$(en)(C_6H_{11}NC)_2]^+$ and $[Cu(tmen)(C_6H_{11}NC)_2]^+,^{28}$ carbonylated solutions of copper(I)–histamine allowed the isolation of $[Cu(hm)(C_6H_{11}NC)](BPh_4)$ only. This suggests that the NH group of an adjacent complex would compete either with the solvent or with a basic isocyanide. Therefore histamine provides, at least in the solid state, three different nitrogens for each copper, which may require in all these complexes a tetracoordination. On this basis, a polymeric structure for

$[Cu(hm)(C_6H_{11}NC)]^+$ is suggested as for II, in which histamine shows the third bonding mode observed in these complexes.

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Molybdoarsinate Heteropoly Complexes. Structure of the Hydrogen Tetramolybdodimethylarsinate(2−) Anion by X-ray and Neutron Diffraction[1]

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Seven salts of the heteropoly molybdate anions $R_2AsMo_4O_{15}H^{2-}$ ($R = CH_3$, C_2H_5, C_6H_5) have been synthesized and characterized by spectroscopic measurements. The structure of $[(CN_3H_6)_2AsMo_4O_{15}H]\cdot H_2O$ ($P2_1/c$, $a = 8.531$ (2) Å, $b = 8.527$ (2) Å, $c = 30.129$ (5) Å, $\beta = 95.49$ (2)°) has been determined by single-crystal X-ray and neutron diffraction and refined to final consistency indices R and R_w of 0.043 and 0.063 for the X-ray data and 0.047 and 0.037 for the neutron data. The anion may be viewed as a ring of face- and edge-shared MoO_6 octahedra capped by the tetrahedral $(CH_3)_2AsO_2^-$ group. At the base of the anion is an oxygen that is asymmetrically shared by all four Mo atoms (Mo–O = 2.360–2.927 Å). The single anionic proton required by the stoichiometry is located on the basal oxygen, with an O–H bond length of 0.991 (5) Å. The unique hydrogen participates in a hydrogen bond to a water molecule which is 1.779 (5) Å away from the hydrogen.

Introduction

A novel class of heteropoly compounds containing organic groups covalently bound to a surface heteroatom has attracted much attention.[4–10] Some representatives of this class are $(CN_3H_6)_5[(C_6H_5As)_2W_6O_{25}H]\cdot 2H_2O$,[5] $Na[N(CH_3)_4][(N-H_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$,[6] $K_4[\alpha-(\eta^5-C_5H_5)Ti(PW_{11}O_{39})]$,[7] $[(C_5H_5)Fe(CO)_2Ge]_2W_{11}PO_{40}{}^{3-}$,[8] $(CN_3H_6)_4[(C_6H_5As)_2-Mo_6O_{25}H_2]\cdot 4H_2O$,[9a,b] and $H_4[(p-H_2NC_6H_4As)_4Mo_{12}O_{46}]\cdot 10CH_3CN\cdot H_2O$.[10] These few examples illustrate the diversity in heteroatom, organic group, and overall composition which allows these compounds to exhibit a promising mixture of properties inherent to ionic metal oxides and covalent organic groups. We report here the synthesis and structural characterization of some of these organometalates which have the

general formula $R_2AsMo_4O_{15}H^{2-}$. Salts of anions with this stoichiometry were first prepared by Rosenheim and Bilecki.[11]

Since the formula indicated a totally new structural type, single-crystal X-ray and subsequent neutron diffraction measurements were undertaken on $(CN_3H_6)_2[(CH_3)_2As-Mo_4O_{15}H]\cdot H_2O$. Following our preliminary report[12] of the X-ray structure we learned of an independent determination by Matsumoto.[13] Klemperer et al.[14] have reported the ^{17}O NMR spectra of the dimethyl and diphenyl derivatives. Recently, an analogous structure has been reported[15] for the tetra-*n*-butylammonium salt of $[H_2CMo_4O_{15}H]^{3-}$ and has been proposed[16] for $Mo_5O_{17}H^{3-}$.

Experimental Section

Preparation of Complexes. Tetramolybdodimethylarsinate: Guanidinium Salt. Dimethylarsinic acid (1.4 g, 0.01 mol) and sodium molybdate (9.8 g, 0.04 mol) were dissolved in 50 mL of water, and the solution was boiled for 15 min. After being cooled, the solution

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was filtered, the pH was adjusted to 4.5 with dilute sulfuric acid, and a solution of guanidinium chloride (4.6 g, 0.05 mol) was added while the solution was stirred. A crystalline precipitate was obtained, which was filtered off and subsequently washed with cold water and air-dried. The crude product was dissolved in 50 mL of hot water, and the solution was filtered. Upon cooling and reduction of the volume, the crystalline product was filtered and washed with cold water. The yield was 5.5 g. Anal. Calcd for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$: C, 5.53; H, 2.42; N, 9.68; As, 8.63; Mo, 44.24; H_2O, 2.07. Found: C, 5.50; H, 2.47; N, 9.71; As, 8.90; Mo, 43.85; H_2O, 2.35.

Tetramolybdodimethylarsinate: Sodium Salt. The procedure was analogous to that for the guanidinium salt, up to the point of addition of cation. After the pH was adjusted, the solution was evaporated to approximately one-fifth of its original volume. A white solid formed, which was treated as described for the guanidinium salt, but by using a smaller volume of water. Anal. Calcd for $Na_2(CH_3)_2$-$AsMo_4O_{15}H\cdot 3H_2O$: C, 2.89; Mo, 46.26; H_2O, 6.51. Found: C, 3.00; Mo, 46.20; H_2O, 6.23.

Tetramolybdodimethylarsinate: Tetramethylammonium Salt. To the reaction mixture at pH 4.5 was added tetramethylammonium chloride (5.5 g, 0.05 mol). After evaporation of one-third of the solution, large crystalline plates were obtained. Recrystallization was carried out as for the guanidinium salt. The yield was 5.0 g. Anal. Calcd for $[(CH_3)_4N]_2[(CH_3)_2AsMo_4O_{15}H]\cdot 2H_2O$: C, 13.13; N, 3.06; Mo, 42.00; H_2O, 3.94. Found: C, 13.49; N, 2.90; Mo, 41.30; H_2O, 4.47.

Tetramolybdodimethylarsinate: Potassium Salt. To the acidified solution was added potassium chloride (2.8 g, 0.05 mol). After reduction of the liquid by one-third, a microcrystalline powder was obtained. It was treated as described for the guanidinium salt. The yield was 4.5 g. Anal. Calcd for $K_2(CH_3)_2AsMo_4O_{15}H\cdot 4H_2O$: C, 2.86; As, 8.92; Mo, 45.71; H_2O, 8.57. Found: C, 2.92; As, 9.25; Mo, 44.32; H_2O, 8.93.

Tetramolybdodimethylarsinate: Tetrabutylammonium Salt. An aqueous solution, containing tetrabutylammonium chloride (2.8 g, 0.01 mol) at pH 4.5, was added to the reaction mixture. A white precipitate formed, which was filtered, washed, and air-dried. The product was dissolved in approximately 300 mL of water by boiling for 1 h. The solution was filtered and left to evaporate to about two-thirds of the original volume. A white product was collected and subsequently washed with water and air-dried. The yield was 7.7 g. Anal. Calcd for $[(C_4H_9)_4N]_2[(CH_3)_2AsMo_4O_{15}H]$: C, 33.59; N, 2.30; Mo, 31.62. Found: C, 33.29; N, 2.03; Mo, 32.15.

Tetramolybdodimethylarsinate: Deuterated Tetrabutylammonium Salt. One gram of the sodium salt was dehydrated at 110 °C and dissolved in 20 mL of D_2O, and the solution was left to evaporate almost to dryness in a vacuum desiccator. The procedure was repeated with the solid residue. The second product was filtered and dissolved in 20 mL of D_2O, and tetrabutylammonium chloride (0.3 g, 0.001 mol) dissolved in D_2O was added. The white precipitate was filtered and dried in a desiccator. The yield was 0.5 g.

Tetramolybdodiethylarsinate: Sodium, Potassium, Guanidinium, Tetramethylammonium, and Tetrabutylammonium Salts. These compounds were prepared in the same way as the dimethyl derivatives, using 0.01 mol of diethylarsinic acid in the reaction solution. Anal. Calcd for $(CN_3H_6)_2[(C_2H_5)_2AsMo_4O_{15}H]\cdot H_2O$: C, 8.04; N, 9.37; Mo, 42.85; H_2O, 2.01. Found: C, 7.84; N, 9.66; Mo, 43.35; H_2O, 1.65.

Tetramolybdodiphenylarsinate: Sodium, Potassium, Guanidinium, Tetramethylammonium, Tetrabutylammonium, and Tetraphenylarsonium Salts. The procedure for their preparation was the same as for the dimethyl and diethyl derivatives, using 0.01 mol of diphenylarsinic acid in the reaction solution. Anal. Calcd for $(CN_3H_6)_2[(C_6H_5)_2AsMo_4O_{15}H]$: C, 17.25; N, 8.62; Mo, 39.42. Found: C, 17.25; N, 8.29; Mo, 39.45.

Analyses. Carbon, hydrogen, nitrogen, arsenic, and molybdenum analyses were performed as described previously.[17]

X-ray Structure Determination of $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}-H]\cdot H_2O$. A well-formed colorless block of approximate dimensions $0.3 \times 0.3 \times 0.5$ mm was mounted on a glass fiber. Preliminary Weissenberg and precession photographs of the $0hl$, $1kl$, $h0l$, $h1l$, and $hk0$ zones indicated that the Laue symmetry was $2/m$. The space group $P2_1/c$, No. 14, was uniquely determined from systematic ab-

Table I. Crystal Data for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

space group = $P2_1/c$	$\beta = 95.49\ (2)°$
$Z = 4$	$\mu = 39.1\ cm^{-1}$
$a = 8.531\ (2)$ Å[a]	$\rho_{calcd} = 2.65\ g/cm^3$
$b = 8.527\ (2)$ Å	$\rho_{obsd} = 2.62\ (2)\ g/cm^3$
$c = 30.129\ (5)$ Å	$V = 2182$ Å^3

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

sences of the $0k0$ (k odd) and $h0l$ (l odd) reflections. The same crystal was mounted on the Picker FACS-I diffractometer, and the unit cell parameters and their standard deviations were determined by using Mo $K\alpha$ radiation ($\lambda = 0.709\,30$ Å) from 20 carefully centered high-angle ($2\theta \approx 45°$) reflections.

The intensity data were measured at ambient temperatures by using Mo $K\alpha$ radiation ($\lambda = 0.709\,30$ Å) by the θ–2θ scan technique to a maximum 2θ value of 45°. Each reflection was scanned from 0.75° below $K\alpha_1$ to 0.75° above $K\alpha_2$ at a scan rate of 1°/min. The background was measured by using the stationary crystal–stationary counter method for 10 s at each end of the scan range. The intensities of three standard reflections were measured after every 100 reflections. No significant variation in their intensities was observed over the 2-week period of data collection, although the crystal slowly changed from colorless to dark amber. In all, the intensities of 3096 unique reflections were recorded.

The intensities, I, were corrected for background as follows: $I = [(10C + 5) - 0.5(t_c/t_b)(10B_1 + 10B_2 - 9)]A^i$, where C is the number of raw counts recorded in time t_c, B_1 and B_2 are the background counts obtained in time t_b, A is the attenuator factor, and i is the number of attenuators used. Standard deviations were assigned by $\sigma^2(I) = [10C + 14 + 0.25(t_c/t_b)^2(10B_1 + 10B_2 + 27)]A^i + (pI)^2$. A value of 0.05 was chosen for p, the correction factor to prevent overweighting of strong reflections. The data were also corrected for Lorentz and polarization effects. Only those 2579 reflections having $I \geq 2\sigma(I)$ were used in solution and refinement of the structure.[18] A linear absorption coefficient of 39 cm^{-1} was calculated, but no absorption corrections were applied.

Solution and Refinement of X-ray Data. The positions of the four Mo atoms and the As atoms were located with some difficulty by analysis of the Patterson function. On the basis of their positions, a structure factor calculation was carried out, where the atomic scattering factors were taken from standard sources.[19] The values for the anomalous corrections were also taken from standard tabulations.[20]

The structure was refined by least-squares techniques minimizing the function of $w(|F_o| - |F_c|)^2$, 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 refinement of all nonhydrogen atoms using anisotropic temperature factors, 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 0.045 and 0.066. During the last cycle of refinement, the position of no atom shifted by more than 0.0032 Å. In the final difference map, the largest peak was 1.1 e/Å^3. However, this density could not be correlated with a chemically reasonable hydrogen position.

The model for the structure was varied slightly when ionic scattering factors for Mo(6+) and O(1−) were introduced.[21] The values of R and R_w were reduced to 0.043 and 0.063 after five cycles of anisotropic refinement. In the last cycle, the greatest atomic shift was 0.00076 Å. A subsequent difference Fourier map showed no peak greater than 1.0 e/Å^3. The final positional and anisotropic thermal parameters from this refinement have been deposited. A table of the final values of $|F_o|$ and $|F_c|$ is available as supplementary material.

Neutron Structure Determination of $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}-H]\cdot H_2O$. A crystal of the complex having dimensions $5 \times 2 \times 1$ mm was grown by seeding a saturated solution maintained at pH 3.5. This crystal was mounted on a quartz rod approximately along the a

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crystallographic axis. Data were collected on the four-circle diffractometer at the NBS research reactor out to a maximum 2θ angle of 106° at a neutron wavelength of 1.230 (1) Å. The longest dimension of the crystal was approximately parallel to the ϕ axis of the diffractometer. In order to determine the proper background for all reflections, in view of the very short c^* axis, we measured the data by either of two methods. When the angle between the reciprocal lattice vector and the c^* axis was less than 45°, an ω scan was employed. When this angle was greater than 45°, a θ–2θ scan was used. Measurement of a few reflections for which this angle was close to 45°, using both methods, established that the integrated intensities were the same, independent of the mode of measurement. Intensity data were obtained and treated by techniques which have been previously reported.[22] Of the 4297 reflections recorded, 3216 unique reflections were used for refinement of the structure. Absorption corrections were not made due to the striated nature of the crystal faces which prevented their identification.

Solution and Refinement of Neutron Data. The final positional and thermal parameters from the X-ray study were taken as starting points for refinement of the neutron data. The scale factor was varied for one cycle, and a structure factor calculation was performed. The scattering length, b, for all atoms, was obtained from standard sources.[23] From the first difference Fourier map, the positions of all 21 hydrogen atoms were located. After exhaustive anisotropic least-squares refinement of all atoms, the values of R and R_w were 0.047 and 0.037. In the final cycle of refinement, no parameter shifted by more than its standard deviation. A final difference map showed no feature greater than 10% the depth of a hydrogen atom. The final positional and thermal parameters are given in Table II. These were introduced into the X-ray data, and the scale factor was refined, leading to values of 0.064 and 0.081 for R and R_w, respectively.

The results of the neutron diffraction study are in total accord with the X-ray diffraction experiment. All the positional parameters agree within 2.5σ, except for those of O(16) and C(2), which agree within 3.5σ. The thermal parameters differ since the X-ray values include contributions from inaccurate scattering factors, absorption, etc. A table of the final values of $|F_o|$ and $|F_c|$ is available as supplementary material.

Results and Discussion

The tetramolybdoarsinate anions are formed in aqueous solution between pH 3 and 5 from stoichiometric mixtures of the arsinic acid and sodium molybdate and are the only heteropoly species to have been isolated from such solutions. Solutions of the complexes display a UV absorption maximum at ~250 nm (ϵ_{max} ~2 × 10^4 M^{-1} cm^{-1}). Similar maxima were observed for [(RP)$_2$Mo$_5$O$_{21}$]$^{4-}$ and [(RAs)$_2$Mo$_6$O$_{24}$]$^{4-}$ anions.[24] Since the stoichiometry of all the salts prepared indicated an anionic charge of 2–, the anions must contain a proton, which within the pH range of stability of the anion (3–5), is not dissociable. A potentiometric titration of (CN$_3$H$_6$)$_2$[(CH$_3$)$_2$AsMo$_4$O$_{15}$H]·H$_2$O with sodium hydroxide gave a single end point at 6.94 ± 0.15 mequiv of base/mmol of complex, in accord with the reaction

$$(CH_3)_2AsMo_4O_{15}H^{2-} + 7OH^- \rightarrow$$
$$(CH_3)_2AsO_2^- + 4MoO_4^{2-} + 4H_2O$$
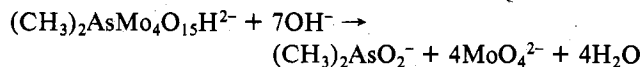
Selected infrared data, obtained in KBr matrices, are presented in Table III. The bands in the molybdenum–oxygen and arsenic–oxygen frequency range, 1000–600 cm^{-1}, are relatively invariant, although some modifications in splittings, positions, and relative intensities occur. These have been attributed to specific cation effects, hydrogen bonding, and organic group effects. Additional bands are observed for the organic groups and cations. With the anhydrous tetrabutylammonium salts in Nujol mulls, the anionic OH stretching mode was observed as a narrow band at 3615 cm^{-1} (value for
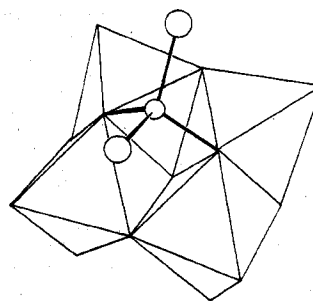

Figure 1. Structure of [(CH$_3$)$_2$AsMo$_4$O$_{15}$H]$^{2-}$ as an assemblage of MoO$_6$ octahedra.

methyl derivative). Confirmation of this assignment was obtained from the deuterated derivative in which the band was shifted to 2645 cm^{-1} (calculated 2632 cm^{-1}).

The anion proton could also be detected by ^{1}H NMR. The spectrum of (Bu$_4$N)$_2$[(CH$_3$)$_2$AsMO$_4$O$_{15}$H] in CDCl$_2$ showed resonances at 2.9 and 1.98 ppm for the dimethylarsinate and OH proton, respectively, as well as the expected cation absorptions. The integrated intensity ratios were satisfactory.[25] The 1.98-ppm resonance disappeared upon addition of a drop of methanol to the solution, indicating the lability of the OH proton.

Polarograms (dropping-mercury electrode) and cyclic voltammograms (wax-impregnated graphite electrode) of the methyl derivative in aqueous solution (1.0 M NaClO$_4$, pH 4.75, acetate buffer) showed an irreversible four-electron reduction, $E_{1/2}$ = –0.62 V vs. SCE. The absence of the characteristic reversible one-electron reductions to heteropoly "blue" species is consistent[25] with the *cis*-dioxo (type II) feature found in the structure of the polyanion.

The structural data for (CN$_3$H$_6$)$_2$[(CH$_3$)$_2$AsMo$_4$O$_{15}$H]·H$_2$O reveal a highly symmetrical and compact anion. The anion consists of four alternately face- and edge-shared octahedra capped by the (CH$_3$)$_2$AsO$_2$ group which bridges the apices of the face-sharing octahedra. This arrangement is depicted in Figure 1. The presence of face sharing is an unusual feature of the anion, since only in rare cases has this been observed in heteropoly complexes.[5,9,15,27]

Since the X-ray and neutron results are essentially identical, only the anionic distances and angles from the neutron refinement are presented in Table IV. For the terminal oxygens O(1), O(2), O(4), O(7), O(8), O(10), O(11), and O(15), the average Mo–O distance is 1.707 Å, for doubly bridging oxygens O(3), O(5), O(9), and O(13), the average distance is 1.923 Å, and for triply bridging oxygens O(12) and O(14), the average Mo–O distance is 2.290 Å, all of which are comparable to those in other heteropoly complexes such as Na$_2$[N(CH$_3$)$_4$]$_2$[(CH$_3$As)$_2$Mo$_6$O$_{24}$]·6H$_2$O.[24] The four Mo atoms form a rectangle of average dimensions of 3.163 × 3.347 Å and average Mo–Mo–Mo angles of 90°. The shorter edges are between face-sharing Mo octahedra, while the longer edges lie between edge-sharing Mo octahedra. The diminution in Mo–Mo distances for face-sharing octahedra has been previously observed in the CeMo$_{12}$O$_{42}$$^{8-}$ anion,[27] where the corresponding distances average 3.164 (2) Å.

However, one exception to the regular geometry of the anion is quite apparent. At the base of the anion is an oxygen O(6) that is simultaneously shared by all four Mo atoms. Three of the four Mo–O distances average 2.371 Å, but the fourth is considerably longer (2.540 Å). The results of a least-squares plane calculation involving the four Mo atoms indicate that no Mo atom is more than 0.01 Å from a plane,[28] while O(6)

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Table II. Final Positional and Anisotropic Thermal Parameters ($\times 10^4$) for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	59 (3)[a,b]	59 (3)	5.6 (2)	−14 (2)	−29.5 (6)	−1.4 (6)
Mo(2)	51 (3)	65 (3)	6.1 (2)	−14 (2)	4.0 (6)	−1.2 (6)
Mo(3)	55 (3)	60 (3)	6.7 (1)	7 (2)	4.1 (7)	−5.0 (6)
Mo(4)	53 (3)	56 (2)	6.0 (2)	10 (2)	2.0 (6)	0.1 (6)
As	45 (3)	60 (2)	6.2 (2)	10 (2)	1.3 (6)	1.9 (6)
O(1)	85 (4)	149 (5)	8.7 (3)	−28 (4)	−6.8 (9)	3.3 (10)
O(2)	135 (5)	73 (3)	8.6 (3)	−9 (3)	12.3 (10)	7.0 (8)
O(3)	74 (3)	74 (3)	5.5 (2)	−14 (3)	3.8 (8)	1.0 (7)
O(4)	126 (5)	66 (3)	9.5 (3)	3 (3)	−0.8 (10)	3.1 (8)
O(5)	74 (4)	56 (3)	6.8 (3)	−11 (3)	5.5 (8)	−2.5 (7)
O(6)	48 (3)	67 (3)	6.7 (3)	0 (3)	2.3 (8)	0.6 (8)
O(7)	59 (4)	145 (4)	9.4 (3)	−5 (4)	−1.1 (9)	−4.8 (10)
O(8)	117 (5)	90 (3)	9.7 (3)	−27 (4)	13.6 (10)	3.4 (9)
O(9)	58 (3)	77 (3)	7.6 (3)	−4 (3)	8.4 (8)	−3.8 (8)
O(10)	90 (4)	74 (3)	15.3 (4)	11 (3)	11.2 (11)	−3.4 (10)
O(11)	119 (5)	139 (4)	7.1 (3)	−24 (4)	4.8 (10)	−11.7 (9)
O(12)	50 (3)	66 (3)	5.6 (2)	2 (3)	3.2 (7)	−0.1 (7)
O(13)	47 (3)	78 (3)	5.9 (3)	−12 (3)	1.7 (7)	−1.5 (7)
O(14)	52 (3)	66 (3)	5.9 (2)	3 (3)	3.4 (7)	0.7 (7)
O(15)	68 (4)	134 (4)	9.7 (3)	−33 (4)	7.7 (9)	−0.7 (10)
O(16)	76 (4)	95 (4)	9.1 (4)	−5 (4)	2.1 (10)	−0.6 (10)
N(1)	176 (4)	117 (3)	18.5 (4)	−55 (3)	−19.0 (10)	2.5 (9)
N(2)	138 (3)	93 (3)	13.3 (3)	−1 (3)	−9.2 (8)	−1.4 (7)
N(3)	124 (3)	89 (3)	13.7 (3)	−8 (3)	−7.4 (8)	0.7 (7)
N(4)	101 (3)	148 (3)	7.0 (2)	51 (3)	3.1 (6)	3.5 (6)
N(5)	101 (3)	192 (4)	7.5 (2)	−6 (3)	1.3 (7)	11.2 (7)
N(6)	88 (3)	117 (3)	10.2 (2)	35 (2)	1.7 (7)	0.1 (7)
C(1)	60 (8)	120 (3)	8.4 (3)	−8 (3)	−2.4 (8)	5.3 (9)
C(2)	149 (5)	55 (3)	11.0 (3)	29 (4)	−0.6 (11)	3.6 (8)
C(3)	87 (3)	91 (3)	8.4 (3)	−22 (3)	−1.8 (8)	0.7 (7)
C(4)	68 (3)	93 (3)	7.5 (2)	−3 (3)	2.2 (7)	1.1 (7)
H(1)	89 (7)	102 (6)	8.2 (5)	11 (6)	2 (2)	3 (1)
H(2)	229 (13)	210 (10)	8.8 (6)	41 (9)	5 (2)	−8 (2)
H(3)	117 (8)	168 (9)	14.2 (7)	−31 (8)	7 (2)	0 (2)
H(4)	500 (28)	144 (11)	43.3 (22)	60 (15)	79 (7)	−12 (4)
H(5)	608 (29)	142 (10)	15.5 (9)	25 (12)	−2 (4)	2 (3)
H(6)	361 (21)	95 (9)	55.9 (25)	14 (12)	−91 (7)	−6 (4)
H(7)	175 (11)	316 (14)	19.0 (9)	−108 (11)	−11 (3)	29 (3)
H(8)	160 (11)	513 (22)	13.8 (8)	−93 (13)	1 (3)	−37 (4)
H(9)	159 (10)	198 (11)	34.4 (15)	15 (10)	−43 (3)	8 (3)
H(10)	161 (9)	207 (9)	9.2 (6)	82 (8)	7 (2)	0 (2)
H(11)	141 (9)	173 (9)	12.9 (7)	42 (8)	−6 (2)	9 (2)
H(12)	160 (10)	258 (12)	10.2 (6)	−1 (9)	−7 (2)	19 (2)
H(13)	168 (11)	347 (15)	10.6 (7)	41 (12)	14 (2)	16 (3)
H(14)	141 (8)	159 (8)	6.9 (5)	51 (7)	5 (2)	4 (2)
H(15)	167 (10)	249 (11)	9.5 (6)	104 (9)	6 (2)	2 (2)
H(16)	188 (12)	158 (9)	18.5 (9)	−4 (9)	−18 (3)	3 (2)
H(17)	212 (12)	134 (8)	23.9 (11)	16 (9)	−27 (2)	−11 (3)
H(18)	344 (20)	142 (11)	32.5 (9)	76 (12)	−36 (4)	−3 (3)
H(19)	189 (11)	124 (8)	16.1 (8)	21 (8)	−5 (2)	5 (2)
H(20)	268 (16)	208 (16)	29.1 (14)	−95 (12)	−45 (4)	4 (3)
H(21)	160 (10)	170 (10)	19.5 (10)	−7 (9)	19 (3)	−4 (2)

atom	x	y	z	atom	x	y	z
Mo(1)	0.1718 (2)[a]	0.1156 (2)	0.445 91 (6)	N(6)	0.2291 (2)	0.1511 (2)	0.222 56 (6)
Mo(2)	0.3705 (2)	0.1076 (2)	0.355 01 (6)	C(1)	0.2212 (3)	0.0614 (3)	0.307 47 (8)
Mo(3)	0.1900 (2)	−0.1993 (2)	0.320 33 (6)	C(2)	−0.0346 (3)	0.3602 (2)	0.343 85 (8)
Mo(4)	−0.0036 (2)	−0.1943 (2)	0.411 43 (6)	C(3)	0.3340 (3)	−0.3758 (2)	0.536 80 (7)
As	−0.0367 (2)	0.1377 (2)	0.341 25 (6)	C(4)	0.3540 (3)	0.0903 (2)	0.205 87 (7)
O(1)	0.3467 (3)	0.0938 (3)	0.478 16 (8)	H(1)	0.3303 (5)	−0.1551 (5)	0.409 4 (1)
O(2)	0.0770 (3)	0.2637 (3)	0.470 03 (8)	H(2)	0.4892 (7)	−0.1821 (7)	0.470 4 (2)
O(3)	0.0721 (3)	−0.0735 (3)	0.462 24 (7)	H(3)	0.5878 (6)	−0.1997 (6)	0.431 2 (2)
O(4)	0.0798 (3)	−0.3687 (3)	0.427 73 (9)	H(4)	−0.1281 (13)	0.3937 (7)	0.359 2 (3)
O(5)	0.2540 (3)	0.2193 (2)	0.396 03 (8)	H(5)	−0.0489 (12)	0.4021 (8)	0.311 9 (2)
O(6)	0.2440 (3)	−0.0956 (2)	0.392 66 (7)	H(6)	0.0613 (11)	0.3985 (7)	0.360 4 (4)
O(7)	0.5414 (3)	0.0766 (3)	0.388 39 (9)	H(7)	−0.2756 (8)	−0.0235 (9)	0.326 7 (2)
O(8)	0.4124 (3)	0.2535 (3)	0.319 29 (9)	H(8)	−0.1899 (8)	0.0131 (11)	0.278 0 (2)
O(9)	0.3775 (3)	−0.0760 (3)	0.317 17 (8)	H(9)	−0.2987 (8)	0.1528 (8)	0.299 6 (3)
O(10)	0.2747 (3)	−0.3754 (3)	0.334 69 (10)	H(10)	0.2076 (6)	0.1263 (6)	0.253 3 (2)
O(11)	0.1166 (3)	0.2178 (3)	0.265 87 (8)	H(11)	0.1483 (6)	0.2063 (6)	0.202 0 (2)
O(12)	0.1263 (3)	0.0684 (2)	0.319 13 (7)	H(12)	0.3034 (7)	0.1804 (7)	0.143 1 (2)
O(13)	−0.0050 (3)	−0.2133 (3)	0.347 39 (7)	H(13)	0.4780 (7)	0.0894 (9)	0.153 0 (2)
O(14)	−0.0302 (3)	0.0655 (3)	0.314 15 (7)	H(14)	0.4360 (6)	−0.0217 (5)	0.262 1 (1)
O(15)	−0.2018 (3)	−0.2193 (3)	0.415 40 (9)	H(15)	0.5366 (7)	−0.0561 (7)	0.215 8 (2)
O(16)	0.5050 (3)	0.2657 (3)	0.057 35 (9)	H(16)	0.2011 (8)	0.1920 (6)	0.515 0 (2)

Table II *(Continued)*

atom	x	y	z	atom	x	y	z
N(1)	0.2411 (3)	0.4827 (2)	0.516 21 (8)	H(17)	0.3622 (8)	0.1499 (6)	0.551 2 (2)
N(2)	0.4646 (2)	-0.4225 (2)	0.561 35 (6)	H(18)	0.2628 (10)	-0.5940 (7)	0.520 8 (3)
N(3)	0.3006 (2)	-0.2261 (2)	0.532 06 (6)	H(19)	0.4965 (7)	-0.5374 (6)	0.560 6 (2)
N(4)	0.4575 (2)	0.0057 (2)	0.230 75 (5)	H(20)	0.1565 (9)	-0.4531 (8)	0.494 5 (3)
N(5)	0.3758 (2)	0.1138 (2)	0.163 06 (6)	H(21)	0.5427 (9)	-0.3477 (7)	0.573 9 (2)

^{a} The standard error in parentheses after each parameter refers to the last decimal place given. ^{b} The form of the anisotropic ellipsoid is $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. IR Absorption Frequencies (cm^{-1}) for the Tetramolybdodiorganoarsinates^a

	R								
	CH$_3$			C$_2$H$_5$			C$_6$H$_5$		
assignt	Na$^+$	[C(NH$_2$)$_3$]$^+$	[N(C$_4$H$_9$)$_4$]$^+$	Na$^+$	[C(NH$_2$)$_3$]$^+$	[N(C$_4$H$_9$)$_4$]$^+$	Na$^+$	[C(NH$_2$)$_3$]$^+$	[N(C$_4$H$_9$)$_4$]$^+$
ν(As–CH$_3$)		1280	1280	1290		1265			
ν(As–C$_6$H$_5$)								1090	1098
ν(Mo–O)	960	955 sh	955 sh	970		960 sh	960	960	960 sh
terminal	930	940 s	945 s	950	950	948 s	950	950	950 s
	920	910 s	920 s	930	920	923 s	920	925	925 s
ν(As–O)			850 sh	870		885 sh	880	885	885 sh
	830	825 n	835 n		830	832 n	830	830	832 s
	800	795 n	810 n	790	810	810 n			
ν(Mo–O)						768 sh			
bridging					750	745 s	750	745	750 sh
	720	710 b	715 sh	730	720	710 sh	710	715	710 sh
			670 sh	670	670	665 w			

^{a} s = strong; sh = shoulder; n = narrow; w = weak; b = broad.
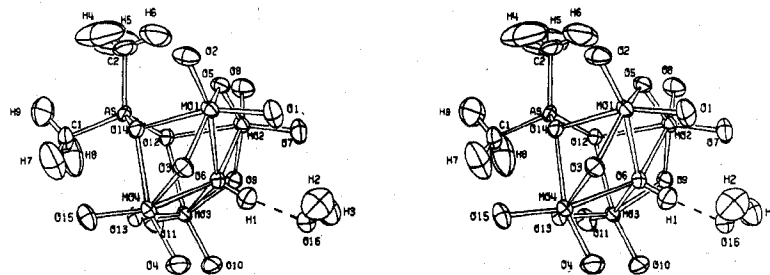
Figure 2. Stereoscopic view of [(CH$_3$)$_2$AsMo$_4$O$_{15}$H]$^{2-}$·H$_2$O illustrating the numbering scheme. Ellipsoids have been drawn at the 50% probability level.

is 0.73 Å below the plane of the Mo atoms. The ordered asymmetry of the basal oxygen, as well as the presence of a water of hydration 2.8 Å from O(6), led us to postulate from the X-ray data that the anionic hydrogen H(1) was bonded to the unique oxygen O(6).[12] Presumably the water molecule of crystallization was hydrogen bonded to O(6) through H(1).

As predicted, the neutron data unambiguously show that the H(1) is located on O(6) and hydrogen bonded to the H$_2$O molecule. A stereoscopic view of the anion which illustrates the site of protonation as well as the anionic numbering scheme is presented as Figure 2. The O(6)–H(1) distance is 0.991(5) Å, which agrees well with the OH distance in alcohols as determined by neutron diffraction. For example, the OH distance in α-resorcinol is 1.02 Å, while in pentaerythritol the analogous distance is 0.94 Å.[29] A summary of bond distances and angles about the unique oxygen is given in Table V. The distance of H(1) to O(16) is 1.779 (5) Å, which is comparable to the OH···O distances obtained by neutron diffraction for α-resorcinol (1.73 Å) and for pentaerythritol (1.81 Å), both of which exhibit hydrogen bonding.[29]

The geometry about the (CH$_3$)$_2$AsO$_2$ group is almost perfectly tetrahedral. The average of the angles about As remains unchanged from uncoordinated dimethylarsinic acid (109.4°).[30] The average As–C distance is 1.930 Å, while the

average As–O distance is 1.704 Å. The As–O distances cannot be compared to those of dimethylarsinic acid, since the acid exists only as dimers. The average C–H distance is 1.021 Å, though the distances of C(1) to H(7), H(8), and H(9) are slightly longer than those of C(2) to H(4), H(5), and H(6). In the former, the average C–H distance is 0.994 Å, as compared to 1.044 Å in the second methyl group. Distances and angles for the (CH$_3$)$_2$AsO$_2$ moiety are shown in Table VI.

The cations are planar and are involved in an extensive hydrogen-bonded network with the water molecules and oxygens of the anion. Their geometry agrees with previous structural work on guanidinium salts.[31] Distances and angles for the cations are found in Table VII, and a list of probable hydrogen bonds is given in Table VIII. The NH···O distances range from 1.838 to 2.281 Å, while the OH···O distances are 1.908 (6) and 2.081 (6) Å, all of which lie within the expected range for hydrogen bonds.[29]

As in [(CH$_3$As)$_2$Mo$_6$O$_{24}$]$^{4-}$,[24] [CH$_3$AsMo$_6$O$_{21}$(OH)$_2$]$^{2-}$,[13] [(C$_6$H$_5$As)$_2$Mo$_6$O$_{25}$H$_2$]$^{4-}$,[9] and [(C$_6$H$_5$As)$_2$W$_6$O$_{25}$H]$^{5-}$,[5] the structure of [(CH$_3$)$_2$AsMo$_4$O$_{15}$H]$^{2-}$ is well adapted to the dimensions of the organoarsenic tetrahedron. Recently Day et al.[15] have reported the structure of (Bu$_4$N)$_3$[H$_2$CMo$_4$O$_{15}$H], the anion of which is isostructural with the dimethylarsinate complex. Bond lengths around the carbon atom in this anion are consistent with its being viewed as an acetal derivative. The O···O distance in (CH$_3$)$_2$AsO$_2$ (2.73 Å) is significantly larger than that in H$_2$CO$_2$ (2.35 Å). Thus, although there is

(28) Distances from plane: Mo(1), -0.012 (1); Mo(2), 0.012 (1); Mo(3), -0.012 (1); Mo(4), 0.011 (1); O(6), 0.725 (7) Å.

(29) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

(30) Trotter, J.; Zobel, T. *J. Chem. Soc.* **1965**, 4466.

(31) Schein, B. J. *J. Chem. Phys.* **1967**, *47*, 5183.

Table IV. Selected Anionic Distances (Å) and Angles (Deg) for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

Distances

Terminal Oxygens

Mo(1)–O(1)	1.711 (3)[a]	Mo(3)–O(10)	1.704 (3)
Mo(1)–O(2)	1.699 (3)	Mo(3)–O(11)	1.707 (3)
Mo(2)–O(7)	1.711 (3)	Mo(4)–O(4)	1.701 (3)
Mo(2)–O(8)	1.705 (3)	Mo(4)–O(15)	1.719 (3)

Doubly Shared Oxygens

Mo(1)–O(3)	1.910 (3)	Mo(3)–O(9)	1.924 (3)
Mo(1)–O(5)	1.932 (3)	Mo(3)–O(13)	1.925 (3)
Mo(2)–O(5)	1.912 (3)	Mo(4)–O(3)	1.906 (3)
Mo(2)–O(9)	1.941 (3)	Mo(4)–O(13)	1.935 (3)

Triply Shared Oxygens

Mo(1)–O(14)	2.252 (3)	Mo(3)–O(12)	2.346 (3)
Mo(2)–O(12)	2.278 (3)	Mo(4)–O(14)	2.283 (3)

Unique Basal Oxygen

Mo(1)–O(6)	2.527 (3)	Mo(3)–O(6)	2.360 (3)
Mo(2)–O(6)	2.385 (3)	Mo(4)–O(6)	2.392 (3)

Nonbonded

Mo(1)–Mo(2)	3.357 (3)	Mo(2)–As	3.468 (3)
Mo(1)–Mo(4)	3.163 (3)	Mo(3)–Mo(4)	3.336 (3)
Mo(1)–As	3.474 (3)	Mo(3)–As	3.468 (3)
Mo(2)–Mo(3)	3.163 (3)	Mo(4)–As	3.529 (3)

Angles

Around Mo(1)

O(1)–Mo(1)–O(2)	105.2 (2)[a]	O(2)–Mo(1)–O(14)	94.2 (1)
O(1)–Mo(1)–O(3)	98.5 (1)	O(3)–Mo(1)–O(5)	71.8 (1)
O(1)–Mo(1)–O(5)	97.4 (2)	O(3)–Mo(1)–O(6)	72.7 (1)
O(1)–Mo(1)–O(6)	91.7 (1)	O(3)–Mo(1)–O(14)	71.8 (1)
O(1)–Mo(1)–O(14)	160.2 (2)	O(5)–Mo(1)–O(6)	72.7 (1)
O(2)–Mo(1)–O(3)	106.0 (1)	O(5)–Mo(1)–O(14)	81.9 (1)
O(2)–Mo(1)–O(5)	102.5 (1)	O(6)–Mo(1)–O(14)	69.0 (1)
O(2)–Mo(1)–O(6)	162.9 (1)		

Around Mo(2)

O(5)–Mo(2)–O(6)	76.5 (1)	O(6)–Mo(2)–O(12)	71.6 (1)
O(5)–Mo(2)–O(7)	99.4 (1)	O(7)–Mo(2)–O(8)	105.4 (2)
O(5)–Mo(2)–O(8)	101.4 (1)	O(7)–Mo(2)–O(9)	98.5 (1)
O(5)–Mo(2)–O(9)	145.9 (1)	O(7)–Mo(2)–O(12)	161.0 (2)
O(5)–Mo(2)–O(12)	82.6 (1)	O(8)–Mo(2)–O(9)	101.4 (1)
O(6)–Mo(2)–O(7)	90.4 (1)	O(8)–Mo(2)–O(12)	92.6 (1)
O(6)–Mo(2)–O(8)	164.1 (2)	O(9)–Mo(2)–O(12)	71.4 (1)
O(6)–Mo(2)–O(9)	74.6 (1)		

Around Mo(3)

O(6)–Mo(3)–O(9)	75.6 (1)	O(9)–Mo(3)–O(13)	144.2 (1)
O(6)–Mo(3)–O(10)	93.2 (1)	O(10)–Mo(3)–O(11)	105.7 (2)
O(6)–Mo(3)–O(11)	161.0 (2)	O(10)–Mo(3)–O(12)	162.4 (2)
O(6)–Mo(3)–O(12)	71.0 (1)	O(10)–Mo(3)–O(13)	101.6 (1)
O(6)–Mo(3)–O(13)	74.4 (1)	O(11)–Mo(3)–O(12)	90.7 (1)
O(9)–Mo(3)–O(10)	99.2 (1)	O(11)–Mo(3)–O(13)	98.6 (2)
O(9)–Mo(3)–O(11)	103.5 (2)	O(12)–Mo(3)–O(13)	81.9 (1)
O(9)–Mo(3)–O(12)	70.1 (1)		

Around Mo(4)

O(3)–Mo(4)–O(4)	98.1 (1)	O(4)–Mo(4)–O(15)	105.0 (2)
O(3)–Mo(4)–O(6)	76.1 (1)	O(6)–Mo(4)–O(13)	73.4 (1)
O(3)–Mo(4)–O(13)	144.6 (1)	O(6)–Mo(4)–O(14)	71.0 (1)
O(3)–Mo(4)–O(14)	71.2 (1)	O(6)–Mo(4)–O(15)	163.1 (2)
O(3)–Mo(4)–O(15)	105.7 (1)	O(13)–Mo(4)–O(14)	82.1 (1)
O(4)–Mo(4)–O(6)	91.2 (1)	O(13)–Mo(4)–O(15)	98.4 (1)
O(4)–Mo(4)–O(13)	100.2 (1)	O(14)–Mo(4)–O(15)	93.4 (1)
O(4)–Mo(4)–O(14)	160.8 (2)		

M–M–M

Mo(1)–Mo(2)–Mo(3)	91.0 (1)	Mo(3)–Mo(4)–Mo(1)	91.4 (1)
Mo(2)–Mo(3)–Mo(4)	88.9 (1)	Mo(4)–Mo(1)–Mo(2)	88.6 (1)

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

Table V. Distances (Å) and Angles (Deg) about the Unique Oxygen in $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

Distances

Mo(1)–O(6)	2.527 (3)[a]	H(1)–O(6)	0.991 (5)
Mo(2)–O(6)	2.385 (3)	H(1)–O(16)	1.779 (5)
Mo(3)–O(6)	2.360 (3)	H(2)–O(16)	0.945 (6)
Mo(4)–O(6)	2.392 (3)	H(3)–O(16)	0.941 (7)

Angles

H(1)–O(6)–Mo(1)	104.9 (3)	H(1)–O(6)–Mo(4)	109.2 (3)
H(1)–O(6)–Mo(2)	105.4 (3)	H(2)–O(16)–H(3)	105.9 (4)
H(1)–O(6)–Mo(3)	110.3 (3)		

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

Table VI. Distances (Å) and Angles (Deg) for the $(CH_3)_2AsO_2$ Group in $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

Distances

As–O(12)	1.704 (3)[a]	H(8)–C(1)	1.037 (7)
As–O(14)	1.704 (3)	H(9)–C(1)	1.034 (7)
As–C(1)	1.906 (3)	H(4)–C(2)	1.023 (7)
As–C(2)	1.899 (3)	H(5)–C(2)	1.001 (10)
H(7)–C(1)	1.060 (7)	H(6)–C(2)	0.972 (9)

Angles

O(5)–As–O(12)	67.9 (1)	C(1)–As–C(2)	111.5 (1)
O(5)–As–O(14)	67.0 (1)	H(7)–C(1)–H(9)	109.7 (6)
O(5)–As–C(2)	74.7 (1)	H(7)–C(1)–H(8)	111.0 (6)
O(12)–As–O(14)	106.6 (1)	H(8)–C(1)–H(9)	108.2 (7)
O(12)–As–C(1)	109.6 (1)	H(4)–C(2)–H(5)	107.8 (8)
O(12)–As–C(2)	111.0 (2)	H(4)–C(2)–H(6)	109.7 (9)
O(14)–As–C(1)	109.1 (1)	H(5)–C(2)–H(6)	112.5 (8)
O(14)–As–C(2)	108.8 (1)		

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

Table VII. Distances (Å) and Angles (Deg) for the $CN_3H_6^+$ Cations in $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

Distances

C(3)–N(1)	1.322 (3)[a]	N(2)–H(19)	1.018 (6)
C(3)–N(2)	1.338 (3)	N(3)–H(17)	0.986 (7)
C(3)–N(3)	1.313 (2)	N(3)–H(16)	0.993 (7)
C(4)–N(4)	1.317 (3)	N(4)–H(15)	0.998 (6)
C(4)–N(5)	1.336 (3)	N(4)–H(14)	1.007 (5)
C(4)–N(6)	1.326 (2)	N(5)–H(13)	0.972 (7)
N(1)–H(18)	0.947 (7)	N(5)–H(12)	0.998 (6)
N(1)–H(20)	0.961 (8)	N(6)–H(10)	0.985 (6)
N(2)–H(21)	0.972 (7)	N(6)–H(11)	0.999 (6)

Angles

N(1)–C(3)–N(2)	119.0 (2)	H(18)–N(1)–H(20)	118.2 (6)
N(1)–C(3)–N(3)	120.4 (2)	H(21)–N(2)–H(19)	117.7 (5)
N(2)–C(3)–N(3)	120.6 (2)	H(16)–N(3)–H(17)	119.4 (5)
N(4)–C(4)–N(5)	119.0 (2)	H(14)–N(4)–H(15)	119.6 (4)
N(4)–C(4)–N(6)	121.2 (2)	H(12)–N(5)–H(13)	117.1 (5)
N(5)–C(4)–N(6)	119.9 (2)	H(10)–N(6)–H(11)	120.2 (4)

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

of spectroscopic data, to have the tetramolybdoarsinate structure with MoO_4^{2-} (O···O = 2.89 Å[32]) instead of $R_2AsO_2^{2-}$.

The presence of constitutional protons in polyanion structures has been recognized for many years. Examples of anions with nontitratable protons are metadodecatungstate, $H_2W_{12}O_{40}^{6-}$, paradodecatungstate, $H_2W_{12}O_{42}^{10-}$, and numerous heteropoly anions, $CrMo_6O_{24}H_6^{3-}$, $Co_2Mo_{10}O_{38}H_4^{6-}$, etc. One may view these species as being derived from hypothetical unprotonated anions $W_{12}O_{40}^{8-}$ etc. or as being complexes incorporating bridging hydroxide groups.[33] Both viewpoints

no confirmed example of an analogous phosphinate complex, the dimensions of $R_2PO_2^-$ (O···O = 2.49 Å) do not preclude such a possibility. The unstable isopoly molybdate anion $Mo_5O_{17}H^{3-}$, reported by Klemperer,[16] is believed, on the basis

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Table VIII. Probable Hydrogen Bonds in
$(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$

atoms	symmetry operation	dist, Å
H(2)–O(1)	$1-x, -y, 1-z$	2.081 (6)[a]
H(3)–O(15)	$x-1, y, z$	1.908 (6)
H(10)–O(12)	x, y, z	2.218 (6)
H(11)–O(13)	$-x, y - \frac{1}{2}, \frac{1}{2} - z$	1.985 (5)
H(12)–O(15)	$-x, y - \frac{1}{2}, \frac{1}{2} - z$	2.072 (6)
H(13)–O(10)	$1-x, y - \frac{1}{2}, \frac{1}{2} - z$	2.129 (7)
H(14)–O(9)	x, y, z	1.838 (5)
H(15)–O(8)	$1-x, \frac{1}{2} + y, \frac{1}{2} - z$	2.007 (6)
H(16)–O(3)	x, y, z	2.103 (6)
H(17)–O(7)	$1-x, -y, 1-z$	2.024 (7)
H(19)–O(16)	$x, -y - \frac{1}{2}, z - \frac{1}{2}$	1.951 (6)
H(20)–O(4)	x, y, z	2.176 (8)
H(21)–O(5)	$1-x, -y, 1-z$	2.174 (6)

[a] The standard error in parentheses after each parameter refers to the last decimal place given.

offer advantages and both have their limitations. In polyanion structures, where the locations of the protons are known, the latter are found to be attached to those sterically accessible oxygen atoms that bridge the most metal atoms. This is not surprising since M–O bond lengths to such oxygens are likely to be long and will result in low total bond orders at the oxygen and therefore a relatively high negative charge. Klemperer and Shum have verified this principle in their ^{17}O NMR study[34] of the protonation of $V_{10}O_{28}^{6-}$. In the tetramolybdoarsinate structure, the proton is attached to the unusual

four-coordinate oxygen. The Mo–O bond lengths to this oxygen atom are very long and imply a low ($<0.2^{35}$) bond order. The asymmetric position of the oxygen in the Mo_4 frame is considered to result from the presence of the hydrogen-bonded water molecule which lies toward the longest Mo–O(H) bond. In the structure of $(Bu_4N)_3CH_2Mo_4O_{15}H$, which has no such water molecule, the corresponding oxygen atom is more nearly equidistant from the four molybdenum atoms.

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Meshing Ability of Bulky Tertiary Phosphines. X-ray Structure of *cis*-Bis(di-*tert*-butylphenylphosphine)dichloroplatinum(II)

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The square-planar platinum(II) complex $PtCl_2(P(t\text{-}Bu)_2Ph)_2$, containing two bulky phosphines cis to each other, has been studied by X-ray diffraction methods. The crystals are monoclinic of space group $P2_1/c$, with $a = 11.211$ (1) Å, $b = 14.621$ (1) Å, $c = 18.157$ (2) Å, $\beta = 102.38$ (2)°, and $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by least squares to a conventional R factor of 0.059, on the basis of 2427 intensities above background. The square-planar coordination is very distorted with P–Pt–P and Cl–Pt–Cl angles of 107.3 (4) and 84.2 (3)°, respectively. The mean Pt–P and Pt–Cl distances are 2.358 (6) and 2.333 (5) Å. The stability of the complex, in spite of the cis relation of the two phosphines, is explained as having recourse to the variable-aperture cone model. The substituent orientation about the Pt–P bonds allows for a good fitting of protrusions and hollows without severe steric hindrance.

Introduction

Electronic properties and size of the ligands play an important role in the reactions catalyzed by transition-metal phosphine complexes.[1] The cone angle introduced by Tolman is a simple criterion to measure the ligand size. The steric demand of the ligand may also be measured in terms of solid cone angles.[2]

Di-*tert*-butylphenylphosphine $P(t\text{-}Bu)_2Ph$ is a very bulky ligand which has a ligand cone angle $\theta = 170°$ and a solid cone angle $\Omega = 4.55$ rad, respectively. With this phosphine the only

zerovalent PtL_n stable complex is PtL_2, and no appreciable quantity of PtL_3 is formed in solution even in the presence of a large excess of free phosphine.[3] For these reasons one expects that only the trans isomer will be stable in the square-planar complex $PtCl_2L_2$. Recently an orange crystalline product which analyzes as $PtCl_2(P(t\text{-}Bu)_2Ph)_2$ has been isolated in our laboratory. As the color is different from the yellow *trans*-$PtCl_2(P(t\text{-}Bu)_2Ph)_2$ described by Shaw,[4] the crystals were studied by X-ray diffraction methods. The compound proved to be the unexpected *cis*-$PtCl_2(P(t\text{-}Bu)_2Ph)_2$.

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