Heteropolyanions of Methylarsonate and Dimethylarsinate: The Crystal Structures of Guanidinium Hexamolybdomethylarsonate Hexahydrate, $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ and Guanidinium Tetramolybdodimethylarsinate Monohydrate, $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$

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The crystal and molecular structures of polymolybdo complexes of methylarsonate and dimethylarsinate have been determined by the X-ray diffraction technique. The crystal of $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ is trigonal, with the space group R3 and the cell dimensions of $a=9.653(6)$ Å, $\alpha=87.01(15)°$, and $Z=1$. The anion is an assemblage of six MoO_6 octahedra and a tetrahedral CH_3AsO_3 group. The six MoO_6 octahedra constitute a ring with alternate edge- and corner-sharing, and the tetrahedral CH_3AsO_3 group joins the anion, with its three oxygen atoms shared with the ring. Each molybdenum atom has two terminal oxygen atoms in the *cis* position and is coordinated by one water molecule. $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$ crystallizes in the space group $P2_1/c$ of the monoclinic system, with the cell dimensions of $a=8.530(5)$, $b=8.532(4)$, $c=30.121(15)$ Å, $\beta=95.50(16)°$, and $Z=4$. The $Mo_4O_{14}(OH)$ moiety in the $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$ anion is formed with two face- and two edge-sharings of MoO_6 octahedra into an almost flat rectangle. The oxygen atom located at the center of the anion and bonded to all the four molybdenum atoms is protonated and is, in fact, a hydroxyl group.

It is well known that arsenic acid reacts with molybdic acid to yield various heteropoly acids. Some of them have been structurally elucidated by X-ray diffraction: $AsMo_{12}O_{40}^{3-}$ with the Keggin structure,[1,2] $H_4AsMo_{12}O_{50}^{4-}$ [3] with the "reversed" Keggin structure, $AsMo_9O_{34}^{9-}$,[4] $As_2Mo_{18}O_{62}^{6-}$,[5,6] and $As_2Mo_5O_{23}^{6-}$.[7] Alkyl- or arylarsonic acids and -arsinic acids, $RAsO_3H_2$ and R_2AsO_2H, seem to be similar to phosphoric or arsenic acid in their chemical properties in the following respects: they form dimers of the pyrophosphoric-acid type and are weak acids (the pK values of $RAsO_3H_2$ are 3—4, whereas pK_1 is 2.1 for phosphoric acid and 2.3 for arsenic acid). In view of the fact that the heteropolyanions containing phosphorus or arsenic atoms are formed through dehydration between phosphoric or arsenic acid and molybdic acid, these organo-arsenic acids can be expected to react with molybdic acid to give organo-heteropolyanions.

Such anions are noteworthy from the following points of view: the organo-heteropolyanions have their heteroatoms, that is, As(V) in the present case, partly coordinated by organic groups. Therefore, the arsenic atoms can not be coordinated by four oxygen atoms, unlike those in non-alkylated arsenic acids, as long as the former keep their coordination number of 4. Otherwise, they may increase the coordination number from 4 to 6. Whichever of the two may be the case, new structural types may be expected for these anions. Recently, the present author has reported the crystal and molecular structure of $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2\cdot 4H_2O$,[8] whose anion's interconversion with $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$ in an aqueous solution[9] has added valuable knowledge concerning the intermediate species involved in the formation of these anions and the pH regions where they are stable.

In this paper the author will report on the crystal and molecular structures of guanidinium polymolybdomethylarsonate and polymolybdodimethylarsinate, $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ and $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$. The first synthetic description of these complexes was made by Gibbs as early as in 1883[10] and later by Rosenheim and Bilecki,[11] but their analytical results are unsatisfactory and the molecular formulae they gave seem doubtful. As for the heteropolyanions containing methylarsonic acid, the synthesis and the structure of $[(CH_3As)_2Mo_6O_{24}]^{4-}$ have recently been reported,[12] but the author has independently obtained a hexamolybdomethylarsonate anion which seems to have a different molecular formula, *i.e.*, $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$. Thus, the formation conditions and structural differences of these anions are of interest and would give information about the reactions occurring in an aqueous solution containing molybdic acid and methylarsonic acid. On the other hand, regarding the heteropolyanion containing dimethylarsinic acid, a short communication on the crystal structure of $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$ recently appeared;[13] it briefly discusses the anion's structure. In this paper, the whole crystal structure, together with the anion's structure, will be discussed, and the full and detailed data on the bond distances, bond angles, and the crystal packings, including the network of hydrogen bondings, will be presented.

Experimental

$(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$. Preparation: 4.3 g (0.03 mol) of MoO_3 was gradually added to 75 cm^3 of a boiling aqueous solution containing 1.46 g (5 mmol) of $Na_2AsCH_3O_3$, and the pH of the solution was decreased to *ca.* 2 with HCl. After the solution has been boiled for a few minutes, it was filtered to remove a small amount of unreacted MoO_3 and the filtrate was condensed on a water bath to 12.5 cm^3. The addition of 1 g of CN_3H_6Cl to the solution readily gave a lolorless precipitate, which was subsequently filtered, recrystallized from hot water, and air-dried. The reaction is expressed as follows:

$$CH_3AsO_3^{2-} + 6MoO_3 + 6H_6O \longrightarrow [CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$$

Found: C, 2.69; H, 2.94; N, 6.48%. Calcd for $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$: C, 2.73; H, 2.80; N, 6.37%.

The addition of $(CH_3)_4NBr$ or KCl instead of CN_3H_6Cl

Table 1. Final positional parameters ($\times 10^4$) for $(CN_3H_6)_6[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$, with their estimated standard deviations in parentheses

	x	y	z
Mo (1)	40 (6)	2265 (6)	−2956 (6)
Mo (2)	2965 (5)	−145 (6)	−2245 (5)
As	300[a]	= x	= x
C	1345 (58)	= x	= x
O (1)	844 (35)	629 (36)	−1312 (37)
O (2)	2041 (69)	1381 (71)	−3223 (70)
O (3)	1373 (53)	3538 (60)	−1545 (61)
O (4)	392 (58)	3612 (56)	−4156 (56)
O (5)	−1155 (76)	2718 (82)	−1584 (76)
O (6)	−882 (53)	949 (55)	−3863 (51)
O (7)	3735 (36)	787 (42)	−1203 (36)
O (8)	4185 (54)	−435 (63)	−3482 (51)
O (9)	1429 (46)	−1577 (48)	−3345 (46)
C (1)	3204 (306)	= x	= x
C (2)	−3133 (243)	= x	= x
N (1)	2079 (85)	4063 (99)	3206 (106)
N (2)	−1890 (92)	−3994 (72)	−3146 (87)
H_2O (1)	−4040 (53)	2496 (53)	−4076 (50)
H_2O (2)	−2273 (64)	4035 (59)	4161 (59)

a) The coordinates for As are arbitrarily fixed at 300.

precipitated the corresponding salts of the anion. The potassium salt was recrystallized from hot water. However, the tetramethylammonium salt is insoluble in most aqueous and organic solvents. The addition of $(n\text{-}C_4H_9)_4NBr$ to the solution gave a yellow-green precipitate, which was a mixture of several polyanions. By the fractional recrystallization of this mixture from CH_3NO_2, the $[(CH_3As)_4Mo_{12}O_{46}]^{4-}$ anion was obtained together with other polyanions, such as $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$ and $Mo_6O_{19}^{2-}$. The $[(CH_3As)_4Mo_{12}O_{46}]^{4-}$[12] and $Mo_6O_{19}^{2-}$[14] anions were identified by elemental analyses and IR spectra.

Crystal Data: Although many kinds of salts of the $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$ anion were prepared, as has been described above, most of them were obtained in powder or microcrystalline form. Among them, guanidinium salt seemed likely to give a single crystal of an appropriate size, though it would not do so easily. Thus, attempts were made to obtain it by a diffusion method, and a crystal with approximate dimensions of $0.1\times 0.08\times 0.08$ mm was used for X-ray measurements. Although this crystal gives slightly smeared diffraction spots, it is fairly stable in air and against X-ray irradiation, at least for the period of X-ray data collection. Such smeared spots have been observed in other isopoly- and heteropolyanions; they are probably attributed to the loose packings of large anions and the existence of easily mobile water of crystallization occupying the cavities between the large anions.[15,16] Although a crystal structure analysis with a high precision can not be expected for this crystal, X-ray measurement was undertaken, because at least the structure of the anion could be elucidated and this would be valuable information for the chemistry of heteropolyanions containing methylarsonic acid. The lattice constants were refined with twelve 2θ values measured on a diffractometer with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). The crystal data for $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ are: trigonal, R3, $a=9.653(6)$ Å, $\alpha=87.01(15)°$, $V=895.9$ Å^3, $M.W.=1338.0$, $Z=1$, $D_m=2.45$ g cm^{-3}, $D_x=2.48$, $\mu=13.3$ cm^{-1}.

Table 2. Final temperature factors for $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ with their estimated standard deviations

The β_{ij}'s are defined by $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. ($\times 10^4$ for Mo and As and $\times 10^3$ for the others).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo (1)	73 (7)	50 (6)	46 (6)	19 (5)	11 (5)	27 (4)
Mo (2)	27 (5)	76 (7)	35 (5)	12 (5)	18 (4)	11 (4)
As	12 (3)	12 (3)	12 (3)	4 (3)	4 (3)	4 (3)
C	5 (4)	5 (4)	5 (4)	−1 (4)	−1 (4)	−1 (4)
O (1)	3 (4)	2 (4)	3 (4)	2 (3)	2 (3)	0 (3)
O (2)	12 (9)	15 (9)	14 (9)	8 (8)	−3 (7)	−6 (8)
O (3)	5 (5)	11 (7)	13 (8)	−1 (5)	5 (5)	1 (6)
O (4)	11 (7)	9 (7)	9 (7)	1 (6)	3 (6)	5 (6)
O (5)	14 (9)	18 (10)	13 (9)	4 (8)	8 (7)	−1 (8)
O (6)	8 (6)	11 (7)	7 (6)	0 (5)	2 (5)	2 (5)
O (7)	2 (4)	6 (5)	2 (3)	5 (3)	3 (3)	3 (3)
O (8)	8 (6)	14 (8)	6 (6)	2 (6)	5 (5)	−1 (5)
O (9)	6 (5)	7 (5)	6 (5)	3 (4)	2 (4)	1 (4)
C (1)	29 (16)	29 (16)	29 (16)	12 (11)	12 (11)	12 (11)
C (2)	9 (19)	9 (19)	9 (19)	7 (23)	7 (23)	7 (23)
N (1)	18 (12)	32 (17)	37 (19)	10 (12)	23 (13)	24 (15)
N (2)	30 (16)	11 (10)	24 (14)	14 (11)	13 (12)	8 (9)
H_6O (1)	12 (7)	13 (7)	11 (6)	0 (5)	−2 (5)	5 (5)
H_6O (2)	18 (8)	13 (7)	15 (8)	−4 (7)	−6 (7)	4 (6)

Data Collection: All the intensities were measured on a Philips automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The ω-2θ scan mode was employed with the scan rate of 1 ° min^{-1} in 2θ. The scan width was determined for each reflection according to this formula $\omega=(1.4+0.6\tan\theta)°$. Background counts of 20 s were taken at each scan end. Three standard reflections were monitored every 3 h, but no significant intensity loss was observed throughout the data collection. The data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied. The intensities were collected up to $2\theta=60°$, of which 1094 independent reflections with $|F_o|\geq 3\sigma(|F_o|)$ were used for the structural analysis.

Solution and Refinement of the Structure: Two independent molybdenum atoms were located from the Patterson map, and successive Fourier syntheses revealed the positions of all non-hydrogen atoms in the anion. At this stage, a problem arose concerning the space group of this crystal. Although this anion itself is, strictly speaking, dissymmetric, a close examination of the atomic coordinates (Table 1) exhibits that this anion is approximately centrosymmetrical except the part of the As–C bond. For instance, many atoms in the anion are related to each other nearly centrosymmetrically, *i.e.*, Mo(1) and Mo(2), O(3) and O(9), O(4) and O(8), and O(6) and O(7). Moreover, when the structure analysis had proceeded further, it was found that the cations and water molecules also occupy centrosymmetric positions (C(1) and C(2), N(1) and N(2), and H_2O(1) and H_2O(2)). As the R3 and R$\bar{3}$ space groups can not be distinguished from the systematic absence of reflection, two different refinements were attempted, one based on the R3 space group, and the other, on R$\bar{3}$, assuming a statistical distribution of the anions in the right-handed and left-handed orientations, with an equal weight for each. Disorder of

Table 3. Final positional coordinates ($\times 10^4$) for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$, with their estimated standard deviations in parentheses

	x	y	z
Mo (1)	1896 (2)	1989 (2)	3202 (1)
Mo (2)	3606 (2)	−1073 (2)	3550 (1)
Mo (3)	1720 (2)	−1161 (2)	4458 (1)
Mo (4)	−32 (2)	1942 (2)	4114 (1)
As	−367 (2)	−1375 (2)	3413 (1)
O (1)	3744 (16)	748 (15)	3155 (4)
O (2)	4120 (22)	−2518 (18)	3180 (5)
O (3)	5407 (20)	−764 (19)	3887 (5)
O (4)	2458 (15)	952 (14)	3923 (4)
O (5)	2546 (16)	−2190 (15)	3961 (4)
O (6)	3508 (20)	−932 (19)	4778 (5)
O (7)	737 (19)	−2628 (17)	4712 (5)
O (8)	683 (16)	735 (15)	4629 (4)
O (9)	807 (18)	3671 (17)	4282 (5)
O (10)	−298 (16)	−656 (14)	3920 (5)
O (11)	−2029 (17)	2197 (17)	4153 (5)
O (12)	−67 (15)	2138 (14)	3472 (4)
O (13)	2752 (18)	3723 (18)	3349 (6)
O (14)	1175 (19)	2176 (19)	2654 (5)
O (15)	1205 (15)	−703 (15)	3186 (4)
O (16)	4960 (17)	2335 (16)	4434 (5)
C (1)	−348 (37)	−3636 (24)	3435 (10)
C (2)	−2220 (27)	−623 (26)	3063 (8)
C (3)	6612 (30)	6234 (27)	4634 (8)
C (4)	6446 (25)	4093 (23)	2942 (7)
N (1)	5352 (26)	5770 (23)	4392 (7)
N (2)	7651 (31)	5169 (27)	4841 (8)
N (3)	6996 (25)	7738 (22)	4691 (7)
N (4)	6263 (24)	3873 (23)	3374 (7)
N (5)	7708 (22)	3476 (21)	2766 (6)
N (6)	5401 (23)	4940 (22)	2686 (6)

Table 4. Final temperature factors ($\times 10^4$) for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$, with their estimated standard deviations

The β_{ij}'s are defined by: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo (1)	48 (2)	29 (2)	5 (1)	6 (2)	5 (1)	3 (1)
Mo (2)	46 (2)	31 (2)	4 (1)	12 (2)	4 (1)	1 (1)
Mo (3)	54 (2)	28 (2)	4 (1)	11 (2)	3 (1)	1 (1)
Mo (4)	46 (2)	23 (2)	4 (1)	10 (1)	3 (1)	0 (1)
As	45 (2)	26 (2)	4 (1)	−7 (2)	2 (1)	−1 (1)
O (1)	64 (17)	39 (15)	4 (1)	18 (13)	11 (4)	1 (3)
O (2)	184 (29)	50 (19)	6 (2)	−22 (19)	20 (6)	0 (4)
O (3)	68 (23)	81 (22)	10 (2)	−1 (18)	1 (5)	4 (5)
O (4)	38 (16)	37 (15)	5 (1)	4 (12)	3 (3)	−1 (3)
O (5)	73 (18)	39 (15)	4 (1)	7 (14)	5 (4)	1 (4)
O (6)	92 (24)	93 (23)	7 (2)	18 (19)	−2 (5)	−3 (5)
O (7)	106 (23)	34 (17)	9 (2)	39 (16)	12 (5)	2 (4)
O (8)	65 (17)	37 (15)	5 (1)	31 (13)	10 (4)	1 (4)
O (9)	80 (20)	30 (17)	12 (2)	20 (16)	−12 (5)	−4 (5)
O (10)	56 (17)	13 (14)	7 (2)	−13 (13)	−2 (4)	−1 (4)
O (11)	56 (19)	53 (18)	9 (2)	22 (15)	9 (4)	−2 (5)
O (12)	46 (16)	9 (13)	6 (1)	2 (12)	1 (4)	0 (4)
O (13)	45 (20)	52 (19)	16 (2)	17 (17)	−3 (5)	−2 (6)
O (14)	77 (22)	114 (23)	7 (2)	15 (19)	8 (5)	7 (5)
O (15)	31 (15)	38 (15)	6 (2)	6 (13)	3 (3)	−4 (4)
O (16)	54 (18)	33 (17)	10 (2)	−11 (14)	2 (4)	1 (4)
C (1)	107 (48)	19 (22)	18 (3)	17 (27)	10 (11)	−2 (7)
C (2)	79 (30)	63 (27)	10 (3)	−10 (24)	0 (7)	−1 (7)
C (3)	115 (35)	54 (28)	9 (3)	45 (27)	−3 (8)	−4 (8)
C (4)	82 (27)	51 (24)	5 (2)	1 (21)	−1 (6)	0 (6)
N (1)	120 (32)	52 (25)	11 (3)	17 (23)	−8 (7)	−3 (7)
N (2)	183 (42)	62 (30)	16 (3)	52 (30)	−24 (10)	0 (9)
N (3)	100 (30)	47 (24)	11 (3)	−15 (22)	−7 (7)	1 (6)
N (4)	94 (28)	79 (25)	8 (2)	−13 (23)	4 (6)	8 (6)
N (5)	69 (23)	55 (22)	8 (2)	23 (19)	4 (5)	1 (6)
N (6)	88 (26)	72 (24)	6 (2)	33 (21)	4 (6)	0 (6)

this kind has sometimes been observed in crystals of isopoly- and heteropoly acids and their salts,[16,17] and is considered as one of their specific properties. The R value for R3 was 0.20, whereas that for $R\bar{3}$ was 0.21. Therefore the R3 space group was assumed to be the true one. After several cycles of refinement with isotropic temperature factors by the block-diagonal least-squares method using the UNICS program,[18] anisotropic temperature factors were applied for all the atoms; further refinements reduced the R value to 0.16 ($R=\sum||F_o|-|F_c||/\sum|F_o|$). All the cations and water of crystallization were located on the basis of the difference synthesis, and the structure was finally refined to $R=0.14$. Although the final R value is not low enough, this is because of the unsatisfactory quality of the crystal, as has been mentioned, and does not basically obviate the elucidated anion's structure.

The atomic coordinates and temperature factors are listed in Tables 1 and 2. The final F_o-F_c table is available at the Office of Chemical Society of Japan as Document No. 7930A. The atomic scattering factors were taken from Ref. 19, while the corrections of the effect of the anomalous dispersion for molybdenum and arsenic atoms were based on Ref. 20. The calculation was performed on a HITAC 8700/8800 computer at the Computer Center of the University of Tokyo.

$(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$. *Preparation*: This compound was prepared according to the method described in Ref. 11. Found: C, 5.41; H, 2.51; N, 9.90; Mo, 45.52%. Calcd for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$: C, 5.54; H, 2.44; N, 9.68; Mo, 44.22%.

Cyrstal Data: A colorless rectangular crystal with the approximate dimensions of $0.2\times0.2\times0.1$ mm was used. The cell dimensions were obtained from twelve 2θ values measured on a diffractometer with Mo $K\alpha$ radiation. The crystal data for $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$ are: monoclinic $P2_1/c$, $a=8.530(5)$ Å, $b=8.532(4)$, $c=30.121(15)$, $\beta=95.50(16)°$, $M.W.=867.9$, $Z=4$, $D_m=2.63$ g cm^{-3}, $D_x=2.64$, $\mu=41.0$ cm^{-1}.

Data Collection: All the intensity measurements were performed on a Rigaku four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The conditions for the data collection were basically the same as those described above. The scan rate was 2° min^{-1} in 2θ, and the scan range was determined according to this formula: $\omega=(1.4+0.6\tan\theta)°$. A background count was made for 10 s at the end of each scan. Three standard reflections, monitored every 50 measurements, remained essentially constant during the data collection. The data were corrected for Lorentz and polarization effects. Absorption and extinction cor-

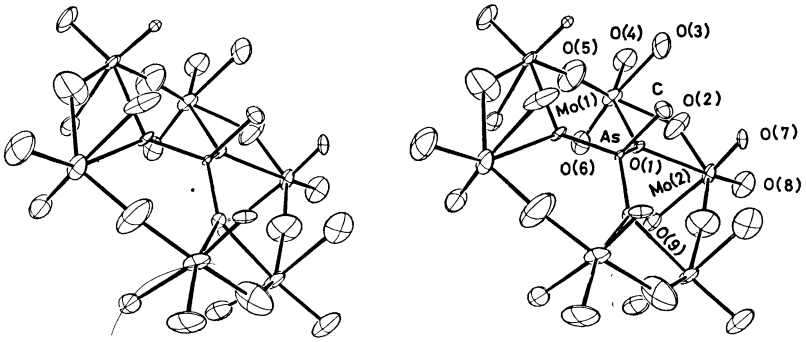


Fig. 1. Stereoscopic view of the $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$ anion with vibrational ellipsoids drawn at the 30% probability level. (ORTEP Johnson, 1971)

Table 5. The bond lengths for the anion and the cations in $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$, with their estimated standard deviations in parentheses

	l/Å		l/Å
MO(1)-O(1)	2.33(4)	Mo(2)-O(1)	2.29(4)
O(2)	2.08(7)	O(2)	1.91(7)
O(3)	2.35(6)	O(7)	1.62(4)
O(4)	1.73(6)	O(8)	1.66(5)
O(5)	1.77(8)	O(9)	2.40(5)
O(6)	1.87(6)	O(5′)	1.72(7)
As-O(1)	1.64(4)	Mo(1)···Mo(2)	3.63(1)
C	1.84(6)	Mo(1)···Mo(2′)	3.48(1)
C(1)-N(1)	1.33(27)		
C(2)-N(2)	1.42(24)		

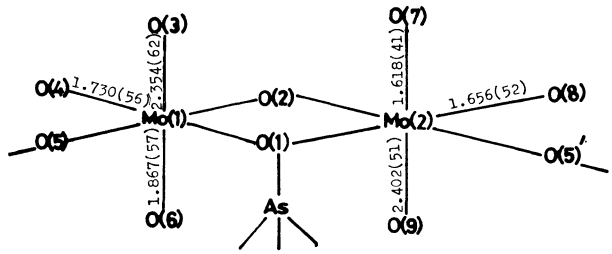
The prime refers to the transformation, (y, z, x).

rections were not applied. 5222 independent reflections with $|F_o| \geq 3\sigma(|F_o|)$ up to $2\theta=60°$ were used for the computation.

Solution and Refinement of the Structure: The coordinates for the four independent molybdenum atoms were deduced from the Patterson map. All the remaining non-hydrogen atoms were located from the successive Fourier maps. A few cycles of refinement with individual isotropic temperature factors for all the atoms, followed by several further cycles of anisotropic refinement, resulted in a final R value of 0.091. The final coordinates and temperature factors are listed in Tables 3 and 4, while the F_o-F_c table is kept at the office of this Bulletin as Document No. 7930B.

Description of the Structure and Discussion

$(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$. The structure of the anion is illustrated in Fig. 1. The anion consists of six MoO_6 octahedra, which form a ring by alternate corner- and edge-sharing (the shared corner is O(5) and the shared edge is O(1)–O(2)), and a CH_3AsO_3 tetrahedron connected to the ring with its three oxygen atoms shared with the ring. The six molybdenum atoms are not coplanar and deviate from the best plane by about 0.4 Å, upward and downward alternately. Only Mo(1), Mo(2), As, C, and the nine oxygen atoms coordinated to these molybdenum and arsenic atoms are crystallographically independent; the remaining part of the anion is related



∠ O(3)-Mo(1)-O(4) 82.5(2.3)° ∠ O(8)-Mo(2)-O(9) 90.4(2.1)°
∠ O(4)-Mo(1)-O(6) 107.4(2.4)° ∠ O(7)-Mo(2)-O(8) 102.7(2.2)°
∠ O(3)-Mo(1)-O(6) 168.5(2.2)° ∠ O(7)-Mo(2)-O(9) 166.6(1.8)°

Fig. 2. The geometry of the terminal oxygen atoms around Mo(1) and Mo(2) in the $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$ anion.

to the independent atoms by a three-fold axis which coincides with the As–C bond axis. The bond lengths in the anion and cations are listed in Table 5. It is noteworthy that each molybdenum atom seemingly possesses three terminal oxygen atoms. However, for the reasons to be presented below, it is concluded that each molybdenum atom is surrounded not by three terminal oxygen atoms, but by two terminal ones and a water molecule. One of the reasons is concerned with the distances of the terminal Mo–O bonds. As is illustrated in Fig. 2, the Mo(1)–O(3) and Mo(2)–O(9) distances are obviously longer than the other four terminal ones (Mo(1)–O(4), Mo(1)–O(6), Mo(2)–O(7), and Mo(2)–O(8)). The distances, 2.35 Å for Mo(1)–O(3) and 2.40 Å for Mo(2)–O(9), are comparable to the Mo–OH_2 distances of 2.28 Å in $MoO_3\cdot 2H_2O$[21] and of 2.33 Å in $K_2(Mo_2O_5(C_2O_4)_2(H_2O)_2)$.[22] The second reason is concerned with the arrangement of the oxygen atoms coordinated to the molybdenum atoms and the bond angles. In the present polyanion, the three terminal oxygen atoms occupy the *mer* position, whereas the mononuclear and binuclear oxo-complexes of Mo(VI) with three terminal oxygen atoms investigated thus far possess the oxygen atoms in the *fac* position.[22,23] The angles between these three Mo–O bonds are given in Fig. 2. It is generally accepted that the repulsion between two terminal oxygen atoms always, without exception, causes fairly large O(terminal)–Mo–O(terminal) bond angles, ranging from 101° to 108°,[22,24] while the O(terminal)–Mo–H_2O angle in $K_2(Mo_2O_5(C_2O_4)_2(H_2O)_2)$ is reduced to

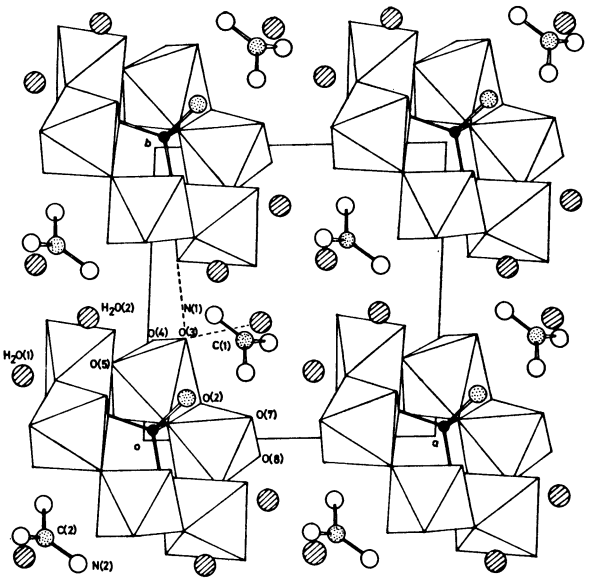


Fig. 3. The crystal structure of $(CN_3H_6)_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ viewed normal to a and b axes.

85.50°.[22] Considering the fact that the O(3)–Mo(1)–O(4) and O(8)–Mo(2)–O(9) angles in the present anion are as small as the latter, O(3) and O(9) can be identified as water molecules without any risk of serious mistake. This assignment is also supproted by the fact that each molybdenum atom is coordinated by two terminal oxygen atoms in the cis position, which is the usual geometry not only in polyacids but also in mono- and binuclear oxo-complexes of Mo(VI). Trans terminal oxygens have been found only in d^2 complexes, such as in $(MoO_2(CN)_4)^{4-}$,[25] but not in Mo(VI) complexes.

Although there have been some reports concerning the coordination of water molecules to heteroatoms in polyanions and their substitution reactions,[26,27] the present anion would seem to be one of the few examples of water molecules coordinating to addenda atoms, that is, molybdenums; another example is found in $Na_3[PMo_9O_{31}(H_2O)_3]\cdot nH_2O$.[28]

The crystal structure is shown in Fig. 3, while selected interionic distances are listed in Table 6. The anions, water molecules, and cations form a three-dimensional network of hydrogen bondings.

$(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$. Figure 4 illustrates the structure of the $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$ anion, which consists of four MoO_6 octahedra joined to form a flat group of Mo_4O_{15}, with two face-sharings (the shared faces are O(4)–O(8)–O(10) and O(1)–O(4)–O(15)) and two edge-sharings (the shared edges are O(4)–O(5) and O(4)–O(12)). A $(CH_3)_2AsO_2$ tetrahedron shares two oxygen atoms (O(10) and O(15)) with the Mo_4O_{15} moiety. The bond lengths and angles in the anion are listed in Tables 7 and 8. O(4) is common to all four octahedra, and the Mo(*n*)–O(4) (*n*=1, 2, 3, and 4) bond lengths are noticeably large; the distance of Mo(3)–O(4) is 2.538 Å in the present work, one of the largest Mo–O lengths recorded, so far as the author knows. Not many examples of face-sharing of octahedra, as is seen in the present anion, are known, either; other examples

Table 6. Bond lengths in the $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$ anion and in the guanidinium cations, $CN_3H_6^+$, with their estimated standard deviations in parentheses

	l/Å		*l*/Å
Mo(1)–O(1)	1.916(14)	Mo(2)–O(1)	1.960(14)
O(4)	2.351(15)	O(2)	1.720(17)
O(12)	1.934(15)	O(3)	1.709(19)
O(13)	1.690(16)	O(4)	2.369(15)
O(14)	1.713(17)	O(5)	1.911(16)
O(15)	2.371(13)	O(15)	2.326(15)
Mo(3)–O(4)	2.538(14)	Mo(4)–O(4)	2.407(15)
O(5)	1.926(16)	O(8)	1.912(15)
O(6)	1.736(19)	O(9)	1.696(15)
O(7)	1.726(16)	O(10)	2.298(13)
O(8)	1.938(14)	O(11)	1.732(15)
O(10)	2.290(17)	O(12)	1.939(14)
Mo(1)···Mo(2)	3.163(5)	As–O(10)	1.642(15)
Mo(2)···Mo(3)	3.353(9)	O(15)	1.665(15)
Mo(3)···Mo(4)	3.166(5)	C(1)	1.930(20)
Mo(4)···Mo(1)	3.334(9)	C(2)	1.924(25)
C(3)–N(1)	1.30(3)	C(4)–N(4)	1.34(3)
N(2)	1.38(3)	N(5)	1.35(3)
N(3)	1.33(3)	N(6)	1.33(3)
O(1)–O(2)	2.81(2)	O(5)–O(10)	2.75(2)
O(3)	2.82(2)	O(15)	2.81(2)
O(4)	2.66(2)	O(6)–O(7)	2.76(2)
O(13)	2.76(2)	O(8)	2.80(2)
O(14)	2.82(2)	O(7)–O(8)	2.88(2)
O(15)	2.51(2)	O(10)	2.98(2)
O(2)–O(3)	2.74(2)	O(8)–O(9)	2.72(2)
O(5)	2.83(2)	O(10)	2.52(2)
O(15)	2.93(2)	O(11)	2.89(2)
O(3)–O(4)	2.92(2)	O(9)–O(11)	2.72(2)
O(5)	2.75(2)	O(12)	2.81(2)
O(4)–O(5)	2.68(2)	O(10)–O(11)	2.97(2)
O(6)	3.10(2)	O(12)	2.76(2)
O(8)	2.73(2)	O(11)–O(12)	2.77(2)
O(9)	2.97(2)	O(12)–O(13)	2.81(2)
O(10)	2.72(2)	O(14)	2.77(2)
O(12)	2.64(2)	O(15)	2.83(2)
O(13)	2.96(2)	O(13)–O(14)	2.72(2)
O(15)	2.76(2)	O(14)–O(15)	2.93(2)
O(5)–O(6)	2.74(2)		
O(7)	2.88(2)		
C(1)···C(2)	3.17(3)		
O(10)···O(15)	2.66(2)		
C(1)–O(10)	2.93(4)		
O(15)	2.96(3)		
C(2)–O(10)	2.92(3)		
O(15)	2.91(3)		

are the Mo_2O_9 part of the mannitol-molybdate complex, $H_2Mo_2O_9C_6H_8(OH)_2$,[29] and the molybdocerate anion, $[CeMo_{12}O_{42}]^{8-}$.[30]

Considering the fact that the distances of As–O (terminal) are generally smaller than those of the As–O(bridging) distances in pyroarsenic acids,[31,33,34] the As–O(bridging) distances in the present anion are

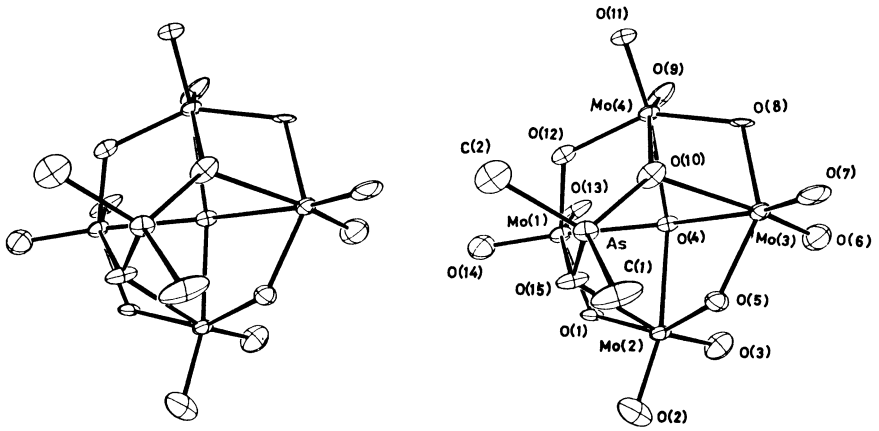


Fig. 4. The structure of the $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$ anion.
The vibrational ellipsoids are drawn at the 50% probability level. (ORTEP Johnson, 1971)

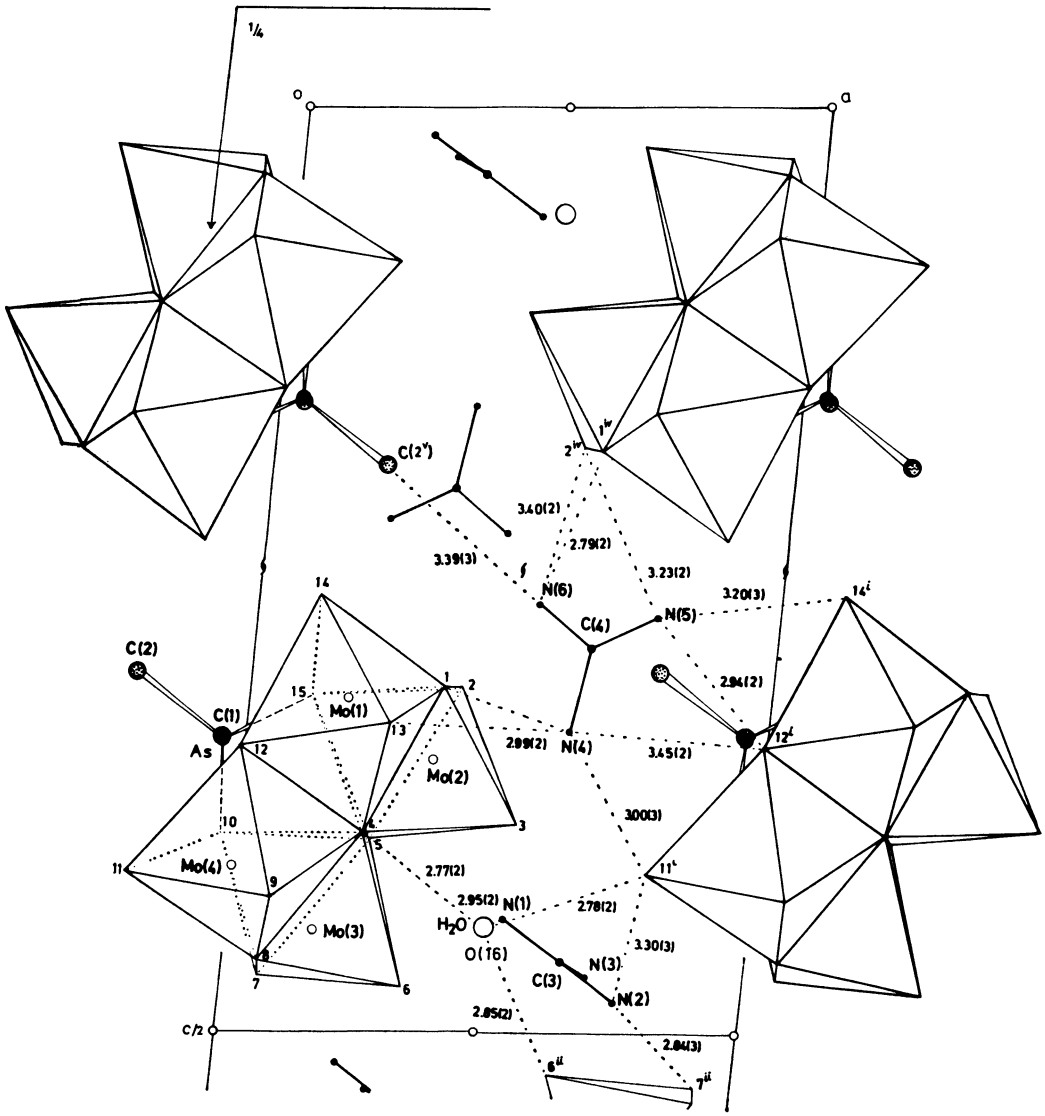


Fig. 5. The crystal structure of $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$ viewed along b axis.

rather short, with lengths comparable to the As–O (terminal) distances. The O–As–O angles do not deviate significantly from the usual values in AsO_4^{3-} anions.[32,34]

It is of interest to know where the unique hydrogen atom is located and what kind of role it plays in the crystal. Barkigia *et al.* reported[13] that IR absorption is observed at 3615 cm^{-1} in unhydrated tetrabutylammonium salt; this absorption can be identified as O–H stretching. They also reported that the anion

Table 7. Bond angles in the $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$ anion and in the guanidinium cations with their estimated standard deviations in parentheses

	θ/°		θ/°
O(1)-Mo(1)-O(4)	76.3(5)	O(5)-Mo(3)-O(7)	104.1(6)
O(12)	145.0(6)	O(8)	142.9(6)
O(13)	99.5(6)	O(10)	80.9(5)
O(14)	101.7(7)	O(6)-Mo(3)-O(7)	105.9(7)
O(15)	70.6(5)	O(8)	99.0(6)
O(4)-Mo(1)-O(12)	75.3(5)	O(10)	158.9(6)
O(13)	92.5(6)	O(7)-Mo(3)-O(8)	103.5(6)
O(14)	161.4(6)	O(10)	94.9(6)
O(15)	90.2(6)	O(8)-Mo(3)-O(10)	72.5(5)
O(12)-Mo(1)-O(13)	101.7(6)	O(4)-Mo(4)-O(8)	77.6(5)
O(14)	98.8(6)	O(9)	91.1(6)
O(15)	81.3(5)	O(10)	70.6(4)
O(13)-Mo(1)-O(14)	106.1(7)	O(11)	163.0(6)
O(15)	97.2(6)	O(12)	73.8(5)
O(14)-Mo(1)-O(15)	90.2(6)	O(8)-Mo(4)-O(9)	97.7(6)
O(1)-Mo(2)-O(2)	99.2(6)	O(10)	72.7(5)
O(3)	100.1(6)	O(11)	104.7(6)
O(4)	75.1(5)	O(12)	146.0(5)
O(5)	145.9(6)	O(9)-Mo(4)-O(10)	160.7(6)
O(15)	71.0(5)	O(11)	105.1(7)
O(2)-Mo(2)-O(3)	106.2(7)	O(12)	100.8(6)
O(4)	163.6(6)	O(10)-Mo(4)-O(11)	93.7(6)
O(5)	102.3(7)	O(12)	80.7(5)
O(15)	91.6(6)	O(11)-Mo(4)-O(12)	97.7(6)
O(4)-Mo(2)-O(4)	90.0(6)	O(10)-As-O(15)	107.2(7)
O(5)	98.9(7)	C(1)	110.0(7)
O(15)	161.3(6)	C(2)	109.9(8)
O(4)-Mo(2)-O(5)	76.9(5)	O(15)-As-C(1)	110.7(7)
O(15)	72.0(4)	C(2)	108.1(8)
O(5)-Mo(2)-O(15)	82.3(5)	C(1)-As-C(2)	110.8(9)
O(4)-Mo(3)-O(5)	72.5(5)	N(1)-C(3)-N(2)	121.0(21)
O(6)	90.8(6)	N(3)	123.1(20)
O(7)	163.3(6)	N(2)-C(3)-N(3)	115.9(18)
O(8)	73.9(5)	N(4)-C(4)-N(5)	119.9(19)
O(10)	68.4(4)	N(6)	120.2(20)
O(5)-Mo(3)-O(6)	96.7(7)	N(5)-C(4)-N(6)	119.9(19)

can not be neutralized by alkali; instead, it is directly decomposed. On the other hand, a close contact of 2.77(2) Å is observed between O(4) and the water molecule O(16), which suggests a hydrogen bonding. These facts all together lead to the conclusion that O(4) is, in fact, a hydroxyl group and is hydrogen-bonded to O(16).

Guanidinium cations are almost flat triangles. The close contacts between nitrogen and oxygen atoms in the polyanions water molecules suggest probable hydrogen bondings (see Fig. 5). Table 9 lists the interionic distances less than 3 Å.

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References

1) K. Nishikawa, unpublished data.
2) J. F. Keggin, *Proc. R. Soc. London, Ser. A*, **114**, 75 (1934).
3) H. Nishikawa and Y. Sasaki, *Chem. Lett.*, **1974**, 1185.
4) R. Strandberg, *Acta Chem. Scand., Sect. A*, **28**, 217 (1974).
5) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953).
6) K. Y. Matsumoto and Y. Sasaki, *Chem. Commun.*, **1975**, 691.
7) R. Strandberg, *Acta Chem. Scand.*, **27**, 1004 (1973).
8) K. Y. Matsumoto, *Bull. Chem. Soc. Jpn.*, **51**, 492 (1978).
9) W. Kwak, L. M. Rajkovic, M. T. Pope, C. O. Quicksall, K. Y. Matsumoto, and Y. Sasaki, *J. Am. Chem. Soc.*, **99**, 6463 (1977).
10) W. Gibbs, *Am. Chem. J.*, **5**, 363 (1883).
11) A. Rosenheim and R. Bilecki, *Chem. Ber.*, **4**, 543 (1913).
12) W. Kwak, L. M. Rajković, J. K. Stalick, M. T. Pope, and C. O. Quicksall, *Inorg. Chem.*, **15**, 2778 (1976).
13) K. M. Barkigia, L. M. Rajković, M. T. Pope, and C. O. Quicksall, *J. Am. Chem. Soc.*, **97**, 4146 (1975).

Table 8. Interionic distances less than 3 Å in $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$, with their estimated standard deviations in parentheses

		l/Å
O(16)	·····O(4)	2.77(2)
	O(11^{i})	2.78(2)
	O(6^{ii})	2.86(2)
N(1)	·····O(16)	2.95(2)
N(2)	·····O(7^{ii})	2.84(3)
N(3)	·····O(3^{iii})	2.95(3)
N(4)	·····O(13)	2.99(3)
N(5)	·····O(12^{i})	2.94(3)
N(6)	·····O(2^{iii})	2.90(3)
	O(1^{iv})	2.93(3)

Symmetry code

i	$1.0+x$,	y,	z
ii	$1.0-x$,	$-y$,	$1.0-z$
iii	x,	$1.0+y$,	z
iv	$1.0-x$,	$0.5+y$,	$0.5-z$

14) V. R. Mattes, H. Bierbüsse, and J. Fuchs, *Z. Anorg. Allg. Chem.*, **385**, 230 (1971).
15) K. Y. Matsumoto, A. Kobayashi, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **48**, 3146 (1975).
16) Y. Sasaki and K. Matsumoto, *Kagaku No Ryoiki*, **29**, 853 (1975).
17) D. D. Dexter and J. V. Silverton, *J. Am. Chem. Soc.*, **90**, 3589 (1968).
18) "The Universal Crystallographic Computation Program System," Crystallographic Society of Japan (1967).
19) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.
20) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
21) B. Krebs, *Acta Crystallogr., Sect. B*, **28**, 2222 (1972).
22) F. A. Cotton, S. M. Morehous, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).
23) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).
24) A. Perloff, *Inorg. Chem.*, **9**, 2228 (1970).
25) V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, **90**, 3374 (1968).
26) L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, **92**, 3794 (1970).
27) T. J. R. Weakley, H. T. Evans, Jr., J. S. Showell, G. F. Tourné, and C. M. Tourné, *J. Chem. Soc. Chem. Commun.*, **1973**, 139.
28) H. d'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).
29) L. Pettersson, Ph. D. Thesis, Umeå University (1974).
30) D. D. Dexter and J. V. Silverton, *J. Am. Chem. Soc.*, **90**, 3589 (1968).
31) K. Y. Leung and C. Calvo, *Can. J. Chem.*, **51**, 2082 (1073).
32) G. Ferraris and M. F. Angela, *Acta Crystallogr., Sect. B*, **29**, 286 (1973).
33) M. Catti and G. Ferraris, *Acta Crystallogr., Sect. B*, **29**, 90 (1973).
34) G. Ferraris and M. F. Angela, *Acta Crystallogr., Sect. B*, **29**, 859 (1973).