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The Crystal Structure of Tetraphenylarsonium Oxotetrabromoaquomolybdate

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The crystal and molecular structure of $[(C_6H_5)_4As]^+[MoOBr_4(H_2O)]^-$ has been investigated by X-ray diffraction and infrared studies. Tetraphenylarsonium oxotetrabromoaquomolybdate forms brown tetragonal crystals with $a=b=13{\cdot}14$, $c=7{\cdot}89$ Å, and space group $P4/n$. There are two formula units per unit cell. The anion was found to have effectively $4mm$ (C_{4v}) symmetry, while that of the cation was $\bar{4}$ (S_4). It has been shown by infrared absorption spectra that the water molecule attached to the anion was very loosely bound, entering or leaving the lattice as the ambient conditions were varied. The presence of this water molecule has the effect of altering the strength of the Mo=O bond. Initially the structure was solved by two-dimensional Patterson and Fourier functions, and was refined by three-dimensional Fourier and least-squares methods to a residual of 0·11.

Introduction

The purpose of the investigation was to elucidate the molecular geometry of the anion, which was initially thought to consist of the dimeric ion $[Mo_2Br_8]^{2-}$. Early in the investigation the assumption was invalidated and the presence of oxygen in the anion was suspected. Support for a double bond between Mo and O came from the infrared spectra of the solid, run on a Nujol mull, which showed a sharp band at 1007 cm^{-1} when the mull was prepared in a dry box. This band was assigned to a Mo=O stretching frequency (Barraclough, Lewis & Nyholm, 1959).

At a later stage in the analysis a three-dimensional difference Fourier synthesis showed another well resolved peak close to the molybdenum atom of about the weight of an oxygen atom. Further infrared spectroscopic studies showed that when the Nujol mull was prepared in the atmosphere, or exposed to the atmosphere for any length of time, bands appeared in the 2–3μ region indicating the presence of water. At the same time the intensity of the band at 1007 cm^{-1} decreased while another band appeared at 981 cm^{-1}. As the crystals used for the collection of the intensity data had not been protected from the atmosphere, it was inferred that water had entered the structure and the anion was $[MoOBr_4(H_2O)]$. The structure was refined on this basis.

Experimental

The crystalline specimen was provided by Dr M. H. B. Stiddard of the Department of Chemistry, University College, London, who also suggested the problem. The crystals were brown, well formed, tetragonal prisms about 0·2 × 0·2 × 0·2 mm, with the (100) faces predominant. Both the (001) and (111) faces, although smaller, were also clearly defined.

Unit-cell parameters were initially determined from Weissenberg and rotation photographs and later refined from powder photographs. The powder contained aluminum ($a=4{\cdot}049$ Å) as a standard and Cu $K\alpha$ radiation (1·5418 Å) was used. The dimensions found were:

$$a=b=13{\cdot}14\pm0{\cdot}01,\ c=7{\cdot}89\pm0{\cdot}01\ \text{Å}\,.$$

Density determinations were made on four crystals by flotation in a mixture of bromoform and benzene, and the mean value observed was $2{\cdot}05\pm0{\cdot}05$ g.cm^{-3} compared with a calculated density of 2·031 g.cm^{-3} for two formula units per unit cell.

The only systematic absences observed were for $hk0$ when $h+k\neq2n$, giving the possible space groups $P4/n$ or $P4/nmm$. As the Laue symmetry was $4/m$ and not $4/mmm$, the space group was uniquely determined as $P4/n$.

Partial three-dimensional data were collected photographically with Ni-filtered Cu $K\alpha$ radiation, for which the linear absorption coefficient was $\mu=140$ cm^{-1}. Data for $0kl$, $hk0$ to $hk4$ were recorded with equi-inclination Weissenberg settings and four-film multiple packs. It was necessary to use a fresh crystal for each layer as it was observed that a primitive cubic powder pattern ($a=4{\cdot}04$ Å) became superimposed on the photographs after the crystals had been exposed to the X-ray beam for a few days. Each crystal used was of approximately the same size and shape and no absorption corrections were attempted. Intensities were estimated visually and the usual Lorentz and polarization factors were applied together with spot-elongation corrections for the upper layers. All computation was carried out on the Portsmouth College Elliott 803 computer using the Fourier program written by Dr R. M. Simmons, and the structure factor and least-squares program written by Dr G. A. Mair.

Structure analysis

With only two formula units per unit cell the Mo and As atoms occupy special positions, and since previous workers had shown the cation to have $\bar{4}$ symmetry

(Mooney, 1940; Palenik, 1966) it was assumed that the arsenic atom was located at $\frac{1}{4},\frac{3}{4},\frac{1}{2}$ and the molybdenum atom at $\frac{1}{4},\frac{1}{4},z$. The Patterson projection along [001] (Fig. 1), revealed the x and y coordinates of the bromine atoms, and the heavy-atom technique was applied to locate the carbon atoms of the phenyl groups in this projection. After three cycles of least-squares refinement a difference Fourier synthesis showed only one well resolved peak at $\frac{1}{4},\frac{1}{4}$, and this was assigned to oxygen after investigation of the infrared spectrum. Four further cycles of refinement reduced the residual to 0·092.

Table 1. *Observed and calculated structure factors*

Asterisks denote unobserved reflexions not included in the refinement.

h	k	l	F_o	F_c
0	2	0	70.5	-86.3
	4		13.9	-3.0
	6		55.7	-53.0
	8		51.9	49.5
	10		43.6	-41.9
	12		40.9	43.0
	14		11.1	-12.8
1	1	0	42.7	-40.3
	3		*	6.1
	5		36.2	-38.0
	7		9.3	-11.3
	9		18.6	18.4
	11		26.9	23.8
	13		20.4	-15.7
2	0	0	70.5	-86.2
	2		21.3	22.4
	4		113.3	-127.8
	6		62.1	64.6
	8		14.8	14.3
	10		45.5	43.2
	12		40.8	-41.8
	14		11.1	9.7
3	1	0	50.1	-54.8
	3		65.9	-65.6
	5		95.5	102.4
	7		30.6	31.3
	9		22.3	-18.9
	11		17.6	-14.0
4	0	0	13.9	-3.0
	2		26.9	-23.7
	4		97.4	102.1
	6		48.2	-47.8
	8		39.0	37.8
	10		48.2	-48.1
5	1	0	17.6	17.7
	3		11.1	8.5
	5		*	-3.9
	7		*	10.0
	9		45.5	-47.2
6	0	0	55.7	-53.0
	2		97.4	98.3
	4		9.3	-8.4
	6		*	-9.2
	8		59.4	-63.6
	10		39.0	35.1
7	1	0	64.0	69.0
	3		26.9	-24.5
	5		40.8	-39.0
	7		*	-1.5
8	0	0	52.0	49.6
	2		93.7	-97.7
	4		34.3	32.2
	6		35.3	-33.0
	8		39.0	39.7
9	1	0	15.8	-15.6
	3		*	1.3
	5		20.4	-19.2
	7		21.3	17.2
	9		17.6	16.0
10	0	0	44.0	-42.0
	2		*	-1.6
	4		21.3	-19.7
	6		52.9	55.3
	8		21.3	-19.6
11	1	0	12.1	-11.1
	3		21.3	19.7
	5		25.0	24.7
	7		12.1	-11.2
12	0	0	40.8	42.9
	2		*	0
	4		21.3	19.4
	6		20.4	-23.2
13	1	0	12.1	-13.2
	3		12.1	13.9
14	0	0	11.1	-13.2
	2		18.6	22.5
	4		20.4	-26.5
0	0	1	103.9	-93.5
	1		66.8	-84.1
	2		39.9	39.2
	3		62.2	-67.4
	4		13.0	11.7
	5		4.7	2.1
	6		37.1	36.0
	7		51.0	50.8
	8		27.8	-27.0
	9		18.6	-14.0
	10		22.3	22.1
	11		22.3	21.4
	12		25.0	-23.3
1	0	1	66.8	-84.0
	1		*	-4.8
	2		72.4	73.5
	3		37.1	39.4
	4		33.4	-34.4
	5		17.6	-16.9
	6		29.7	28.9
	7		21.3	22.4
	8		20.4	20.2
	9		26.9	-22.8
	10		16.7	14.8
	11		*	-10.1
	12		39.9	42.7
2	0	1	39.9	39.1
	1		41.7	40.1
	2		52.9	44.7
	3		72.4	-72.5
	4		81.6	79.6
2	5	1	61.2	66.8
	6		39.0	-37.7
	7		17.6	17.9
	8		7.4	-2.0
	9		17.6	-14.5
	10		16.7	-19.0
	11		40.8	-38.4
	12		21.3	20.7
3	0	1	62.2	67.2
	1		40.8	50.7
	2		39.0	33.5
	3		*	3.9
	4		88.1	95.4
	5		22.3	-22.0
	6		45.5	-44.4
	7		19.5	-19.2
	8		18.6	-12.0
	9		20.5	22.4
	10		17.6	-14.9
	11		*	1.9
	12		21.3	13.9
4	0	1	13.0	11.5
	1		51.9	55.7
	2		11.1	-11.2
	3		54.7	53.4
	4		40.1	-37.8
	5		49.2	-46.6
	6		18.6	16.0
	7		6.5	7.9
	8		26.0	-22.3
	9		25.0	-24.5
	10		23.2	24.6
	11		7.4	9.9
5	0	1	4.6	2.4
	1		26.0	-26.4
	2		*	3.3
	3		*	5.0
	4		27.8	-24.0
	5		22.3	-18.6
	6		*	-2.4
	7		*	5.5
	8		33.4	-34.8
	9		*	4.9
	10		21.3	24.3
6	0	1	37.1	35.8
	1		46.4	55.1
	2		50.1	-51.5
	3		40.8	-39.8
	4		17.6	14.4
	5		35.3	-34.5
	6		*	-1.3
	7		23.2	-18.5
	8		33.4	34.4
	9		35.3	49.2
	10		22.3	-21.5
7	0	1	51.0	51.0
	1		9.3	-10.4
	2		68.4	-75.3
	3		*	2.5
	4		*	-1.3
	5		33.4	33.4
	6		6.5	11.8
	7		*	-6.3
	8		28.8	28.7
8	0	1	27.8	-26.9
	1		42.7	-51.1
	2		40.8	44.5
	3		21.3	24.4
	4		12.1	-11.1
	5		*	7.2
	6		6.5	17.7
	7		23.2	21.5
	8		22.3	-19.3
9	0	1	18.6	-13.7
	1		11.1	-11.3
	2		17.6	22.4
	3		*	3.6
	4		14.8	-14.1
	5		*	-2.8
	6		37.1	33.6
	7		*	0.2
	8		*	-5.6
	9		22.3	-17.2
10	0	1	22.3	21.8
	1		*	-0.2
	2		*	-6.7
	3		*	7.6
	4		*	8.9
	5		31.4	30.6
	6		34.3	-33.0
	7		29.7	-30.7
	8		25.0	13.8
11	0	1	22.3	21.1
	1		12.1	16.1
	2		12.1	11.7
	3		14.8	-16.5
	4		*	3.8
	5		*	-2.1
	6		24.1	-24.5
0	0	2	92.8	-96.2
	1		74.4	75.3
	2		10.2	-5.5
	3		52.3	54.7
	4		50.9	49.5
	5		20.4	-16.4
	6		15.8	-6.1
	7		20.4	-16.1
	8		8.4	-8.4
0	9	2	*	0
	10		*	0.1
	11		13.0	-10.6
1	0	2	72.4	75.3
	1		66.8	67.5
	2		26.7	-23.2
	3		26.0	-24.9
	4		28.8	25.3
	5		57.5	57.0
	6		16.7	-12.8
	7		25.0	-23.5
	8		28.8	-27.7
	9		18.6	16.2
	10		*	-3.1
	11		32.5	-33.7
	12		21.3	25.7
	13		15.8	21.2
2	0	2	10.2	-5.9
	1		38.4	36.5
	2		18.6	14.3
	3		*	3.8
	4		31.5	27.1
	5		40.8	-40.5
	6		*	0.1
	7		39.9	-34.8
	8		31.5	-29.0
	9		16.7	14.7
	10		*	-5.1
	11		21.3	20.0
	12		*	19.8
	13		8.4	-5.5
3	0	2	52.3	54.8
	1		9.3	-11.2
	2		46.4	-34.5
	3		73.3	67.7
	4		60.3	-63.5
	5		88.1	-90.0
	6		28.8	22.0
	7		16.7	14.4
	8		30.6	28.4
	9		12.1	-9.2
	10		*	5.3
	11		26.9	24.5
4	0	2	50.9	49.6
	1		55.7	-55.9
	2		26.9	-23.2
	3		32.5	-33.0
	4		18.6	-19.3
	5		39.0	44.7
	6		*	-3.4
	7		*	1.9
	8		*	5.4
	9		26.9	23.3
5	0	2	20.4	-16.4
	1		30.6	29.9
	2		13.0	8.2
	3		33.4	-34.6
	4		*	-2.5
	5		18.6	19.2
	6		19.5	16.7
	7		33.4	-30.9
	8		20.4	17.5
	9		41.7	40.7
	10		24.1	-17.3
	11		16.7	-15.2
	12		13.9	-12.8
6	0	2	15.8	-6.1
	1		27.8	-25.0
	2		18.6	-20.1
	3		*	4.5
	4		18.6	-15.2
	5		43.6	41.9
	6		23.2	17.2
	7		*	0.6
	8		17.6	16.2
	9		39.9	-38.2
7	0	2	20.4	-16.2
	1		60.3	-61.6
	2		52.9	52.9
	3		39.9	41.0
	4		*	5.1
	5		*	2.3
	6		22.3	-20.9
	7		31.5	29.8
	8		16.7	-13.0
	9		28.8	-30.4
	10		*	0.2
8	0	2	8.4	-8.4
	1		47.3	44.4
	2		26.9	26.3
	3		17.6	-12.6
	4		*	5.4
	5		*	-9.9
	6		*	-4.8
	7		13.0	-10.1
9	1	2	30.6	30.5
	2		*	-3.3
	3		27.8	-26.2
	4		*	-5.1
	5		26.9	26.9
	6		26.9	-22.4
	7		25.0	-28.6
10	1	2	*	-0.2
	2		20.4	21.5
	3		21.3	-23.7
	4		*	-2.6
	5		20.4	-17.3
	6		18.6	-16.7
10	7	2	18.6	16.7
11	0	2	13.0	-10.7
	1		13.9	-11.5
	2		22.3	-20.8
	3		12.1	9.9
	4		*	-1.7
	5		29.7	-29.3
	6		17.6	15.3
	7		18.6	18.3
12	1	2	*	3.3
	2		13.9	-12.2
13	1	2	18.6	18.4
	3		13.0	-19.1
	5		13.0	13.1
0	0	3	103.9	95.7
	1		41.7	36.5
	2		12.1	9.5
	3		27.8	-26.7
	4		68.6	-69.7
	5		12.1	13.5
	6		13.9	-5.5
	7		30.6	-30.4
	8		*	0.6
	9		17.6	17.3
	10		*	1.2
	11		8.4	-8.0
	12		13.9	11.7
	13		8.4	9.9
1	0	3	41.7	36.8
	1		71.4	-75.9
	2		13.0	-16.6
	3		26.9	24.7
	4		23.2	21.2
	5		38.0	-37.9
	6		20.4	-20.2
	7		14.8	11.4
	8		*	8.2
	9		*	-0.9
	10		*	-12.0
	11		39.9	42.4
	12		17.6	10.2
2	0	3	12.1	9.4
	1		13.9	-15.2
	2		13.9	-12.7
	3		36.2	35.7
	4		55.7	-55.8
	5		13.0	-15.4
	6		16.7	11.0
	7		10.2	12.1
	8		49.2	49.0
	9		*	10.6
	10		*	0.2
	11		13.9	13.8
3	0	3	27.8	-26.8
	1		26.9	-19.9
	2		*	6.9
	3		62.2	-72.5
	4		24.1	24.0
	5		89.4	91.3
	6		13.9	14.5
	7		5.8	-5.0
	8		*	10.9
	9		*	2.2
	10		*	13.9
	11		26.9	-29.7
	12		14.8	-13.9
4	0	3	68.6	-69.5
	1		10.2	13.2
	2		49.2	55.9
	3		30.6	-32.6
	4		25.0	19.8
	5		26.0	27.7
	6		14.8	10.3
	7		*	-9.3
	8		*	-5.1
	9		*	11.4
	10		*	-6.6
	11		13.0	-9.1
	12		17.6	-19.9
5	0	3	12.1	13.4
	1		11.1	-8.5
	2		13.9	-14.4
	3		41.7	44.5
	4		28.8	26.0
	5		24.1	-20.5
	6		23.2	-22.0
	7		33.4	27.9
	8		31.5	24.3
	9		50.1	-47.0
	10		*	7.7
	11		15.8	12.9
	12		19.5	3.3
6	0	3	13.9	-5.5
	1		24.1	-25.1
	2		26.9	28.9
	3		10.2	9.8
	4		32.5	33.5
	5		40.8	-41.6
	8		27.8	-24.7
	9		12.1	-14.2
7	0	3	30.6	-30.6
	1		66.8	74.2
	2		20.4	24.3
	3		48.2	-49.0
	4		*	-3.6
	5		17.6	-13.6
	6		*	6.3
7	7	3	20.4	-19.2
	8		22.3	-18.3
	9		29.7	28.5
8	1	3	15.8	17.6
	2		33.4	-33.3
	3		11.1	-9.2
	4		19.5	-18.0
	5		19.5	23.2
	6		*	4.6
	7		19.5	-13.6
	8		*	5.5
	9		16.7	13.2
	10		27.8	16.3
9	0	3	17.6	17.2
	1		23.2	-23.9
	2		19.5	-17.4
	3		24.1	20.9
	4		4.6	10.0
	5		31.5	-28.7
	6		5.6	-10.1
	7		26.9	27.8
10	1	3	9.3	-12.8
	2		23.2	-23.3
	3		*	10.0
	4		*	9.2
	5		14.8	-18.3
	6		25.0	25.4
	7		*	6.0
11	0	3	8.4	-8.2
	1		*	1.7
	2		*	4.5
	3		*	3.2
	4		*	-8.8
	5		22.3	28.7
12	0	3	13.9	11.6
13	0	3	8.4	10.0
0	0	4	13.0	-9.5
	1		70.5	-68.7
	2		32.5	-32.9
	3		34.3	-28.1
	4		36.2	38.9
	5		*	-1.5
	6		23.2	-19.0
	7		27.8	27.9
	8		26.9	25.7
	9		11.1	-9.3
	10		13.9	-11.4
	11		16.7	16.2
	12		9.3	5.8
1	0	4	70.5	-68.7
	1		19.5	17.0
	2		34.3	30.6
	3		20.4	-15.4
	4		25.0	-19.3
	5		4.6	7.1
	6		21.3	18.1
	7		*	0.2
	8		14.8	7.4
	9		4.6	-4.1
	10		15.8	14.1
	11		9.3	-10.6
	12		17.6	-28.3
	13		9.3	8.3
2	0	4	32.5	-32.7
	1		14.8	10.0
	2		43.6	48.2
	3		33.4	-34.0
	4		13.0	-10.2
	5		54.7	53.2
	6		22.3	21.0
	7		13.9	12.8
	8		38.0	-36.1
	9		13.0	-11.4
	10		18.6	18.0
	11		25.0	-27.3
	12		17.6	-11.5
	13		10.2	10.7
	14		9.3	10.9
3	0	4	34.3	-28.3
	1		12.1	7.6
	2		*	2.9
	3		21.3	18.9
	4		69.6	75.6
	5		24.1	-21.8
	6		26.0	-25.3
	7		*	1.6
	8		17.6	-14.3
	9		4.6	-5.7
	10		16.7	-12.2
	11		12.1	9.7
	12		12.1	10.6
	14		9.3	-1.5
4	0	4	36.2	38.8
	1		37.1	37.3
	2		43.6	-52.8
	3		22.3	26.3
	4		20.4	19.1
	5		39.9	-39.2
	6		26.0	-25.9
	7		13.9	10.9
	8		14.8	12.2
	9		20.4	-19.8
	10		16.7	-13.0
	11		4.6	7.0
	12		14.8	20.3
	13		3.7	5.1
	14		7.4	-11.5
5	1	4	*	1.2
	2		14.8	10.3
	3		16.7	-17.0
	4		15.8	-16.1
	5		18.6	17.8
	6		4.6	-5.3
	7		*	-6.0
	8		23.2	-23.6
	9		18.6	18.1
	10		17.6	20.7
	11		*	-4.1
	12		14.8	7.9
6	0	4	23.2	-19.1
	1		36.2	38.6
	2		18.6	18.0
	3		23.2	-23.6
	4		35.3	-37.1
	5		23.2	-21.5
	6		43.6	45.1
	7		17.6	-16.5
	8		15.8	-11.5
	9		34.3	35.4
	10		11.1	12.0
	12		7.4	-14.0
7	0	4	27.8	27.5
	1		21.3	-23.0
	2		44.5	-49.7
	3		13.9	13.6
	4		*	-2.8
	5		*	-3.7
	6		9.3	8.7
	7		9.3	-3.4
	8		18.6	22.6
	9		*	-8.2
	10		12.1	-9.8
	11		4.6	3.5
	12		5.6	3.0
8	0	4	26.9	25.8
	1		36.2	-44.8
	2		9.3	-10.2
	3		23.2	21.9
	4		20.4	21.6
	5		*	5.5
	6		12.1	-12.4
	7		15.8	14.0
	8		*	4.1
	9		*	-2.9
	10		14.8	-15.7
	11		*	-0.6
	12		6.5	9.7
9	0	4	11.1	-9.2
	1		3.7	6.8
	2		14.8	14.2
	3		*	-4.0
	4		13.9	-13.1
	5		13.0	13.8
	6		26.0	28.1
	7		*	-5.9
	8		*	-5.1
	9		*	-1.6
10	0	4	13.9	-11.3
	1		3.7	0.1
	2		16.7	19.2
	3		3.7	7.3
	4		19.5	-23.3
	5		19.5	22.5
	6		4.6	6.7
	7		18.6	-20.0
	8		12.1	-10.8
11	0	4	16.7	16.1
	1		*	-2.5
	2		13.9	12.5
	3		4.6	-5.2
	4		*	5.3
	5		4.6	-7.1
12	0	4	9.3	5.6
	1		*	-4.1
	2		13.9	-16.9
	3		*	2.3
	4		13.0	14.4
	5		8.4	-11.2
	6		12.1	-10.0
0	0	5	78.8	-77.2
	1		18.6	20.6
	2		30.6	28.1
	3		49.2	41.1
	4		12.1	-11.0
	5		26.0	-20.4
	6		34.3	33.7
	8		29.9	-28.8
	9		13.0	-8.8
	10		18.6	16.9
1	0	5	18.6	20.4
2	0	5	30.6	28.1
3	0	5	49.2	41.0
4	0	5	12.1	-11.1
5	0	5	26.0	-20.3
6	0	5	34.3	33.8
8	0	5	26.9	-28.8
9	0	5	13.0	-8.8
10	0	5	18.6	17.1

From the Patterson projection along [100] the z coordinates of the molybdenum and bromine atoms were obtained. The electron density along [100] did not resolve the carbon and oxygen atoms owing to overlapping, but it was possible to estimate the z coordinates of these atoms by making use of the y coordinates previously obtained. Refinement of this projection was stopped when the residual reached 0·088.

Three-dimensional structure factors were then calculated with the contributions of all the atoms (except hydrogen) in the formula unit $[(C_6H_5)_4As][MoOBr_4]$. Atomic scattering factors obtained from the tables in *International Tables for X-ray Crystallography* were used for this purpose. Refinement of the structure was carried out by means of the least-squares program of Dr G. A. Mair. This program minimizes $\Sigma\, \omega(F_o - F_c)^2$, using the block-diagonal approximation. The weighting factor applied was $\omega = \frac{1}{1+(F_o-b)^2/a^2}$ with $a=30, b=20$.

After three cycles of refinement with isotropic temperature factors for the heavy atoms ($R=0{\cdot}146$) a three-dimensional difference Fourier synthesis was computed. This revealed no peaks of electron density greater than 0·8 e.Å^{-3} except for a well defined symmetrical peak of height 6·4 e.Å^{-3} situated on the fourfold axis about 2·4 Å above the molybdenum atom. Examination of the infrared spectra of the solid which had been mulled with Nujol in the atmosphere (see discussion) showed that water had entered the structure. Consequently the peak was assigned to the oxygen atom of a water molecule.

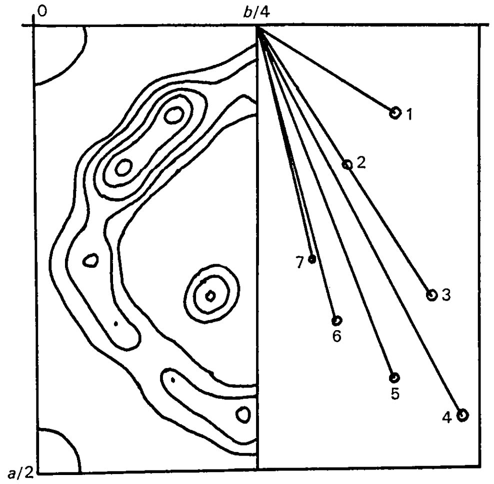


Fig. 1. [001] Patterson projection. (1) Mo–Br, (2) Mo–Br, (3) Br–Br, (4) Br–Br, (5) As–Br, (6) As–Br, (7) Br–Br.

Three more cycles of refinement including this oxygen atom reduced the residual to 0·110, when the positional and vibrational shifts were less than 0·3 times the standard deviation.

A final three-dimensional difference Fourier synthesis showed no significant peaks.

Observed and calculated structure factors are listed in Table 1, and the atomic positions and temperature factors in Table 2.

Discussion of the structure

The crystal structure of $[(C_6H_5)_4As][MoOBr_4(H_2O)]$ is composed of discrete ions. Like ions are stacked head-to-tail along the c axis, none of the intervening volume being occupied by unlike ions (Fig. 2).

The $[(C_6H_5)_4As]^+$ cation has previously been investigated by a number of workers (Cotton & Lippard, 1966; Palenik, 1966, and references therein) and the results of this investigation (Table 3) are in close agreement with those reported previously. Since the contribution of the carbon atoms to the structure factors is comparatively small, the standard deviations of the bond lengths and angles of the phenyl group are naturally larger than those for the heavy atoms of the anions. Also less reliance can be placed on the temperature factors found. However, the As–C distance of 1·91 Å is in agreement with the value found by the workers mentioned above (1·90 and 1·897 Å respectively) while the mean C–C bond length of 1·40 Å in the phenyl rings is close to the accepted value.

The $[MoOBr_4(H_2O)]^-$ anion (Fig. 3) bears a very close relationship to the $[ReOBr_4(H_2O)]^-$ anion investigated by Cotton & Lippard (1965), and Table 4 besides reporting the bond lengths and angles found for the molybdate anion in this investigation also lists, for

Table 2. *Final structure parameters for one molecule*

e.s.d.'s are multiplied by 10^3
Anisotropic temperature factors B_{ij} are defined by
$\exp\{-10^{-3}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$
The numbering of the atoms relates to the projection shown in Fig. 2.

	x/a	y/b	z/c	σ_x	σ_y	σ_z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Mo	0·2500	0·2500	0·2862	0	0	0·6	4·3	4·3	18·2	0·04	0	0	
As	0·7500	0·2500	0·5000	0	0	0·6	3·9	3·9	−3·4	−0·03	0	0	
Br	0·1474	0·0902	0·3267	0·3	0·3	0·6	7·2	5·5	17·3	−4·5	4·75	−2·97	
O	0·250	0·250	0·062	0	0	9							11·8
O(H_2O)	0·250	0·250	0·589	0	0	3							0·6
C(1)	0·866	0·244	0·646	2	2	5							2·9
C(2)	0·940	0·170	0·634	2	2	5							3·2
C(3)	1·018	0·163	0·745	3	3	6							5·1
C(4)	1·019	0·236	0·876	3	3	6							4·6
C(5)	0·947	0·316	0·903	3	3	5							4·4
C(6)	0·867	0·318	0·775	2	2	5							3·7

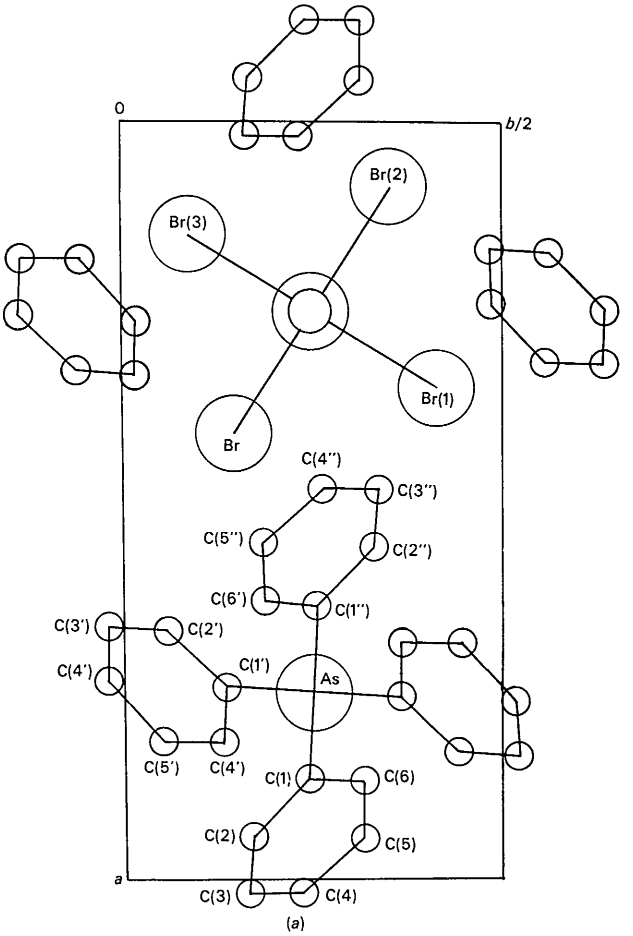
comparison, those found for the rhenate anion by Cotton & Lippard.

As was pointed out in the introduction, the infrared spectra of crystals which have not been exposed to the atmosphere show no evidence of water in the 2–3μ region, but on exposure to the atmosphere water is quickly taken up. The single band at 1007 cm^{-1} for the dry specimen, attributed to the Mo=O stretching frequency, weakens when water is detected, and a second band appears at 981 cm^{-1} (Fig. 4). This water can be removed in part by vacuum drying at 40°C, resulting in the 981 cm^{-1} band weakening and the 1007 cm^{-1} band becoming stronger. The same effect was also observed in the spectra of the isomorphous tetrachloride, but much more markedly. Here the Mo=O band appears at 1012 cm^{-1} when the crystals are dry and 981 cm^{-1} when water is detected in the 2–3μ region, but with the tetrachloride the initial spectrum is completely restored when the crystals are dried in vacuo at 40°C. This doublet in the tetrachloride ion spectrum has been reported previously (Allen, Brisdon, Edwards, Fowles & Williams, 1963) but was not associated with water entering the structure.

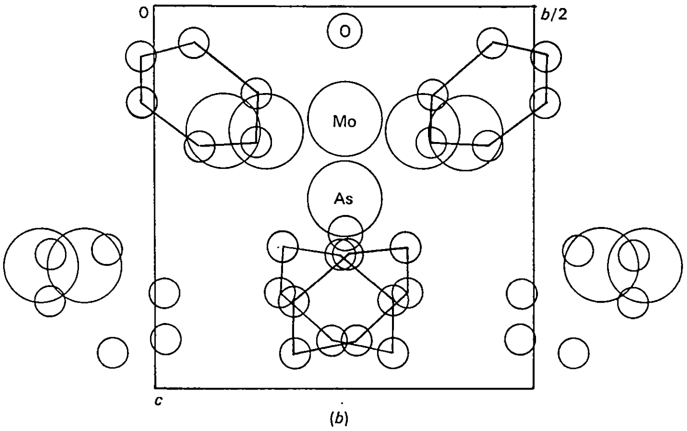
Table 3. *Bond distances and valency angles of* $[(C_6H_5)_4As]^+$

	Length	σ
As—C(1)	1·91 Å	0·03 Å
As—C(2)	2·91	0·03
As—C(6)	2·81	0·04
C(1)-C(2)	1·38	0·04
C(2)-C(3)	1·35	0·06
C(3)-C(4)	1·41	0·06
C(4)-C(5)	1·42	0·05
C(5)-C(6)	1·46	0·06
C(6)-C(1)	1·42	0·05
	Angle	σ
C(1)-As—C(1″)	106°	0·8
C(1)-As—C(1′)	111	0·7
C(1)-C(2)-C(3)	123	2·5
C(2)-C(3)-C(4)	116	2·2
C(3)-C(4)-C(5)	127	3·1
C(4)-C(5)-C(6)	113	2·2
C(5)-C(6)-C(1)	122	1·7
C(6)-C(1)-C(2)	121	2·5

Consequently it is inferred that the gap along the fourfold axis between the $[MoOBr_4]^-$ ions is of an optimum size to accommodate the water molecule, the oxygen of the water being very weakly bound to the molybdenum. Since this water molecule is situated on a fourfold axis the hydrogen atoms must be disordered.



(a)



(b)

Fig. 2. (*a*) Projection of the structure along the *c* axis.
(*b*) Projection of the structure along the *a* axis.

Table 4. *Bond distances and valency angles of* $[\mathrm{MoOBr_4(H_2O)}]^-$ *compared with those of* $[\mathrm{ReOBr_4(H_2O)}]^-$ (*Cotton & Lippard*, 1965)

$[\mathrm{MoOBr_4(H_2O)}]^-$			$[\mathrm{ReOBr_4(H_2O)}]^-$		
	Length	σ		Length	σ
Mo–Br	2·516	0·004	Re–Br	2·51	0·01
Mo–O(H_2O)	2·39	0·03	Re–O(H_2O)	2·32	0·04
Mo–O	1·78	0·07	Re–O	1·71	0·04
Br—O(H_2O)	3·24	0·02			
Br—O	3·26	0·05			
Br—Br(1)	3·530	0·004			
	Angle	σ		Angle	σ
Br–Mo–O(H_2O)	82·6	0·08	Br——Re–O(H_2O)	83·2	0·9
			Br(1)–Re–O(H_2O)	80·5	0·9
Br–Mo–O	97·4	0·2	Br——Re–O	98·4	0·7
			Br(1)–Re–O	97·9	0·8
Br–Mo–Br(1)	89·1	0·04	Br——Re–Br(1)	89·2	0·2
			Br(1)–Re–Br(2)	88·0	0·2

The extra angles quoted for the $[\mathrm{ReOBr_4(H_2O)}]^-$ ion are due to the fact that this ion does not lie on a fourfold axis.

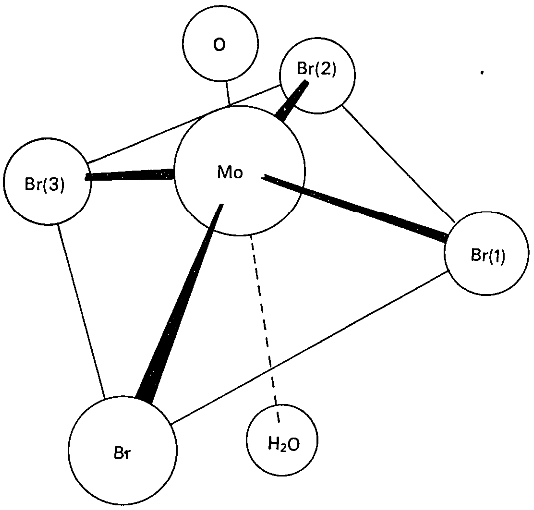


Fig. 3. Sketch of the $[\mathrm{MoOBr_4(H_2O)}]^-$ ion.

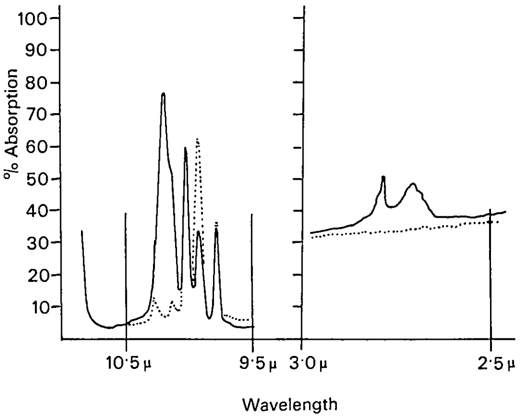


Fig. 4. Absorption spectra in Nujol mull. Dotted line: mulled in dry box; full line: mulled in atmosphere.

The two oxygen atoms contribute relatively little to the structure factors and therefore the accuracy of their positions and thermal parameters is relatively low. Nevertheless it appears that the thermal motion of the Mo=O oxygen ($B = 11{\cdot}8$) is significantly greater than that of the water oxygen ($B = 0{\cdot}6$). This can be accounted for by assuming that water is precisely located in the structure but that the molybdyl oxygen shares in the large thermal motion of the $\mathrm{MoOBr_4}$ group (which is very marked parallel to **c**).

If the value 1·11 Å is used for the tetrahedral covalent radius of the bromine atom (Pauling, 1960) the covalent radius of the molybdenum atom is 1·41 Å.

A preliminary examination has also been made of the diffraction data of $[\mathrm{(C_2H_5)_4N}]^+[\mathrm{MoOBr_4(H_2O)}]^-$ and shows that it is isomorphous with the $[\mathrm{(C_2H_5)_4N}]^+[\mathrm{ReOBr_4(H_2O)}]^-$ reported by Cotton & Lippard (1965). When exposed to X-rays this too shows a powder pattern superimposed on the single-crystal pattern which is identical with that observed superimposed on the $[\mathrm{(C_6H_5)_4As}][\mathrm{MoOBr_4(H_2O)}]$ pattern.

It is intended to investigate the structure of the anhydrous tetrachloride in order to obtain further information on the Mo=O bond. Further work on the breakdown product which gives the cubic powder pattern of $a = 4$ Å is also contemplated.

A complete report on the infrared spectra of the tetrabromide and tetrachloride is being prepared for publication (J. G. Scane and R. M. Stephens).

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