(18)–Mo(1)–O(7)	166.0 (7)
O(8)–Mo(1)–O(7)	83.7 (6)	O(18)–Mo(1)–O(1)	89.5 (7)
O(8)–Mo(1)–O(1)	86.2 (2)	O(18)–Mo(1)–O(2)	99.5 (7)
O(8)–Mo(1)–O(2)	151.6 (6)	O(18)–Mo(1)–O(8)	99.8 (7)
O(6)–Mo(1)–O(7)	89.6 (6)	O(18)–Mo(1)–O(6)	103.1 (8)
O(6)–Mo(1)–O(1)	164.6 (6)		
Around Mo(2)			
O(2)–Mo(2)–O(10)	70.8 (5)	O(5)–Mo(2)–O(11)	102.9 (8)
O(2)–Mo(2)–O(7)	71.9 (5)	O(5)–Mo(2)–O(2)	95.8 (7)
O(10)–Mo(2)–O(7)	77.0 (5)	O(5)–Mo(2)–O(10)	163.2 (7)
O(9)–Mo(2)–O(5)	103.0 (8)	O(5)–Mo(2)–O(7)	89.5 (7)
O(9)–Mo(2)–O(11)	101.6 (7)	O(11)–Mo(2)–O(2)	149.8 (7)
O(9)–Mo(2)–O(2)	96.9 (7)	O(11)–Mo(2)–O(10)	85.9 (6)
O(9)–Mo(2)–O(10)	88.9 (7)	O(11)–Mo(2)–O(7)	71.9 (5)
O(9)–Mo(2)–O(7)	164.3 (7)		
Around Mo(3)			
O(2)–Mo(3)–O(1)	71.3 (6)	O(4)–Mo(3)–O(2)	95.4 (7)
O(2)–Mo(3)–O(10)	71.3 (5)	O(4)–Mo(3)–O(3)	104.2 (7)
O(3)–Mo(3)–O(1)	84.5 (6)	O(24)–Mo(3)–O(1)	89.0 (7)
O(3)–Mo(3)–O(10)	86.6 (7)	O(24)–Mo(3)–O(10)	161.6 (7)
O(3)–Mo(3)–O(2)	150.4 (8)	O(24)–Mo(3)–O(2)	94.7 (7)
O(10)–Mo(3)–O(1)	75.4 (5)	O(24)–Mo(3)–O(3)	101.8 (7)
O(4)–Mo(3)–O(1)	162.5 (7)	O(24)–Mo(3)–O(4)	103.7 (8)
O(4)–Mo(3)–O(10)	89.8 (7)		
Around Mo(4)			
O(11)–Mo(4)–O(15)	149.3 (7)	O(21)–Mo(4)–O(16)	103.1 (8)
O(11)–Mo(4)–O(23)	85.4 (6)	O(21)–Mo(4)–O(11)	102.3 (8)
O(11)–Mo(4)–O(12)	84.1 (6)	O(21)–Mo(4)–O(15)	95.0 (7)
O(15)–Mo(4)–O(23)	71.8 (5)	O(21)–Mo(4)–O(23)	162.4 (7)
O(16)–Mo(4)–O(12)	167.2 (7)	O(21)–Mo(4)–O(12)	86.7 (7)
O(16)–Mo(4)–O(11)	101.5 (8)	O(15)–Mo(4)–O(12)	71.7 (5)
O(16)–Mo(4)–O(15)	98.9 (7)	O(12)–Mo(4)–O(23)	
O(16)–Mo(4)–O(23)	90.7 (7)		
Around Mo(5)			
O(19)–Mo(5)–O(20)	101.9 (8)	O(20)–Mo(5)–O(12)	83.7 (6)
O(19)–Mo(5)–O(8)	100.5 (7)	O(8)–Mo(5)–O(15)	151.2 (6)
O(19)–Mo(5)–O(15)	97.5 (7)	O(8)–Mo(5)–O(22)	85.9 (6)
O(19)–Mo(5)–O(22)	90.9 (6)	O(8)–Mo(5)–O(12)	85.9 (6)
O(19)–Mo(5)–O(12)	167.0 (6)	O(15)–Mo(5)–O(22)	71.5 (6)
O(20)–Mo(5)–O(8)	103.9 (7)	O(15)–Mo(5)–O(12)	72.4 (5)
O(20)–Mo(5)–O(15)	94.0 (7)	O(22)–Mo(5)–O(12)	78.2 (5)
O(20)–Mo(5)–O(22)	162.0 (7)		
Around Mo(6)			
O(17)–Mo(6)–O(14)	103.7 (8)	O(14)–Mo(6)–O(23)	162.3 (7)
O(17)–Mo(6)–O(13)	102.5 (7)	O(13)–Mo(6)–O(15)	149.3 (8)
O(17)–Mo(6)–O(15)	95.9 (7)	O(13)–Mo(6)–O(22)	85.5 (7)
O(17)–Mo(6)–O(22)	161.5 (7)	O(13)–Mo(6)–O(23)	85.0 (6)
O(17)–Mo(6)–O(23)	90.1 (7)	O(15)–Mo(6)–O(22)	70.4 (6)
O(14)–Mo(6)–O(13)	102.5 (7)	O(15)–Mo(6)–O(23)	70.5 (5)
O(14)–Mo(6)–O(15)	96.7 (7)	O(22)–Mo(6)–O(23)	73.9 (5)
O(14)–Mo(6)–O(22)	90.5 (7)		
Around As(1)			
O(23)–As(1)–O(7)	110.2 (7)	O(7)–As(1)–Ph1C1	110.3
O(23)–As(1)–O(22)	108.6 (7)	O(22)–As(1)–Ph1C1	109.2
O(7)–As(1)–O(22)	108.1 (7)	O(23)–As(1)–Ph1C1	110.3
Around As(2)			
O(12)–As(2)–O(1)	110.6 (7)	O(1)–As(2)–Ph2C1	107.3
O(12)–As(2)–O(10)	109.7 (7)	O(10)–As(2)–Ph2C1	111.0
O(1)–As(2)–O(10)	109.5 (7)	O(12)–As(2)–Ph2C1	108.8
In Solvent Molecules			
C1Ac1–C2Ac1–NAc1	173 (4)	C1Ac4–C2Ac4–NAc4	176 (5)
C1Ac2–C2Ac2–NAc2	171 (9)	C1Ac5–C2Ac5–NAc5	177 (5)
C1Ac3–C2Ac3–NAc3	171 (7)		

$\text{As})_4\text{Mo}_{12}\text{O}_{46}]$ in 1 M *p*-toluenesulfonic acid at 0 °C were found to be very similar to those reported by Souchay and Contant for $\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}^{4-}$ under the same conditions, and showed ill-defined waves between –0.15 and –0.38 V vs. SCE (total 16 electrons) followed by a single irreversible 20-electron

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wave at -0.44 V. In 50% aqueous acetonitrile each of the organoarsenate complexes showed a single irreversible wave (dropping mercury electrode) or cathodic peak (cyclic voltammetry, wax-impregnated graphite electrode) at -0.5 to -0.6 V. Electrolysis on a mercury pool cathode at -0.65 V involved the addition of at least 12 electrons per anion and led to amber-colored solutions that have not been examined further.

Acknowledgment. This work has been supported in part by the Office of Naval Research.

Registry No. $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$, 78571-54-7; $(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}$, 78571-53-6; $[(\text{CH}_3\text{As})_4\text{Mo}_{12}\text{O}_{46}](\text{NH}_4)_4$, 78656-72-1; $[(\text{CH}_3\text{As})_4\text{Mo}_{12}\text{O}_{46}][\text{N}(\text{C}_4\text{H}_9)_4]_4$, 78549-89-0; $[(\text{PhAs})_4\text{Mo}_{12}\text{O}_{46}](\text{NH}_4)_4$, 78549-87-8; $[(\text{PhAs})_4\text{Mo}_{12}\text{O}_{46}][\text{N}(\text{C}_4\text{H}_9)_4]_4$, 78571-56-9; $[(\text{HOCH}_2\text{CH}_2\text{As})_4\text{Mo}_{12}\text{O}_{46}][\text{N}(\text{C}_4\text{H}_9)_4]_4$, 78571-52-5; $(\text{NH}_4)_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}$, 78609-75-3; $[\text{N}(\text{C}_4\text{H}_9)_4]_4\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}$, 78624-40-5.

Supplementary Material Available: Listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Structural Rearrangements Accompanying Zinc(II) Complexation Reactions in Aqueous Dimethyl Sulfoxide

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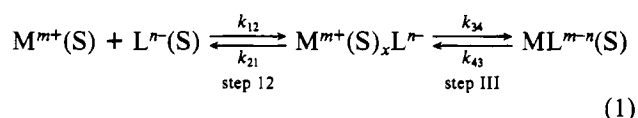
Ultrasonic absorption measurements on $\text{Zn}(\text{NO}_3)_2$ and ZnCl_2 solutions in Me_2SO demonstrate that a conformation change from octahedral to tetrahedral coordination accompanies the addition of the third bound chloride but is absent in the nitrate system. At 25°C and a water mole fraction of 0.59, the ZnNO_3^+ complexation rate constant equals $2.2 \times 10^8 \text{ s}^{-1}$. At 25°C and a water mole fraction of 0.039 and 0.904, the chloride complexation rates are 4.1×10^7 and $3.3 \times 10^7 \text{ s}^{-1}$, respectively.

Introduction

Despite its importance in inorganic and biochemical systems, relatively few kinetic investigations of $\text{Zn}(\text{II})$ complexation studies have been carried out. Many of the complexation investigations utilized the temperature-jump method, and the relaxation times are near the experimental limit of the equipment, thereby requiring lower temperatures for the measurements. Second-order $\text{Zn}(\text{II})$ complexation rates are $4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for pyridine-2-azo-*p*-dimethylaniline (15°C),^{2a} $8.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for murexide (15.5°C),^{2b} greater than $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 1,10-phenanthroline (25°C),³ $8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for 2,2'-bipyridine (20°C),³ and between 5.9×10^7 and $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for glycine and the glycine zwitterions depending upon ionic strengths (25°C).^{4,5} In order to convert second-order complex formation rate constants into ligand penetration rates, the outer-sphere association constants must be measured or calculated. Values of the first-order ligand penetration rates, corresponding to cation solvent-exchange rates, are $3 \times 10^7 \text{ s}^{-1}$ for pyridine-2-azo-*p*-dimethylaniline (15°C),^{2a} between 3×10^7 and $1 \times 10^8 \text{ s}^{-1}$ for acetate and sulfate (25°C),⁶ $2 \times 10^7 \text{ s}^{-1}$ for ammonia (11°C),⁷ and $7 \times 10^8 \text{ s}^{-1}$ for glycine (25°C).⁴ In addition, Swift investigated $\text{Zn}(\text{NO}_3)_2$ complexation in water and found a concentration-independent relaxation with a relaxation time of approximately 0.13 s, attributed to a structural rearrangement involving tetrahedral $\text{Zn}(\text{H}_2\text{O})_4^{2+}$ and another conformation.⁸ In concentrated

glycine, Miceli and Stuehr observed the formation of the bis(glycinato) complex with a relaxation time of the order of 10^{-8} s , coupled to the rate-determining unimolecular rearrangement from a tetrahedral to an octahedral species with a rate constant of 93 s^{-1} .⁴

In principle, ultrasonic relaxation measurements can separate the relaxations corresponding to outer- and inner-sphere complexation via the multistep mechanism



Step 12 involves the diffusion-controlled formation of an outer-sphere ion pair coupled to solvent loss from the inner solvation shell of the ligand. Step III is the loss of solvent from the cation solvation shell followed by cation-ligand bond formation, i.e., the ligand penetration rate. In ultrasonic relaxation measurements, step 12 occurs at high frequency and step III at lower frequency. Darbari, Richelson, and Petrucci studied aqueous ZnCl_2 association reactions using ultrasonics, obtaining only a single relaxation even at high salt concentrations.⁹ Because a single relaxation is inconsistent both with a multistep reaction and with the expected multiple complexation reactions involving Zn^{2+} , ZnCl^+ , ZnCl_2 , ZnCl_3^- , and ZnCl_4^{2-} , the observed relaxation could not be explained in chemical terms. Recently, Tamura has carried out ultrasonic investigations on ZnCl_2 , ZnBr_2 , and $\text{Zn}(\text{NO}_3)_2$ in water, obtaining single relaxations with the halides and no relaxations for the nitrate.¹⁰ Tamura postulates a mechanism involving bis, tris, and tetrakis complexes with the halides coupled to structural changes involving species of coordination numbers 4, 5, and 6. Tamura's model was based upon earlier com-

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