and 1.03 μm^{-1} which, for intensity and energy, correspond to d–d transitions of distorted tetrahedral copper(II) complexes. Also the ESR data, with the high g_3 value of the hyperfine coupling constant, conform to this view, since it has been suggested that these are the features which characterize tetrahedral copper(II) complexes.[28]

The band at 1.46 μm^{-1} in the electronic spectra is very intense and can be assigned to a charge transfer transition, presumably involving the metals and the system of the MeNN and chloride ligands.[29] A low-energy transition was observed also in the mixed valence complexes $[Ni_2X_2(NN)_4]^+$ and it was found to possess polarization properties compatible with Ni–NN charge transfer nature.[2] Since no such band is observed in the corresponding monomeric nickel(II) and copper(II) complexes the lowering of the energy of the absorption can be ascribed to the reduced charge on the metal in the mixed valence compound and to the formation of the dimer.[26]

An alternative interpretation of the spectra may be that the equivalence of the two copper atoms is not retained in the instantaneous vision provided by the electronic specta, a fact similar to that commonly observed in Jahn–Teller distorted copper(II) ions.[30] In this case the 1.46 kcm^{-1} band might be due to an intervalence transition, making the complex, as regards the electronic spectra, a class II mixed valence compound.[29] It is worth noting however that the polarization properties of the mixed valence nickel compound do not confirm this assignment.

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Registry No. $[Cu_2Cl_3(MeNN)_2]$, 60325-89-5.

Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information can be found on any current masthead page.

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Synthesis and Structure of Hexamolybdobis(organoarsonates)

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Five salts of the heteropoly molybdate anion $(RAs)_2Mo_6O_{24}{}^{4-}$ (R = CH_3, C_6H_5, p-$C_6H_4NH_2$) have been synthesized and characterized by spectroscopic measurements. The complexes are stable in aqueous solutions at pH 3–5. The structure of $[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$ ($P\bar{1}$; a = 11.712 (2) Å, b = 11.589 (1) Å, c = 8.331 (1) Å, α = 87.84 (1)°, β = 110.31 (1)°; γ = 112.13 (1)°) has been determined by single-crystal x-ray diffraction. Final consistency indices of 0.043 ($R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$) and 0.072 ($R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) were obtained. The structure of the anion is closely related to that previously reported for $(CH_3P)_2Mo_5O_{21}{}^{4-}$ and consists of a ring of six edge-shared MoO_6 octahedra capped above and below by the $CH_3AsO_3{}^{2-}$ groups.

Introduction

As part of our program to investigate the chemistry of organic derivatives of heteropolyoxometalate complexes, we have previously described molybdenum complexes of monoalkyl- and monoarylphosphonates, $RPO_3{}^{2-}$, and dialkyl- and diarylarsinates, $R_2AsO_2{}^-$. We now report the syntheses, solution properties, and structures of a series of polymolybdate anions based on monoalkyl- and monoarylarsonates, $RAsO_3{}^{2-}$. In 1913[1] Rosenheim and Bilecki isolated organic derivatives of this type with $RAsO_3{}^{2-}$:MoO_3 ratios of 1:3, 1:6, 1:9, and 2:9. In addition, the existence of 2:2, 2:5, and 1:9 complexes

of methylarsonate and molybdate have been claimed on the basis of solution studies.[2,3]

We have prepared several examples of two series of complexes with the As:Mo ratio 1:3 and in this paper we describe those complexes with the general formula $(RAs)_2Mo_6O_{24}{}^{4-}$. Very recently Filowitz and Klemperer[4] have reported the phenyl derivative of this series and proposed its structure from the ^{17}O NMR spectrum.

Experimental Section

Preparation of Complexes. Hexamolybdobis(methylarsonate), Tetramethylammonium–Sodium Double Salt. A solution of sodium

Table I. Analytical Results for $(RAs)_2Mo_6O_{24}{}^{4-}$ Anions

R	CH_3	C_6H_5	C_6H_5	$C_6H_4NH_2$	$C_6H_4NH_2$
Cation	$Me_4N^+Na^+$ [b]	$CH_6N_3^+$	Me_4N^+	$CH_6N_3^+$	Me_4N^+
n^a	6	4	6	2	3
% C found	8.07	12.34	20.21	11.81	20.87
% C calcd	8.32	12.19	20.16	12.07	20.15
% H found	2.74	2.63	4.27	2.95	3.83
% H calcd	2.91	2.68	4.22	2.52	3.97
% N found	1.92	10.84	3.40	11.60	5.08
% N calcd	1.94	10.66	3.36	12.33	5.04
% As found	9.80	9.61	8.98	9.79	10.01
% As calcd	10.39	9.51	8.98	9.43	9.02
% Mo found	39.96	36.61	34.07	36.80	35.15
% Mo calcd	39.93	36.52	34.50	36.15	34.65
Mo:As found	3.18	2.97	2.95	2.92	3.01

a Number of molecules of water of crystallization. b Double salt.

molybdate (21.8 g, 0.09 mol) and sodium methylarsenate[5] (5.6 g, 0.03 mol) in 50 ml of water was adjusted to pH 5 with dilute sulfuric acid. After the solution had been boiled for 20 min, tetramethylammonium chloride (6.6 g, 0.06 mol) was dissolved in the warm solution. The pH of the resulting solution was adjusted to 5 with dilute sulfuric acid and the solution was then boiled for another 10 min. The hot solution was filtered and allowed to evaporate at room temperature. Traces of a mixture of white and yellow material were removed by filtration and in a few days a large number of tiny colorless crystals started to appear. As they were allowed to grow for another few days, large colorless blocks (or sometimes white powder) began to separate. After several days the well-shaped colorless crystals were mechanically separated from the chunky blocks[6] (or white powder). The crystals were dipped in cold water, washed with cold water on a Büchner funnel with suction, and then dried in the air. The yield was 9.3 g, i.e., 44%, based on the molecular formula $[(CH_3)_4N]_2Na_2[(CH_3As)_2\text{-}Mo_6O_{24}]\cdot6H_2O$. The preparation of this salt was not always reproducible and other salts of the heteropoly anion were not obtained. The crude product was dissolved in 60 ml of hot water. After filtration the clear solution was allowed to evaporate at room temperature. A small amount of yellow material which formed overnight was filtered off and the pH of the filtrate was adjusted to 4.5 by the dissolution of a small amount of solid sodium molybdate in the filtrate. When the solution was allowed to evaporate at room temperature, transparent crystals started to separate in 2 days. After 4 days the crystals were collected by filtration and washed with cold water. The transparent crystals became opaque rapidly and finally pulverized upon air-drying. Analytical data for all the new compounds are given in Table I.

Hexamolybdobis(phenylarsonate), Guanidinium Salt. Phenylarsonic acid (4.1 g, 0.02 mol) and sodium molybdate (15.5 g, 0.064 mol) were dissolved successively in ca. 70 ml of water. The slightly cloudy solution was adjusted to pH 4 with dilute sulfuric acid and then boiled for 30 min. The hot solution was filtered and to the filtrate was added 200 ml of pH 4 solution containing guanidinium hydrochloride (3.8 g, 0.04 mol). A small amount of white powder formed and redissolved upon heating. The solution was boiled to reduce its volume to ca. 150 ml and kept at 5 °C overnight. White needles, slightly contaminated with some brown powder, separated and were filtered off and washed with pH 4 water. The yield was 9 g, i.e., 57%, based on the molecular formula $[C(NH_2)_3]_4[(C_6H_5As)_2Mo_6O_{24}]\cdot4H_2O$. The crude product was recrystallized rapidly from hot water, washed with pH 4 water, and dried in the air.

Hexamolybdobis(phenylarsonate), Tetramethylammonium Salt. Phenylarsonic acid (8.8 g, 0.04 mol) and sodium molybdate (29.1 g, 0.12 mol) were dissolved in 130 ml of water. The resulting solution was adjusted to pH 4.7 with dilute sulfuric acid and boiled for 30 min. After cooling of the mixture to room temperature, tetramethylammonium chloride (6.6 g, 0.06 mol) dissolved in 20 ml of water was added. The final solution was readjusted to pH 4.7 with dilute sulfuric acid, boiled for 30 min, and allowed to stand in a refrigerator overnight. After removal of traces of gray powder the solution at pH 4.8 was evaporated on a hot plate until a large amount of white powder had separated. More product was obtained by cooling the solution slowly to room temperature. The crude product was dissolved in a minimum of lukewarm water and the pH adjusted to

Table II. Crystal Data

Formula: $Na_2[N(CH_3)_4]_2\text{-}$ $[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$	$Z = 1$ $V = 976.6$ Å^3
Fw: 1441.92	$\rho_{calcd} = 2.451$ g/cm^3
$a = 11.712$ (2) Å	$\rho_{obsd} = 2.45$ (2) g/cm^3
$b = 11.589$ (1) Å	$\mu = 37.29$ cm^{-1}
$c = 8.331$ (1) Å	$\lambda = 0.70926$Å
$\alpha = 87.84$ (1)°	Crystal faces: $\{010\}$,^{a} $\{1\bar{1}0\}$,
$\beta = 110.31$ (1)°	$\{100\}$,^{a} $\{01\bar{1}\}$,^{a} $\{10\bar{1}\}$, $\{11\bar{1}\}$
$\gamma = 112.13$ (1)°	
$T = 21$ °C	

a Most prominent.

4.8 with sodium hydroxide. The volume of the solution was reduced to ca. 30 ml by heating, and after cooling of the mixture to room temperature the product was filtered off, washed with water, and dried in the air. In most cases three or more recrystallizations were necessary to obtain a pure salt.

Hexamolybdobis(p-aminophenylarsonate), Guanidinium Salt. p-Aminophenylarsonic acid (2.2 g, 0.01 mol) and sodium hydroxide (2 g, 0.025 mol) were dissolved in ca. 100 ml of water and heated to boiling. To the boiling solution molybdenum trioxide (6.5 g, 0.045 mol) was added. The pH of the solution was adjusted to 4 with dilute sulfuric acid. Approximately 50 ml of a pH 4 solution containing guanidinium hydrochloride (4.8 g, 0.05 mol) was added. The initial amorphous yellowish precipitate was filtered off and the solution left to evaporate. After several hours, shiny yellow needles mixed with some yellow microcrystalline powder precipitated out. The needles were mechanically separated from the powder and recrystallized from hot water at pH 4. The product was washed with cold water and dried in the air. The yield was 5 g, i.e., 62%.

Hexamolybdobis(p-aminophenylarsonate), Tetramethylammonium Salt. This salt was prepared in a similar fashion to the guanidinium salt described above.

Analyses. Carbon, hydrogen, nitrogen, arsenic, and molybdenum analyses were performed as described previously.[7]

Physical Measurements. Spectroscopic and electrochemical measurements were carried out as in our previous paper.[7]

Structure Determination of $[(CH_3)_4N]_2Na_2\text{-}[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$. A colorless crystal of approximate dimensions $0.2 \times 0.3 \times 0.4$ mm was mounted on a glass fiber with the ($\bar{1}01$) direction coincident with the goniometer rotation axis. Precession photographs did not show any special symmetry or systematic absences, suggesting space groups $C_1^1\text{-}P1$ or $C_1^2\text{-}P\bar{1}$. A triclinic unit cell was assigned and a Delaunay reduction of the cell parameters failed to indicate any hidden symmetry. Cell dimensions were determined by a least-squares refinement to fit the $\pm2\theta$ values for 24 high-angle reflections centered on the Picker FACS-I diffractometer. Crystallographic data are presented in Table II.

Integrated intensities were measured using Zr-filtered Mo Kα radiation by the θ–2θ scan technique at a takeoff angle of 1.5°. The peaks were scanned from 0.5° on the low-angle side of the Kα_1 peak to 0.5° on the high-angle side of the Kα_2 peak at a rate of 1.0°/min. Stationary-crystal, stationary-counter background counts of 10-s duration were taken at each end of the scan. The diffracted beams were counted using a scintillation counter and were automatically attenuated with Zr foil whenever the count rate exceeded 8000 counts/s. A hemisphere of data (3766 reflections) was collected to $2\theta = 50°$. The intensities of three standard reflections monitored after every 100 reflections remained essentially constant. The intensities were corrected for background and standard deviations were estimated as previously described.[8a] The data were corrected for Lorentz and polarization effects and subsequently for absorption. Transmission coefficients ranged from 0.57 to 0.30. Only the 3175 unique reflections for which $I \geq 2\sigma(I)$ were used in the solution and refinement of the structure.

A Patterson function was computed,[9] and the positions of the three crystallographically independent Mo atoms and the As atom in space group $P\bar{1}$ were determined. Four cycles of least-squares refinement, assuming isotropic thermal parameters of 1.5 Å^2 for each atom, gave consistency indices R_1 and R_2 of 0.258 and 0.377, respectively, where $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. In this and succeeding refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, were taken as

Table III. Final Positional and Thermal Parameters for $Na_2[N(CH_3)_4]_2[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$

Atom	Fractional coordinates			Anisotropic temperature factors $(\times 10^4)^a$					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.552 40 (6)^b	0.772 84 (6)	0 346 22 (8)	37.4 (7)	23.1 (6)	61.1 (12)	10.5 (5)	18.2 (7)	6.3 (6)
Mo(2)	0.797 32 (6)	0.717 76 (6)	0.617 89 (8)	28.4 (7)	29.8 (6)	70.4 (12)	5.9 (5)	13.2 (7)	5.6 (6)
Mo(3)	0.747 58 (6)	0.446 59 (6)	0.780 31 (8)	32.3 (7)	33.1 (6)	55.1 (11)	13.4 (5)	11.0 (7)	2.3 (6)
As	0.478 95 (7)	0.556 10 (6)	0.666 07 (9)	26.1 (7)	22.3 (7)	44.5 (12)	8.3 (6)	10.7 (7)	−0.5 (7)
O(1)	0.525 4 (6)	0.808 7 (6)	0.138 9 (7)	68 (6)	55 (6)	80 (9)	30 (5)	39 (6)	20 (6)
O(2)	0.614 1 (6)	0.914 4 (5)	0.461 6 (8)	68 (7)	32 (5)	105 (10)	9 (5)	29 (7)	14 (6)
O(3)	0.712 0 (5)	0.744 5 (5)	0.387 1 (7)	40 (5)	34 (5)	82 (9)	14 (4)	29 (6)	16 (5)
O(4)	0.585 6 (5)	0.675 3 (5)	0.597 5 (6)	37 (5)	26 (4)	59 (8)	10 (4)	16 (5)	1 (5)
O(5)	0.851 8 (6)	0.860 7 (5)	0.723 1 (8)	52 (6)	35 (5)	124 (11)	31 (5)	33 (7)	−12 (6)
O(6)	0.933 5 (6)	0.711 9 (6)	0.589 0 (8)	45 (6)	73 (6)	123 (11)	24 (5)	43 (7)	12 (7)
O(7)	0.792 2 (5)	0.622 3 (5)	0.811 3 (7)	38 (5)	33 (5)	64 (9)	8 (4)	11 (6)	−6 (5)
O(8)	0.673 2 (5)	0.504 9 (5)	0.490 1 (7)	27 (5)	34 (5)	65 (8)	8 (4)	−2 (5)	1 (5)
O(9)	0.880 2 (5)	0.440 4 (6)	0.742 0 (7)	39 (6)	74 (6)	92 (10)	26 (5)	25 (6)	2 (6)
O(10)	0.770 9 (6)	0.414 3 (5)	0.989 0 (7)	65 (6)	56 (5)	59 (9)	28 (5)	15 (6)	13 (6)
O(11)	0.624 2 (5)	0.285 2 (5)	0.655 9 (7)	44 (5)	32 (5)	66 (9)	19 (4)	22 (6)	3 (5)
O(12)	0.541 1 (5)	0.445 1 (5)	0.734 4 (6)	34 (5)	27 (4)	62 (8)	15 (4)	13 (5)	−2 (5)
C(1)	0.466 5 (9)	0.625 5 (8)	0.857 9 (10)	64 (9)	51 (8)	82 (14)	26 (7)	31 (9)	−16 (8)
C(2)	0.644 4 (10)	−0.016 8 (11)	−0.146 7 (13)	71 (11)	95 (11)	99 (16)	19 (9)	−6 (11)	−27 (11)
C(3)	0.869 8 (11)	0.143 6 (10)	−0.066 8 (14)	101 (13)	86 (11)	164 (21)	23 (10)	74 (14)	56 (12)
C(4)	0.822 7 (11)	−0.042 4 (10)	0.087 9 (15)	89 (12)	90 (11)	210 (23)	64 (10)	48 (14)	79 (14)
C(5)	0.743 7 (12)	0.121 5 (11)	0.124 8 (15)	128 (15)	82 (11)	173 (22)	47 (11)	66 (15)	−18 (12)
N	0.769 8 (7)	0.054 2 (7)	0.000 8 (9)	51 (7)	50 (7)	88 (12)	24 (6)	16 (8)	20 (7)
Na	0.041 3 (3)	0.656 0 (3)	0.426 3 (4)	57 (3)	54 (3)	122 (6)	25 (3)	34 (4)	15 (4)
aq(1)	0.258 2 (8)	0.816 9 (6)	0.505 4 (10)	117 (9)	59 (7)	226 (17)	12 (6)	106 (11)	−7 (8)
aq(2)	−0.139 9 (6)	0.453 6 (6)	0.360 0 (7)	59 (6)	56 (6)	89 (10)	22 (5)	8 (7)	10 (6)
aq(3)	−0.121 8 (8)	0.708 1 (7)	0.193 9 (9)	119 (10)	89 (8)	152 (14)	56 (7)	35 (9)	24 (8)

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Numbers in parentheses in this table and succeeding tables are estimated standard deviations in the last significant figures.
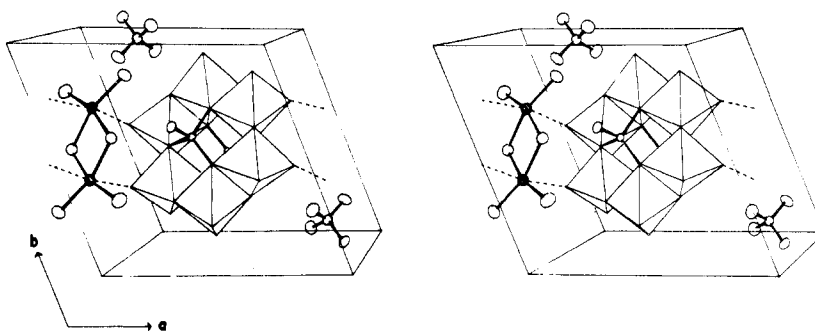

Figure 1. Stereoscopic view of the unit cell of $Na_2[N(CH_3)_4]_2[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$. The anions show MoO_6 octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. Sodium ions are shaded.

$4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors, including the anomalous terms for Mo and As, were taken from the usual tabulation.[10] A difference Fourier map gave the positions of all remaining nonhydrogen atoms. Two cycles of isotropic least-squares refinement, followed by three cycles refining anisotropic thermal parameters for each atom in addition to the positional parameters, resulted in values of $R_1 = 0.069$ and $R_2 = 0.097$. The intensities were next corrected for absorption, and two additional cycles of full-matrix refinement lowered the consistency indices to $R_1 = 0.043$ and $R_2 = 0.072$. The standard deviation in an observation of unit weight was 2.5. A final difference Fourier map contained, as the most significant feature, a ring of electron density of 0.5 e/Å^3 in the vicinity of the expected positions of the methyl group hydrogen atoms of the anion. No attempt was made, however, to include hydrogen atoms in the model of the structure. The lack of residual electron density, coupled with the successful structure refinement, supports the choice of the centric space group $P\bar{1}$.

Table III presents the final positional and thermal parameters, along with the corresponding standard deviations. A table of the final values of $|F_o|$ and $|F_c|$ is available as supplementary material.

Results and Discussion

Description of the Structure. The structure consists of $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anions, $[N(CH_3)_4]^+$ cations, and Na^+ cations coordinated by the water molecules to form $[Na_2(H_2O)_6]^{2+}$ dimers. Figure 1 presents a stereoscopic view of

the contents of the unit cell. Both the $[Na_2(H_2O)_6]^{2+}$ dimers and the molybdate anion are located on inversion centers and are linked together through terminal oxygens on the anion to form a chain running along the a axis. Selected bond distances and angles are given in Table IV. There are no unusually short nonbonded distances, the closest approach of anions being only 3.65 Å between O(9) and O(10). The water–anion distances range between 2.78 and 2.88 Å.

The $[N(CH_3)_4]^+$ cation has the usual tetrahedral geometry with C–N–C angles ranging from 106.4 to 111.2°. The average N–C bond distance is 1.504 Å. The coordination geometry about the sodium dimer is that of two distorted octahedra sharing an edge. The sodium–water and sodium–oxygen distances, which range from 2.37 to 2.44 Å, correspond to those found in a similar cation described in a previous paper.[8]

A stereoscopic drawing of the $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion is presented in Figure 2. It is conveniently described as a fragment of a close-packed oxide lattice with Mo atoms in selected octahedral sites and two CH$_3$As groups bound to its exterior surface through stable covalent bonds. Alternatively (see Figure 1) it may be viewed as six distorted octahedra joined together by edge sharing to form a flat metal oxide ring, which is capped, top and bottom, by the CH$_3$As groups. This

Table IV. Selected Distances (Å) and Angles (Deg) for $Na_2[N(CH_3)_4]_2[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$

$[N(CH_3)_4]^+$

Distances

N–C(2)	1.502 (11)	N–C(4)	1.520 (11)	N–C(5)	1.493 (12)
N–C(3)	1.503 (12)				

Angles

C(2)–N–C(3)	109.7 (8)	C(2)–N–C(5)	110.8 (8)	C(3)–N–C(5)	111.2 (8)
C(2)–N–C(4)	106.4 (8)	C(3)–N–C(4)	108.2 (7)	C(4)–N–C(5)	110.4 (8)

$Na^+(aq)$

Distances

Na–aq(1)	2.393 (8)	Na–aq(2)'^{a}	2.371 (7)	Na–O(6)	2.392 (7)
Na–aq(2)	2.417 (7)	Na–aq(3)	2.444 (8)	Na–O(9)'	2.417 (7)

Angles

aq(1)–Na–aq(2)	162.6 (3)	aq(2)–Na–aq(2)'	80.4 (2)	aq(2)'–Na–O(6)	95.5 (2)
aq(1)–Na–aq(2)'	85.9 (3)	aq(2)–Na–aq(3)	81.6 (2)	aq(2)'–Na–O(9)'	81.0 (2)
aq(1)–Na–aq(3)	112.2 (3)	aq(2)–Na–O(6)	85.7 (2)	aq(3)–Na–O(6)	80.5 (3)
aq(1)–Na–O(6)	106.6 (3)	aq(2)–Na–O(9)'	83.6 (2)	aq(3)–Na–O(9)'	99.7 (3)
aq(1)–Na–O(9)'	83.6 (2)	aq(2)'–Na–aq(3)	161.8 (3)	O(6)–Na–O(9)'	169.1 (3)

$[(CH_3As)_2Mo_6O_{24}]^{4-}$

Distances

Mo(1)–Mo(2)	3.244 (1)	Mo(1)–Mo(1)'	6.571 (1)	As–Mo(3)	3.640 (1)
Mo(2)–Mo(3)	3.300 (1)	Mo(2)–Mo(2)'	6.527 (2)	As–Mo(1)'	3.691 (1)
Mo(3)–Mo(1)'	3.290 (1)	Mo(3)–Mo(3)'	6.568 (2)	As–Mo(2)'	3.695 (1)
Mo(1)–Mo(3)	5.687 (1)	As–Mo(1)	3.689 (1)	As–Mo(3)'	3.737 (1)
Mo(2)–Mo(1)'	5.689 (1)	As–Mo(2)	3.646 (1)	As–As'	3.360 (1)
Mo(3)–Mo(2)'	5.655 (2)				

Terminal Oxygen

Mo(1)–O(1)	1.709 (6)	Mo(2)–O(5)	1.687 (5)	Mo(3)–O(9)	1.718 (5)
Mo(1)–O(2)	1.698 (6)	Mo(2)–O(6)	1.719 (5)	Mo(3)–O(10)	1.713 (5)

Oxygen Doubly Shared by Two Mo Atoms

Mo(1)–O(3)	1.931 (5)	Mo(2)–O(3)	1.909 (5)	Mo(3)–O(7)	1.905 (5)
Mo(1)–O(11)'	1.912 (5)	Mo(2)–O(7)	1.925 (5)	Mo(3)–O(11)	1.931 (5)

Oxygen Triply Shared by Two Mo Atoms and One As Atom

Mo(1)–O(4)	2.324 (5)	Mo(2)–O(4)	2.284 (5)	Mo(3)–O(8)	2.433 (5)
Mo(1)–O(12)'	2.358 (5)	Mo(2)–O(8)	2.398 (5)	Mo(3)–O(12)	2.306 (5)
As–O(4)	1.711 (5)	As–O(12)	1.695 (5)	As–C(1)	1.890 (8)
As–O(8)'	1.697 (5)				

Angles

O(1)–Mo(1)–O(2)	103.5 (3)	O(3)–Mo(2)–O(4)	75.7 (2)	O(7)–Mo(3)–O(8)	75.4 (2)
O(1)–Mo(1)–O(3)	98.0 (2)	O(3)–Mo(2)–O(5)	101.5 (2)	O(7)–Mo(3)–O(9)	102.4 (3)
O(1)–Mo(1)–O(4)	164.9 (2)	O(3)–Mo(2)–O(6)	96.7 (3)	O(7)–Mo(3)–O(10)	99.1 (2)
O(1)–Mo(1)–O(11)'	99.7 (2)	O(3)–Mo(2)–O(7)	149.7 (2)	O(7)–Mo(3)–O(11)	148.4 (2)
O(1)–Mo(1)–O(12)'	93.5 (2)	O(3)–Mo(2)–O(8)	79.9 (2)	O(7)–Mo(3)–O(12)	80.6 (2)
O(2)–Mo(1)–O(3)	101.0 (3)	O(4)–Mo(2)–O(5)	91.7 (2)	O(8)–Mo(3)–O(9)	87.8 (2)
O(2)–Mo(1)–O(4)	90.9 (2)	O(4)–Mo(2)–O(6)	163.1 (2)	O(8)–Mo(3)–O(10)	166.5 (2)
O(2)–Mo(1)–O(11)'	98.6 (3)	O(4)–Mo(2)–O(7)	80.4 (2)	O(8)–Mo(3)–O(11)	79.3 (2)
O(2)–Mo(1)–O(12)'	162.4 (2)	O(4)–Mo(2)–O(8)	74.6 (2)	O(8)–Mo(3)–O(12)	74.8 (2)
O(3)–Mo(1)–O(4)	74.4 (2)	O(5)–Mo(2)–O(6)	104.7 (3)	O(9)–Mo(3)–O(10)	105.5 (3)
O(3)–Mo(1)–O(11)'	149.6 (2)	O(5)–Mo(2)–O(7)	97.6 (3)	O(9)–Mo(3)–O(11)	95.2 (2)
O(3)–Mo(1)–O(12)'	80.7 (2)	O(5)–Mo(2)–O(8)	165.5 (2)	O(9)–Mo(3)–O(12)	161.1 (2)
O(4)–Mo(1)–O(11)'	82.4 (2)	O(6)–Mo(2)–O(7)	101.1 (3)	O(10)–Mo(3)–O(11)	101.3 (2)
O(4)–Mo(1)–O(12)'	72.6 (2)	O(6)–Mo(2)–O(8)	89.4 (2)	O(10)–Mo(3)–O(12)	92.3 (2)
O(11)'–Mo(1)–O(12)'	73.8 (2)	O(7)–Mo(2)–O(8)	75.9 (2)	O(11)–Mo(3)–O(12)	74.7 (2)
C(1)–As–O(4)	106.9 (3)	C(1)–As–O(12)	107.4 (3)	O(4)–As–O(12)	110.4 (2)
C(1)–As–O(8)'	109.0 (3)	O(4)–As–O(8)'	111.0 (3)	O(8)'–As–O(12)	111.8 (2)

^{a} Primed atoms are related to the corresponding unprimed atoms by a center of symmetry.

highly symmetrical anion exhibits approximately D_{3d} symmetry. The metal oxide portion of the anion resembles the previously reported structures[11] of the heteropoly molybdates, $(XMo_6O_{24})^{n-}$. The average distances of 1.707, 1.919, and 2.351 Å for Mo–O(terminal), Mo–O(doubly shared), and Mo–O(triply shared) bonds compare favorably with those found in $TeMo_6O_{24}^{6-}$.[12] The geometry about the As is very close to tetrahedral with angles in the CH_3AsO_3 group ranging from 106.9 to 111.8°. The As–C distance of 1.89 Å and the average As–O distance of 1.70 Å are consistent with values found in free organoarsenates.[13]

Solution Properties. On the preparative scale the alkyl- and arylarsonatomolybdate complexes are formed both with sodium molybdate and with molybdenum trioxide in aqueous solutions at pH 4–5. In aqueous solutions of spectroscopic concentration (ca. 5×10^{-4} M), though, they appear to be the predominant species in slightly more acidic media, i.e., pH 3–4. The analytical data for the complex salts are in good agreement with the empirical formula $[(RAs)_2Mo_6O_{24}]^{4-}$ (Table I) and the structure determination also confirms this molecular stoichiometry. The uv spectra of all three complexes have an absorption peak at about 250 nm. The electronic transition
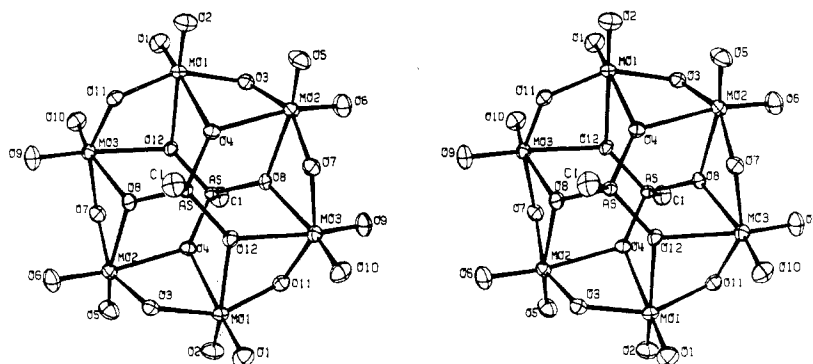
Figure 2. Stereoscopic view of the $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion with vibrational ellipsoids drawn at the 50% probability level.

Table V. Infrared Absorption Frequencies (cm^{-1}) for $(RAs)_2Mo_6O_{24}{}^{4-}$ Anions

$R = CH_3{}^a$	$R = C_6H_5{}^b$	$R = C_6H_5{}^c$	$R = C_6H_4NH_2{}^b$	$R = C_6H_4NH_2{}^c$	Tentative assignment
1249 m^d	1083 m	1088 m	1092 m	1094 m	ν(As–C)
949 s		943 s	950 s, sh	950 s, b	
922 s	930 sh	928 w			ν(Mo–O terminal)
919 s	890 s				
899 s		891 s, b	900 s	910 s, b	
862 w					
849 w					ν(As–O)
	822 s	825 s, b	830 s, b	840 s	
785 s, b	794 s, b	797 s, b	795 s	800 s, sh	
667 sh, n					ν(Mo–O bridging)
657 s, b	655 s, b	660 s, b	665 s, n	675 s, b	

^{a} Tetramethylammonium–sodium salt. ^{b} Guanidinium salt. ^{c} Tetramethylammonium salt. ^{d} Key: s, strong; m, medium; w, weak; b, broad; n, narrow; sh, shoulder.

energy and the extinction coefficients are very close to the corresponding values for the $[(RP)_2Mo_5O_{21}]^{4-}$ anions with extinction coefficients $(3.5-5) \times 10^4 M^{-1} cm^{-1}$.

From all of the compounds reported by Rosenheim and co-workers,[1] only the salts formulated $[C(NH_2)_3]_2[(p\text{-}NH_2C_6H_4As)(MoO_4)_3]\cdot5H_2O$ and $[C(NH_2)_3]_2[(p\text{-}HOC_6H_4As)(MoO_4)_3]\cdot2H_2O$ appear to correspond to $[(RAs)_2Mo_6O_{24}]^{4-}$. No methyl derivative was reported. Although neither $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$ nor $[(NH_2C_6H_4As)_2Mo_6O_{24}]^{4-}$ crystallizes easily with small inorganic cations such as Na^+, K^+, and NH_4^+, their guanidinium and tetramethylammonium salts can be relatively readily separated from the reaction solutions. Isolation of the tetramethylammonium–sodium double salt of the $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion proved to be more difficult. Compared to our previous syntheses of various salts of the $[(RP)_2Mo_5O_{21}]^{4-}$[7] and $[(R_2As)Mo_4O_{15}H]^{2-}$[14] anions, the preparation of the compounds reported here appears to be more sensitive to pH, temperature, precipitating conditions, concentration, etc., and isolation of pure crystalline material is time consuming.

The infrared absorption spectra of all three complexes are characteristic of the anion, and the main bands are listed in Table V.

The proton magnetic resonance spectrum of an analyzed sample of $[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}]\cdot6H_2O$ in aqueous solution at pH 4 shows the anion methyl resonance at 2.20 ppm, about 0.30 ppm downfield from that of the free methylarsonate anion under the same conditions. The ratio of the integrated intensities of the cation:anion methyl resonances was 4.2 ± 0.2 and confirms the above stoichiometry. The slightly high value is probably a result of traces of $(CH_3)_4NCl$ in the bulk sample rather than partial hydrolysis of $AsCH_3$ to $AsOH$ in the anion.

Polarography of 5×10^{-4} M solutions of the molybdoarsonate complexes at pH 3–4 revealed single irreversible waves at –0.6 to –0.7 V vs. SCE and indicates that the anions are not reducible to mixed-valence, "heteropoly blue" species.

This behavior is consistent with the type II structure adopted by the complexes.[15]

Conclusions

The new complexes bear an obvious structural similarity to the 2:5 molybdophosphonate anions that we have reported previously.[7,8] In both structures a ring of MoO_6 octahedra is spanned by RXO_3 tripod groups, and the difference in stoichiometry appears to be dictated by the dimensions of $RPO_3{}^{2-}$ and $RAsO_3{}^{2-}$. As we[8] and others[4] have independently pointed out, the appropriate O···O distances across the six-membered Mo_6O_{24} ring closely match the nonbonded O···O separation in an $AsO_4{}^{3-}$ tetrahedron (2.86 Å), whereas the smaller, buckled, edge- and corner-shared Mo_5O_{21} ring is needed to accommodate $PO_4{}^{3-}$ or $RPO_3{}^{2-}$ groups (O···O = 2.53 Å).[16] The structure of the $S_2Mo_5O_{21}{}^{4-}$ anion[17] is consistent with this principle (O···O for $SO_3{}^{2-}$ is 2.41 Å)[18] and it is probable that $Se_2Mo_5O_{21}{}^{4-}$ (O···O = 2.61 Å)[18] has a similar structure. On the other hand the compound originally formulated as $(NH_4)_4Sb_2W_5O_{21}\cdot H_2O$ has recently been shown[19] to contain an Sb_8W_{21} structure based on fragments of a β Keggin (XW_{12}) molecule. Such a structure is compatible with the larger size of Sb(III) vis-à-vis As.

Complexes of molybdate and inorganic arsenate with the 1:3 stoichiometry are known. Contant[20] showed the existence of 2:6 and 4:12 anions, and Nishikawa and Sasaki[21] have recently determined the crystal structure of the ammonium salt of the latter complex. From potentiometric measurements, Pettersson[22] concluded that both 2:5 and 2:6 complexes of arsenate and molybdate exist, the former in very small relative amounts, in aqueous solution at pH 3–6. Pettersson also proposed a structure for the 2:6 complex analogous to the one reported here. As mentioned above, Filowitz and Klemperer[4] showed that the ^{17}O NMR spectra of $(OAs)_2Mo_6O_{24}{}^{6-}$ and $(C_6H_5As)_2Mo_6O_{24}{}^{4-}$ were consistent with the Pettersson structure.

In their original study Rosenheim and Bilecki[1] reported the following compounds with a 1:3 stoichiometry: [C(N-

H$_2$)$_3$]H[(C$_6$H$_5$As)(MoO$_4$)$_3$], [C(NH$_2$)$_3$]$_2$[(p-NH$_2$C$_6$H$_4$As)(MoO$_4$)$_3$]·H$_2$O, and [C(NH$_2$)$_3$]$_2$[(p-HOC$_6$H$_4$As)(MoO$_4$)$_3$]·2H$_2$O. The latter two salts almost certainly contain 2:6 anions of the type reported here. The first salt however is probably not an acid salt as written but, we believe, contains a tetrameric (4:12) anion analogous to the molybdoarsenate complex [(HOAs)$_4$Mo$_{12}$O$_{46}$]$^{4-}$. We have prepared several such derivatives and reported them elsewhere.[8b,23]

Registry No. [(CH$_3$)$_4$N]$_2$Na$_2$[(CH$_3$As)$_2$Mo$_6$O$_{24}$]·6H$_2$O, 60364-06-9; [C(NH$_2$)$_3$]$_4$[(C$_6$H$_5$As)$_2$Mo$_6$O$_{24}$], 60364-04-7; [(CH$_3$)$_4$N]$_4$[(C$_6$H$_5$As)$_2$Mo$_6$O$_{24}$], 60326-17-2; [C(NH$_2$)$_3$]$_4$[(C$_6$-H$_4$NH$_2$As)$_2$Mo$_6$O$_{24}$], 60364-03-6; [(CH$_3$)$_4$N]$_4$[(C$_6$H$_4$NH$_2$-As)$_2$Mo$_6$O$_{24}$], 60364-02-5; sodium molybdate, 7631-95-0; sodium methylarsonate, 144-21-8; phenylarsonic acid, 98-05-5; p-aminophenylarsonic acid, 98-50-0; molybdenum trioxide, 1313-27-5.

Supplementary Material Available: Listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Interligand Hydrogen Bonding in Metal–Purine Complexes.
Crystal and Molecular Structure of
(N-3,4-Benzosalicylidene-N'-methylethylenediamine)(theophyllinato)(aquo)copper(II)

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This report relates the synthesis and crystal structure of (N-3,4-benzosalicylidene-N'-methylethylenediamine)(theophyllinato)(aquo)copper(II). The complex crystallizes from methanol in the monoclinic system, space group $P2_1/c$, with $a = 18.949 (9)$ Å, $b = 8.279 (2)$ Å, $c = 13.499 (6)$ Å, $\beta = 101.60 (3)°$, $Z = 4$, $V = 2074.5$ Å^3, $d_{\text{measd}} = 1.55 (1)$ g cm^{-3}, and $d_{\text{calcd}} = 1.56$ g cm^{-3}. The 11005 reflections in the $+h$ hemisphere to $2\theta = 55°$ were collected by counter methods on a diffractometer employing Mo K$\bar{\alpha}$ radiation and the θ–2θ scan technique. The 11005 measured reflections were subsequently reduced to a set of 4174 independent, symmetry-averaged reflections with $I > \sigma(I)$, which were used in the structural solution and refinement. The structure was solved by standard heavy-atom Patterson and Fourier methods and has been refined by full-matrix least squares, based on F, to a final R value of 0.068. The copper(II) is in a pseudo-square-pyramidal environment with the tridentate Schiff base and N(7) of the theophyllinato ligand, Cu–N(7) = 2.000 (3) Å, in the equatorial positions and a weakly bound water molecule, Cu–OH$_2$ = 2.740 (3) Å, in the axial position. There are two interligand hydrogen bonds to the O(6) carbonyl oxygen of the theophyllinato ligand, one from the secondary amine of the ethylenediamine terminus of the Schiff base chelate and one from the axially bonded water molecule. The Cu–N(7) vector lies 15.5 (3)° out of the plane of the theophyllinato ligand, probably as a consequence of the axial interligand hydrogen bond. The crystal packing is dominated by intercomplex hydrogen bonding and the formation of two types of stacking dimers between symmetry-related complexes, one employing the naphthylidene ring of the Schiff base and one the theophylline monoanion ring.

Introduction

An integral part of our work on stereoselective metal–ligand and ligand–ligand interactions in chelate–transition metal complexes of purines, pyrimidines, and their nucleosides has centered on copper(II) complexes of the tridentate ligand N-salicylidene-N'-methylethylenediamine. The Cu(II) complex of this Schiff base has one equatorial coordination site available for ligand attachment. The exocyclic oxygen atom of the salicylidene ring is a potential hydrogen-bond acceptor site, and the amino group at the N-methylethyl-

enediamine terminus is a potential hydrogen-bond donor site.

Thus far we have studied the crystal and molecular structures of three complexes of the above Schiff base system: (1) in the theophyllinato complex,[1] the metal binding is at N(7) of the purine and an interligand hydrogen bond is formed between the coordinated secondary amine group on the Schiff base and the exocyclic carbonyl oxygen, O(6), on the coordinated purine atom; (2) in the 9-methyladenine complex,[2] the metal binding site is N(7) and an interligand hydrogen bond is formed between the coordinated salicylidene oxygen