The Crystal Structure of Guanidinium Hexamolybdobis(phenylarsonate) Tetrahydrate, $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$

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(Received August 17, 1977)

Two heteropoly anions, $[C_6H_5AsMo_6O_{21}(H_2O)_6]^{2-}$ and $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$, have been synthesized by the reaction of phenylarsonic acid with molybdenum trioxide in an aqueous solution of pH *ca.* 2. The latter anion has been subjected to crystal-structure analysis as a guanidinium salt, $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$, and a heteropoly anion with a new type of structure has been established. The crystal is monoclinic with the space group of $P2_1$ and cell dimensions of $a=13.754(5)$, $b=15.752(7)$, $c=11.900(5)$ Å, $\beta=115.59(2)°$, $V=2325.3$ Å^3, $D_m=2.25$, $D_x=2.28$ g cm^{-3}, and $Z=2$. The formula of the anion has been proved to be $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$, which is different from the expected formula, $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$, though the latter had previously been proposed on the basis of a ^{17}O NMR study and an independent X-ray investigation of the methyl derivative had confirmed the existence of the $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion. The present anion, $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$, consists of six MoO_6 octahedra, which form a ring with one face-, two corner- and three edge-sharings, the two $C_6H_5AsO_3$ tetrahedra are attached to the ring from above and below, with their three oxygens shared with molybdenums. The two phenyl groups are oriented upwards and downwards from the ring respectively.

In a previous paper[1] the present author reported the structure of two heteropoly molybdates derived from methylarsonic acid and dimethylarsinic acid. That study suggested the possibility that many other such acids with metal-organic group bonds may act as hetero elements to enter poly anions. Thus, the author has continued this preparative and structural study, extending the hetero parts from methyl derivatives to a phenyl derivative of arsenic acid. In this paper the author will report on the crystal structure of $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$; a preparative description of this appeared as early as in 1913,[2] but the analytical results seem unsatisfactory and no further study has been undertaken since.

Experimental

Preparation. Two g (0.01 mol) of $C_6H_5AsO_3H_2$ and 0.8 g of NaOH were dissolved in 500 ml of water and then 8.6 g (0.06 mol) of MoO_3 was gradually added while the solution was heated to boiling. After the solution had then been filtered to remove the small amount of unreacted MoO_3, the filtrate was condensed to 75 ml on a water bath and 2 g of CN_3H_6Cl was added. A colorless precipitate which appeared instantly was filtered out. The reaction of the formation of the heteropoly anion may be described as follows:

$$2C_6H_5AsO_3^{2-} + 6MoO_3 + H_2O \longrightarrow [(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}.$$

The results of elemental analyses are: Found: C, 11.99; H, 2.72; N, 10.38%. Calcd for $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$: C, 12.05; H, 2.79; N, 10.55%.

After the filtrate had stood at room temperature for about a week, colorless, bush-like crystals appeared. Their composition was formulated as $(CN_3H_6)_2[C_6H_5AsMo_6O_{21}(H_2O)_6]\cdot 3H_2O$, and from the IR spectrum the anion was concluded to be analogous to the corresponding methyl derivative reported in a previous paper.[1] The formation reaction may be described as follows:

$$C_6H_5AsO_3^{2-} + 6MoO_3 + 6H_2O \longrightarrow [C_6H_5AsMo_6O_{21}(H_2O)_6]^{2-}.$$

The results of elemental analyses are: Found: C, 7.32; H, 2.65; N, 6.28%. Calcd for $(CN_3H_6)_2[C_6H_5AsMo_6O_{21}(H_2O)_6]\cdot 3H_2O$: C, 7.13; H, 2.63; N, 6.24%.

Crystal Data. The single crystal of $(CN_3H_6)_4[(C_6H_5As)_4Mo_6O_{25}H_2]\cdot 4H_2O$ was obtained by the diffusion method, its approximate dimensions were $0.1\times 0.15\times 1.0$ mm. Preliminary Weissenberg photographs exhibited a monoclinic symmetry, and the observed systematic absence indicated the space group to be $P2_1/m$ or $P2_1$. However, a satisfactory solution for the Patterson map was achieved only when $P2_1$ was assumed, hence, the space group was determined to be $P2_1$. The crystal data are as follows:

$(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$
monoclinic $P2_1$
$a = 13.754(5)$
$b = 15.752(7)$
$c = 11.900(5)$ Å
$\beta = 115.59(2)°$
$V = 2325.3$ Å^3
$M.W. = 1594.2$
$Z = 2$
$D_m = 2.25$
$D_x = 2.28$ g cm^{-3}
$\mu = 16.6$ cm^{-1} (for Mo $K\alpha$ radiation)

Data Collection. All the intensities were measured on a Philips automatic four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used, and the scan mode was ω-2θ, with a scan rate of 2θ 1° min^{-1}. The scan range was calculated for each reflection according to this formula: $\omega=1.4+0.6\tan\theta$, and stationary-crystal, stationary-counter background counts of 20 s were taken at the end of each scan. In order to check the crystal deterioration, three standard reflections were monitored every three hours, but no significant intensity loss was observed throughout the data collection. The data were corrected for the Lorentz and polarization effects. No absorption or extinction corrections were applied. The intensities were collected up to $2\theta=60°$, and 4720 independent reflections with $|F_o|\geq 3\sigma(|F_o|)$ were used for further computation.

Solution and Refinement of the Structure. The coordinates of the molybdenum atoms were determined from the Patterson map, while all the remining non-hydrogen atoms were located from the successive Fourier syntheses. After the structure had been refined with isotropic temperature factors by the block-diagonal least-squares method, anisotropic temperature factors were applied to all the atoms. After the refinement had been

TABLE 1. FINAL POSITIONAL PARAMETERS ($\times 10^4$), WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion	x	y	z
Mo(1)	2421(2)	443(1)	−1169(2)
Mo(2)	642(1)	0(0)	−44(2)
Mo(3)	266(1)	1414(1)	2264(2)
Mo(4)	2646(2)	1870(1)	4406(2)
Mo(5)	4951(1)	1120(1)	3878(2)
Mo(6)	4751(1)	1183(1)	983(2)
As(1)	2386(2)	1811(1)	1213(2)
As(2)	3357(2)	−452(1)	1872(2)
O(1)	3439(11)	1356(8)	−486(12)
O(2)	1455(15)	945(10)	−2419(13)
O(3)	3042(16)	−180(11)	−1835(16)
O(4)	1568(11)	−360(9)	−819(13)
O(5)	1672(11)	1141(8)	42(11)
O(6)	3667(10)	47(8)	773(12)
O(7)	−356(12)	371(10)	−1375(14)
O(8)	2118(12)	−220(8)	1716(13)
O(9)	259(11)	666(8)	1055(13)
O(10)	201(11)	−980(9)	117(16)
O(11)	−494(13)	2227(11)	1395(14)
O(12)	−572(13)	899(13)	2772(17)
O(13)	1130(10)	2047(8)	3780(12)
O(14)	1834(10)	1820(8)	2251(12)
O(15)	1717(11)	509(9)	3555(13)
O(16)	3119(15)	2871(9)	4629(16)
O(17)	2829(14)	1523(9)	5842(13)
O(18)	3799(10)	1252(8)	4316(12)
O(19)	5897(13)	634(9)	5166(15)
O(20)	5398(15)	2153(9)	4092(16)
O(21)	4223(11)	−148(8)	3296(13)
O(22)	5537(10)	838(9)	2696(12)
O(23)	3696(9)	1530(9)	1954(12)
O(24)	5478(13)	599(9)	393(16)
O(25)	5237(13)	2213(9)	1108(16)
C(1)	2240(19)	2913(12)	552(23)
C(2)	1805(19)	3043(15)	−712(24)
C(3)	1769(20)	3968(17)	−1044(24)
C(4)	2087(24)	4568(18)	−276(27)
C(5)	2516(26)	4427(17)	972(31)
C(6)	2611(24)	3589(14)	1432(28)
C(7)	3498(19)	−1635(13)	1757(21)
C(8)	3150(24)	−2011(14)	583(23)
C(9)	3158(28)	−2863(21)	433(34)
C(10)	3666(23)	−3406(18)	1570(28)
C(11)	4302(26)	−2984(19)	2600(28)
C(12)	4254(29)	−2022(21)	2917(32)
Guanidinium cations	x	y	z
C(13)	−1636(20)	170(14)	4744(28)
N(1)	−622(18)	−38(18)	4984(25)
N(2)	−2148(20)	−160(15)	5414(22)
N(3)	−2149(18)	775(14)	3853(21)
C(14)	4469(21)	−763(15)	6491(23)
N(4)	4398(18)	−1244(13)	7311(20)
N(5)	4875(19)	−1051(13)	5770(20)
N(6)	4248(17)	56(12)	6483(20)
C(15)	−1144(22)	2426(16)	−2368(24)
N(7)	−1186(19)	1787(15)	−3047(21)
N(8)	−1374(21)	3226(16)	−2785(23)
N(9)	−782(19)	2236(15)	−1162(20)
C(16)	3946(18)	3433(15)	−1806(22)
N(10)	3783(17)	3977(14)	−2773(20)
N(11)	3599(17)	2623(13)	−2031(18)
N(12)	4384(17)	3753(13)	−652(20)
Water molecules	x	y	z
$H_2O(1)$	234(18)	3791(13)	3019(19)
$H_2O(2)$	1605(14)	−381(12)	5401(16)
$H_2O(3)$	1416(17)	−2005(14)	5239(19)
$H_2O(4)$	441(17)	2210(14)	5642(19)

TABLE 2. FINAL TEMPERATURE FACTORS ($\times 10^4$), WITH THEIR ESTIMATED STANDARD DEVIATIONS

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

$[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	69(1)	22(1)	46(1)	−2(1)	38(1)	−1(1)
Mo(2)	47(1)	15(1)	49(1)	−3(1)	22(1)	−5(1)
Mo(3)	42(1)	23(1)	56(1)	0(1)	28(1)	−6(1)
Mo(4)	53(1)	18(1)	48(1)	2(1)	27(1)	−7(1)
Mo(5)	41(1)	16(1)	52(1)	−1(1)	21(1)	−2(1)
Mo(6)	55(1)	16(1)	62(1)	1(1)	39(1)	4(1)
As(1)	46(1)	12(1)	44(1)	1(1)	26(1)	1(1)
As(2)	44(1)	11(1)	44(1)	−1(1)	25(1)	0(1)
O(1)	55(10)	18(5)	54(12)	0(6)	28(9)	10(7)
O(2)	100(15)	32(7)	35(12)	7(8)	23(11)	12(8)
O(3)	122(18)	37(8)	76(16)	8(10)	71(15)	−10(9)
O(4)	52(10)	26(6)	66(13)	−14(6)	40(10)	−21(8)
O(5)	59(10)	15(4)	38(10)	1(6)	29(8)	3(7)
O(6)	48(9)	16(5)	55(12)	−6(6)	32(9)	−4(7)
O(7)	51(11)	33(7)	62(14)	−6(7)	14(10)	−20(9)
O(8)	72(12)	18(5)	62(13)	0(6)	45(11)	7(7)
O(9)	42(9)	21(5)	64(13)	−9(6)	30(10)	−11(7)
O(10)	44(10)	17(5)	104(17)	−9(6)	41(11)	0(8)
O(11)	58(12)	44(8)	56(14)	15(8)	11(11)	−9(9)
O(12)	54(12)	70(12)	102(19)	−5(10)	53(13)	−6(12)
O(13)	35(8)	16(5)	59(12)	2(5)	29(9)	−5(6)
O(14)	43(9)	12(4)	60(12)	7(5)	30(9)	−6(7)
O(15)	54(10)	22(6)	57(12)	−4(6)	28(10)	−2(7)
O(16)	92(15)	18(6)	91(18)	−10(8)	36(14)	−5(9)
O(17)	97(14)	22(6)	55(13)	1(8)	49(12)	−3(7)
O(18)	45(9)	18(5)	56(12)	−7(6)	33(9)	−14(7)
O(19)	65(12)	17(6)	81(15)	−7(7)	32(11)	−10(8)
O(20)	100(16)	19(6)	93(18)	−10(8)	56(14)	−8(9)
O(21)	45(9)	13(5)	65(13)	−5(5)	29(9)	0(7)
O(22)	33(8)	30(6)	43(11)	20(6)	12(8)	11(7)
O(23)	21(7)	24(5)	47(12)	3(5)	7(8)	1(7)
O(24)	71(12)	26(6)	109(18)	17(7)	69(13)	12(9)
O(25)	67(13)	19(6)	106(18)	−4(7)	41(13)	3(9)
C(1)	68(17)	12(7)	99(24)	4(9)	55(18)	6(11)
C(2)	58(17)	34(10)	99(26)	27(11)	46(18)	24(14)
C(3)	62(18)	38(11)	94(25)	7(11)	41(18)	16(14)
C(4)	112(25)	37(12)	137(31)	24(15)	75(24)	36(17)
C(5)	116(28)	27(11)	146(38)	−16(14)	62(28)	0(17)
C(6)	107(25)	12(8)	124(32)	8(11)	42(24)	20(13)
C(7)	67(17)	20(8)	79(22)	14(10)	46(17)	3(11)
C(8)	119(27)	15(8)	69(23)	20(12)	0(20)	−11(11)

C(9)	113(31)	47(16)	144(40)	−6(18)	45(30)	−15(21)
C(10)	77(21)	35(12)	112(29)	−3(12)	35(21)	2(15)
C(11)	114(27)	45(14)	92(29)	−2(16)	33(24)	3(17)
C(12)	146(33)	46(15)	136(37)	16(18)	82(30)	5(20)

Guanidinium cations

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(13)	66(18)	22(9)	140(32)	−8(10)	52(21)	−16(14)
N(1)	68(17)	57(12)	140(29)	10(13)	44(19)	10(17)
N(2)	106(20)	39(11)	109(25)	15(12)	65(19)	22(13)
N(3)	70(16)	39(10)	94(22)	−1(10)	30(16)	4(13)
C(14)	82(20)	29(9)	79(23)	5(11)	49(19)	5(12)
N(4)	83(17)	30(9)	91(21)	8(10)	52(16)	12(11)
N(5)	102(20)	31(9)	83(21)	3(11)	51(17)	9(11)
N(6)	88(17)	23(7)	98(22)	5(10)	58(17)	−1(11)
C(15)	83(21)	32(11)	85(25)	3(12)	37(20)	4(14)
N(7)	98(19)	40(10)	102(23)	2(12)	49(18)	−6(14)
N(8)	110(22)	44(11)	110(26)	4(13)	56(20)	1(15)
N(9)	84(18)	47(11)	80(21)	2(12)	35(17)	−4(13)
C(16)	48(15)	30(9)	78(22)	−3(10)	27(16)	4(12)
N(10)	71(16)	35(9)	81(20)	−1(10)	29(15)	6(12)
N(11)	71(16)	32(9)	72(19)	−5(10)	32(15)	−3(11)
N(12)	73(16)	34(9)	88(21)	−8(10)	38(16)	−3(12)

Water molecules

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$H_2O(1)$	121(19)	47(10)	101(21)	2(11)	34(17)	2(12)
$H_2O(2)$	75(14)	47(9)	80(17)	−7(9)	33(13)	1(11)
$H_2O(3)$	114(18)	54(10)	106(22)	−15(12)	49(17)	−10(13)
$H_2O(4)$	109(18)	57(11)	119(23)	5(12)	64(17)	7(13)

continiued several more cycles, the final R value was 0.066 ($R=\sum||F_o|-|F_o||/\sum|F_o|$).

The final atomic coordinates and temperature factors are listed in Tables 1 and 2 respectively. The F_o-F_c table is kept at the office of this Bulletin (Document No. 7801). The atomic scattering factors were based on Ref. 3, and the effects of the anomalous dispersion for molybdenum and arsenic were corrected according to Ref. 4. All the calculations were performed on a HITAC 8700/8800 computer at the Computer Center of the University of Tokyo.

Table 3. The bond lengths (Å) in $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion and guanidinium cations, with their estimated standard deviations in parentheses

$[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion

Mo(1)...Mo(2)	3.331(4)	Mo(4)...Mo(5)	3.683(4)
Mo(2)...Mo(3)	3.740(4)	Mo(5)...Mo(6)	3.337(4)
Mo(3)...Mo(4)	3.244(4)	Mo(6)...Mo(1)	3.332(4)
Mo(1)—O(1)	1.925(14)	Mo(2)—O(4)	1.948(19)
O(2)	1.701(15)	O(5)	2.263(15)
O(3)	1.700(22)	O(7)	1.691(14)
O(4)	1.884(17)	O(8)	2.224(13)
O(5)	2.372(17)	O(9)	1.920(18)
O(6)	2.291(13)	O(10)	1.691(16)
Mo(3)—O(9)	1.855(17)	Mo(4)—O(13)	1.908(14)
O(11)	1.693(17)	O(14)	2.314(14)
O(12)	1.718(22)	O(15)	2.478(15)
O(13)	1.952(13)	O(16)	1.683(16)
O(14)	2.255(16)	O(17)	1.706(18)
O(15)	2.393(14)	O(18)	1.903(16)
Mo(5)—O(18)	1.881(17)	Mo(6)—O(22)	1.927(14)
O(19)	1.704(14)	O(23)	2.278(17)
O(20)	1.719(16)	O(24)	1.716(20)
O(21)	2.198(13)	O(25)	1.737(16)
O(22)	1.950(18)	O(1)	1.914(12)
O(23)	2.286(12)	O(6)	2.272(15)
As(1)—O(14)	1.707(18)	As(2)—O(8)	1.673(19)
O(5)	1.685(13)	O(6)	1.724(17)
O(23)	1.687(13)	O(21)	1.666(13)
C(1)	1.881(21)	C(7)	1.885(22)
C(1)—C(2)	1.373(37)	O(8)—O(10)	2.770(19)
C(2)—C(3)	1.506(37)	O(15)	2.726(26)
C(3)—C(4)	1.259(37)	O(21)	2.689(19)
C(4)—C(5)	1.360(49)	O(9)—O(10)	2.803(21)
C(5)—C(6)	1.413(37)	O(11)	2.764(24)
C(6)—C(1)	1.424(33)	O(12)	2.762(30)
C(7)—C(8)	1.398(36)	O(14)	2.712(18)
C(8)—C(9)	1.355(41)	O(15)	2.789(19)
C(9)—C(10)	1.495(44)	O(11)—O(12)	2.687(29)
C(10)—C(11)	1.333(38)	O(13)	2.765(18)
C(11)—C(12)	1.569(47)	O(14)	2.979(23)
C(12)—C(7)	1.458(37)	O(26)	3.022(27)
		O(12)—O(13)	2.785(23)
O(1)—O(2)	2.781(19)	O(15)	2.937(25)
O(3)	2.816(23)	O(13)—O(14)	2.429(25)
O(5)	2.780(25)	O(15)	2.604(21)
O(6)	2.487(20)	O(16)	2.794(23)
O(23)	2.782(22)	O(17)	2.685(18)
O(24)	2.801(22)	O(14)—O(15)	2.629(22)
O(25)	2.736(20)	O(16)	3.091(20)
O(2)—O(3)	2.655(27)	O(18)	2.900(16)
O(4)	2.753(24)	O(23)	2.771(22)
O(5)	2.829(23)	O(15)—O(17)	2.950(20)
O(3)—O(4)	2.788(32)	O(18)	2.855(21)
O(6)	2.862(24)	O(16)—O(17)	2.693(25)
O(4)—O(5)	2.547(21)	O(18)	2.796(22)
O(6)	2.757(18)	O(17)—O(18)	2.712(27)
O(7)	2.689(23)	O(18)—O(19)	2.788(22)
O(8)	2.783(23)	O(20)	2.725(27)
O(10)	2.745(27)	O(21)	2.691(21)
O(5)—O(6)	3.032(20)	O(23)	2.787(22)
O(7)	2.834(20)	O(19)—O(20)	2.658(22)
O(8)	2.800(20)	O(21)	2.706(18)
O(9)	2.795(25)	O(22)	2.780(24)
O(14)	2.757(21)	O(20)—O(22)	2.712(24)
O(23)	2.798(16)	O(23)	2.788(19)
O(6)—O(8)	2.834(27)	O(21)—O(22)	2.696(23)
O(21)	2.775(22)	O(23)	3.001(19)
O(22)	2.884(17)	O(22)—O(23)	2.539(19)
O(23)	2.717(20)	O(24)	2.733(26)
O(24)	2.853(27)	O(25)	2.785(23)
O(7)—O(9)	2.680(23)	O(23)—O(25)	2.917(27)
O(10)	2.657(22)	O(24)—O(25)	2.745(23)
O(8)—O(9)	2.709(22)		

Guanidinium cations

C(13)—N(1)	1.337(38)	C(15)—N(7)	1.280(37)
N(2)	1.371(47)	N(8)	1.337(36)
N(3)	1.369(32)	N(9)	1.335(37)
C(14)—N(4)	1.269(37)	C(16)—N(10)	1.370(33)
N(5)	1.291(43)	N(11)	1.352(31)
N(6)	1.319(32)	N(12)	1.336(32)

TABLE 4. THE BOND ANGLES(°) IN $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ ANION AND GUANIDINIUM CATIONS, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

O(1)—Mo(1)—O(2)	99.97(61)	O(18)—Mo(5)—O(23)	83.35(57)
O(3)	101.75(85)	O(19)—Mo(5)—O(20)	101.89(68)
O(4)	144.40(64)	O(21)	86.83(55)
O(5)	79.89(54)	O(22)	98.86(67)
O(6)	71.70(48)	O(23)	168.70(53)
O(2)—Mo(1)—O(3)	102.62(89)	O(20)—Mo(5)—O(21)	170.92(61)
O(4)	100.21(69)	O(22)	95.14(72)
O(5)	86.29(61)	O(23)	87.03(58)
O(6)	165.91(55)	O(21)—Mo(5)—O(22)	84.01(42)
O(3)—Mo(1)—O(4)	102.05(91)	O(23)	80.85(59)
O(5)	170.41(85)	O(22)—Mo(5)—O(23)	73.17(57)
O(6)	90.39(81)	O(22)—Mo(6)—O(23)	73.74(54)
O(4)—Mo(1)—O(5)	72.50(64)	O(22)—Mo(6)—O(24)	97.05(76)
O(6)	82.04(58)	O(25)	98.83(62)
O(5)—Mo(1)—O(6)	81.11(48)	O(1)	151.98(52)
O(4)—Mo(2)—O(5)	74.01(65)	O(6)	86.34(51)
O(7)	95.02(70)	O(23)—Mo(6)—O(24)	161.40(78)
O(8)	83.40(63)	O(25)	92.19(64)
O(9)	155.04(74)	O(1)	82.68(52)
O(10)	97.65(74)	O(6)	73.33(52)
O(5)—Mo(2)—O(7)	90.36(57)	O(24)—Mo(6)—O(25)	105.36(84)
O(8)	77.22(48)	O(1)	100.89(75)
O(9)	83.42(61)	O(6)	90.23(75)
O(10)	164.50(62)	O(25)—Mo(6)—O(1)	96.96(61)
O(7)—Mo(2)—O(8)	167.45(55)	O(6)	162.72(61)
O(9)	95.66(67)	O(1)—Mo(6)—O(6)	72.32(48)
O(10)	103.55(67)	O(5)—As(1)—O(14)	108.75(69)
O(8)—Mo(2)—O(9)	81.30(59)	O(23)	112.18(57)
O(10)	89.00(59)	C(1)	108.24(74)
O(9)—Mo(2)—O(10)	101.67(71)	O(14)—As(1)—O(23)	109.44(68)
O(9)—Mo(3)—O(11)	102.23(72)	C(1)	107.12(84)
O(12)	101.19(89)	O(23)—As(1)—C(1)	110.95(74)
O(13)	146.94(60)	O(6)—As(2)—O(8)	113.02(81)
O(14)	81.94(62)	O(21)	109.87(68)
O(15)	80.99(57)	C(7)	108.85(83)
O(11)—Mo(3)—O(12)	103.92(92)	O(8)—As(2)—O(21)	107.23(74)
O(13)	98.40(64)	C(7)	109.85(88)
O(14)	96.94(66)	O(21)—As(2)—C(7)	107.89(76)
O(15)	165.00(62)		
O(12)—Mo(3)—O(13)	98.52(83)	C(1)—C(2)—C(3)	112.33(216)
O(14)	157.61(84)	C(2)—C(3)—C(4)	125.39(249)
O(15)	89.63(81)	C(3)—C(4)—C(5)	121.14(257)
O(13)—Mo(3)—O(14)	70.09(52)	C(4)—C(5)—C(6)	120.21(268)
O(15)	72.84(47)	C(5)—C(6)—C(1)	118.04(251)
O(14)—Mo(3)—O(15)	68.81(49)	C(6)—C(1)—C(2)	122.89(207)
O(13)—Mo(4)—O(14)	69.47(50)	C(7)—C(8)—C(9)	122.16(246)
O(15)	71.52(51)	C(8)—C(9)—C(10)	118.34(284)
O(16)	102.02(65)	C(9) C(10)—C(11)	114.41(262)
O(17)	95.78(68)	C(10)—C(11)—C(12)	128.35(262)
O(18)	148.18(60)	C(11)—C(12)—C(7)	105.43(238)
O(14)—Mo(4)—O(15)	66.44(45)	C(12)—C(7)—C(8)	124.38(223)
O(16)	100.10(61)		
O(17)	152.93(64)	N(1)—C(13)—N(2)	122.39(251)
O(18)	86.29(55)	N(2)—C(13)—N(3)	119.21(257)
O(15)—Mo(4)—O(16)	166.29(61)	N(3)—C(13)—N(1)	118.25(286)
O(17)	87.64(64)	N(4)—C(14)—N(5)	120.33(251)
O(18)	80.16(55)	N(5)—C(14)—N(6)	119.84(266)
O(16)—Mo(4)—O(17)	105.26(76)	N(6)—C(14)—N(4)	119.31(276)
O(18)	102.31(69)	N(7)—C(15)—N(8)	124.67(267)
O(17)—Mo(4)—O(18)	97.28(71)	N(8)—C(15)—N(9)	122.09(252)
O(18)—Mo(5)—O(19)	101.97(68)	N(9)—C(15)—N(7)	113.13(237)
O(20)	98.29(72)	N(10)—C(16)—N(11)	120.39(208)
O(21)	82.18(59)	N(11)—C(16)—N(12)	121.46(229)
O(22)	152.23(70)	N(12)—C(16)—N(10)	117.97(208)

Description of the Structure and Discussion

The structure of the anion is depicted in Fig. 1, while the interatomic distances and angles within the anion and guanidinium cations are listed in Tables 3 and 4.

Each molybdenum is octahedrally coordinated by six oxygen atoms, and the anion is constituted of six MoO_6 octahedra and two $C_6H_5AsO_3$ tetrahedra. These octahedra are connected with one face-sharing (the shared face is O(13)–O(14)–O(15)), two corner-sharings (the shared corners are O(9) and O(18)), and three edge-sharings (the shared edges are O(4)–O(5), O(1)–O(6), and O(22)–O(23)) to form a ring. The six molybdenum atoms are not coplanar. Each of the two arsenics is tetrahedrally coordinated by three oxygen atoms and a phenyl group, and each joins the ring through sharing the three oxygens with molybdenums, one arsenic atom from above and the other from below the ring. These two arsenics are not, however, equivalent in their bonding manner. As(1) is bonded to O(5), O(14), and O(23), each of which is shared with two molybdenums besides As(1), whereas As(2) is coordinated by O(6), O(8), and O(21), of which each of O(8) and O(21) is bonded to one molybdenum and O(6) is shared with two molybdenums. There is no significant difference observed between the bond lengths and angles in the two $C_6H_5AsO_3$ tetrahedra of the present anion and those of free arsonic acid.[5]

Just before the present structural analysis had been completed, the ^{17}O NMR spectra of a heteropoly molybdate containing phenylarsonic acid was reported.[6] Based on the similarity of its spectral pattern to that of $[TeMo_6O_{24}]^{6-}$, the formula of the anion was concluded to be $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$, which has one less oxygen than the present anion. Then the problem arose of whether these anions are really different anions or whether they are the same but have been considered to be different merely because of an erroneous interpretation of the experimental results. However, subsequent X-ray structural analysis of the analogous methyl derivative, $[(CH_3As)_2Mo_6O_{24}]^{4-}$, confirmed its formula and structure,[7] which is depicted in Fig. 2, and it was concluded that there are two kinds of heteropoly molybdate anions, both of which have a hetero part to the molybdenum atoms in the ratio 2: 6, but which are different in the number of their oxygens. The $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion is synthesized at pH 4—5 and consists of six MoO_6 octahedra, all of which share

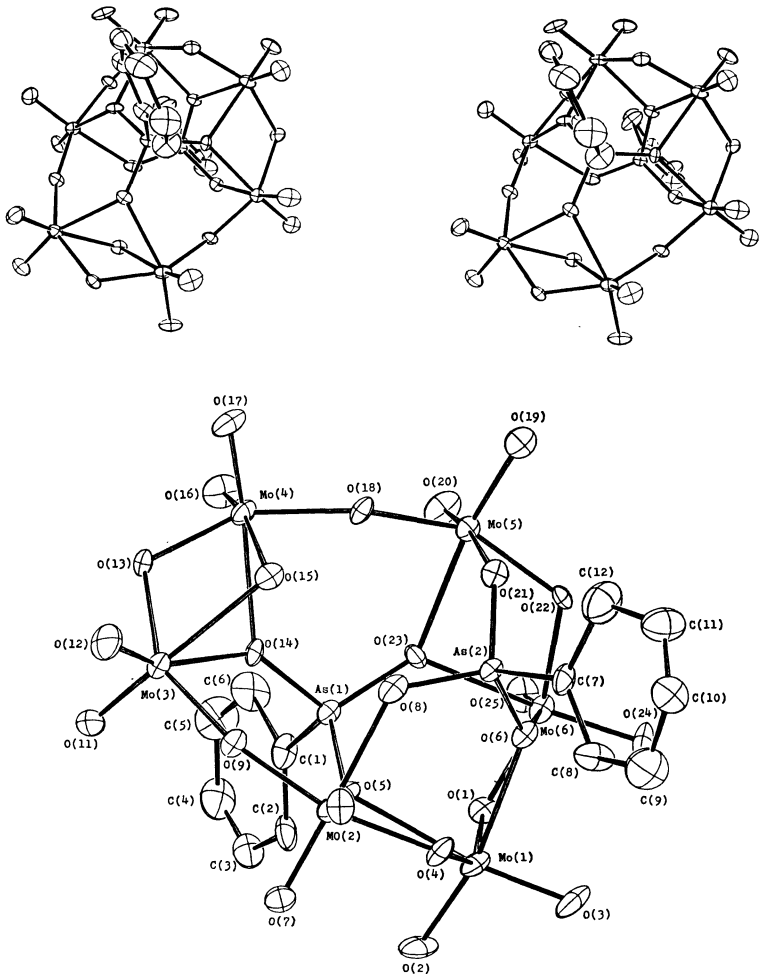

Fig. 1. Stereoscopic view of the $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion, with the vibrational ellipsoids drawn at the 50% probability level (ORTEP, Johnson, 1971).

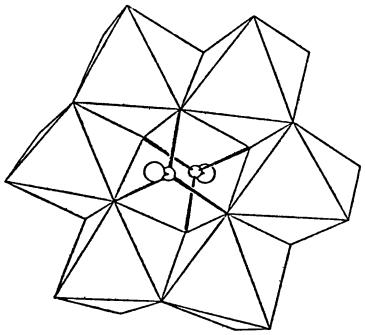

Fig. 2. The structure of the $[(CH_3As)_2Mo_6O_{24}]^{4-}$ anion. All the MoO_6 groups are expressed as octahedra.

edges to form a coplanar ring.

The crystal structure viewed along the b axis is shown in Fig. 3, while the interionic distances are listed in Table 5.

Parallel to the present work, Pope *et al.* have independently studied the same system, consisting of MoO_4^{2-} and $RAsO_3^{2-}$. However, the anions they obtained were $[(RAs)_2Mo_6O_{24}]^{4-}$ and $[(RAs)_4Mo_{12}O_{46}]^{4-}$ (R=CH_3, C_6H_5, and *p*-$NH_2C_6H_4$ for the former and R=CH_3, C_2H_4OH, C_6H_5, and *p*-$NH_2C_6H_4$ for the latter), whose structures have been clarified by the X-ray diffraction technique.[7,8] This system thus exhibits a complicated aspect, giving various heteropolyanions with different ratios of molybdenum to hetero parts depending on the pH of the solution. All these reactions are summarized below, including both the present work and that of Pope *et al.*:

(I) $RAsO_3^{2-} + 6MoO_3 + 6H_2O \xrightarrow{\text{pH 2}} [RAsMo_6O_{21}(H_2O)_6]^{2-}$ [1]

(II) $2RAsO_3^{2-} + 6MoO_3 + H_2O \xrightarrow{\text{pH 2}} [(RAs)_2Mo_6O_{25}H_2]^{4-}$

(III) $4RAsO_3^{2-} + 12MoO_3 + 4H^+ \xrightarrow{\text{pH 2}} [(RAs)_4Mo_{12}O_{46}]^{4-} + 2H_2O$ [8]

(IV) $2RAsO_3^{2-} + 6MoO_3 \xrightarrow{\text{pH 4.5}} [(RAs)_2Mo_6O_{24}]^{4-}$ [8]

Table 5. Interionic distances less than 3.1 Å, with their estimated standard deviations

O(1).....N(11)	2.788(28)
O(7).....N(7)	2.876(28)
O(7).....N(9)	3.028(30)
O(11).....H_2O(1)	3.022(27)
O(11).....N(9)	2.894(32)
O(12).....N(3)	2.968(38)
O(12).....N(1)	3.040(39)
O(13).....H_2O(1)	2.987(25)
O(13).....H_2O(4)	2.772(33)
O(15).....H_2O(2)	2.662(27)
O(17).....N(6)	2.907(27)
O(18).....N(6)	3.035(27)
O(21).....N(5)	3.035(27)
N(1).....H_2O(2)	2.933(34)
H_2O(2).....H_2O(3)	2.570(30)
H_2O(1).....N(1^{i})	2.877(37)
H_2O(1).....N(2^{i})	2.988(31)
H_2O(4).....H_2O(3^{i})	2.620(31)
N(8).....H_2O(3^{ii})	2.917(40)
N(9).....O(10^{ii})	3.045(28)
H_2O(1).....O(4^{ii})	3.034(23)
O(2).....H_2O(4^{iii})	2.909(26)
O(3).....N(4^{iii})	2.922(35)
N(11).....O(17^{iii})	2.867(26)
O(3).....H_2O(2^{iii})	3.034(23)
O(19).....N(2^{iv})	2.859(34)
O(22).....N(3^{iv})	2.873(26)
O(20).....N(5^{v})	2.878(27)
O(25).....N(4^{v})	2.988(28)
O(22).....N(10^{vi})	3.067(26)
O(24).....N(12^{vi})	2.922(26)

Symmetry code

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

The (III) anion is of the same structural type as $[As_4Mo_{12}O_{50}H_4]^{4-}$, in which R groups are replaced

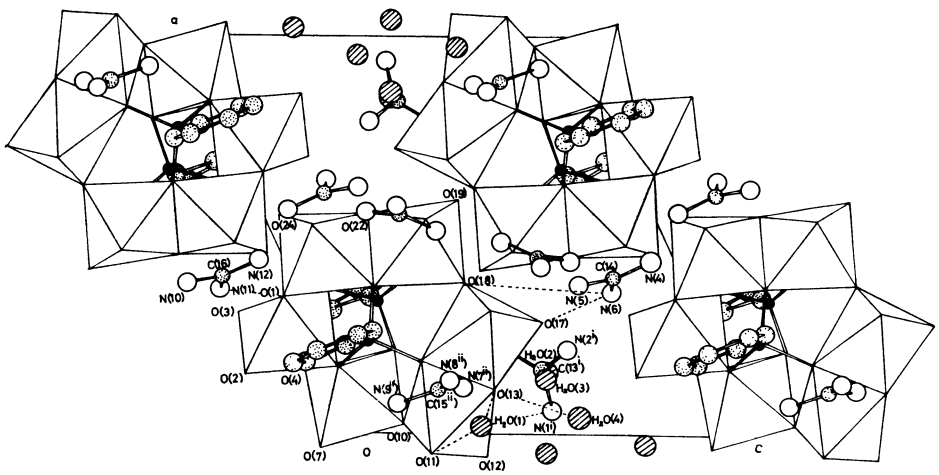

Fig. 3. The crystal structure of $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$ viewed along b axis.

by hydroxyl groups.[9] The (IV) anion is probably structurally analogous to $[As_2Mo_6O_{26}]^{6-}$.[10]

In such a system where two or more anions may be expected to exist in equilibrium with one another, it is of interest and important to know what species is formed and stable in which pH region and what equilibrium relations exist among them in the solution. Although the study attempting to clarify these points is still in progress and has not been completed, an interesting interconversion through dehydration and rehydration has been proved, with the aid of the Raman, IR, and 90 MHz ^1H FT-NMR spectra, to occur between the $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ and $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$ anions when the CD_3CN solution of $(n\text{-}Bu_4N)_4[(C_6H_5As)_2Mo_6O_{25}H_2]$ is kept at 90 °C and then cooled to room temperature, as is expressed in the following:[11]

$$[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-} \xrightarrow[90°C]{-H_2O} [(C_6H_5As)_2Mo_6O_{24}]^{4-}$$

$$\xrightarrow[r.t.]{H_2O} [(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$$

It can not said decisively what the two hydrogen atoms in the $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$ anion are bonded to. However, the above-mentioned interconversion caused by hydration and dehydration and the two anomalously long Mo–O bonds to O(15) (Mo(3)–O(15) is 2.393 Å and Mo(4)–O(15) is 2.478 Å; see Fig. 1 and Table 3) suggest that O(15) is a water molecule and is bridging Mo(3) and Mo(4).

The author wishes to express her thanks to Professor M. T. Pope of Georgetown University, who kindly sent her the IR data and some other helpful information on compounds related to those in the present work. The author is also indebted to Professor Yukiyoshi Sasaki of the University of Tokyo for his continual interest in the present work. Thanks are also due to Prefessor Hisao Kuroya and Dr. K. Matsumoto of Osaka City University for the use of a Philips automatic diffractometer.

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