TABLE IV

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Distances, A		Angles, deg	
Re–S_1	2.32 (1)	S_1–Re–S_6	81.9 (3)
Re–S_2	2.30 (1)	S_2–Re–S_5	81.5 (4)
Re–S_3	2.33 (1)	S_3–Re–S_4	80.9 (4)
Re–S_4	2.32 (1)	Re–S_1–C_1	109 (1)
Re–S_5	2.33 (1)	Re–S_2–C_2	108 (1)
Re–S_6	2.33 (1)	Re–S_3–C_3	111 (1)
S_1–C_1	1.75 (3)	Re–S_4–C_4	107 (1)
S_2–C_2	1.72 (4)	Re–S_5–C_5	109 (1)
S_3–C_3	1.63 (3)	Re–S_6–C_6	110 (1)
S_4–C_4	1.70 (3)	S_1–C_1–C_6	119 (2)
S_5–C_5	1.62 (4)	S_6–C_6–C_1	120 (2)
S_6–C_6	1.70 (2)	S_2–C_2–C_5	119 (3)
		S_5–C_5–C_2	122 (3)
C_1–C_6	1.34 (3)	S_3–C_3–C_4	119 (2)
C_2–C_5	1.33 (3)	S_4–C_4–C_3	122 (2)
C_3–C_4	1.34 (3)	S_1–C_1–R_1C_1	112
C_1–R_1C_1	1.51	S_2–C_2–R_2C_1	112
C_2–R_2C_1	1.52	S_3–C_3–R_3C_1	119
C_3–R_3C_1	1.53	S_4–C_4–R_4C_1	112
C_4–R_4C_1	1.54	S_5–C_5–R_5C_1	118
C_5–R_5C_1	1.53	S_6–C_6–R_6C_1	118
C_6–R_6C_1	1.52		

mentioned above, the W analog and possibly the Mo, Cr, and V analogs of the Re complex probably have the trigonal prismatic configuration. Thus tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium is the first example of what will undoubtedly become a class of trigonal prismatic complexes in transition metal chemistry.

Acknowledgments.—We are indebted to G. N. Schrauzer for the crystals and to H. B. Gray for his helpful and enlightening comments.

TABLE V

THE EQUATIONS OF THE BEST LEAST-SQUARES PLANES THROUGH THE CHELATE RINGS AND THE DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES (A)

(1) The Plane through the Chelate Ring Defined by Re, S_1, S_6, C_1, and C_6

$19.121x - 0.867y + 0.509z = 4.751$ (triclinic coordinates)

Atom	Distance	Atom	Distance
Re	0.000 (2)	C_1	0.03 (4)
S_1	0.003 (11)	C_6	−0.04 (4)
S_6	0.003 (10)		

(2) The Plane through the Chelate Ring Defined by Re, S_2, S_5, C_2, and C_5

$9.457x - 9.213y - 0.213z = 2.190$ (triclinic coordinates)

Atom	Distance	Atom	Distance
Re	0.000 (1)	C_2	−0.08 (3)
S_2	0.007 (8)	C_5	0.04 (2)
S_5	−0.002 (8)		

(3) The Plane through the Chelate Ring Defined by Re, S_3, S_4, C_3, and C_4

$9.730x + 7.465y + 1.718z = 2.586$ (triclinic coordinates)

Atom	Distance	Atom	Distance
Re	0.000 (1)	C_3	−0.05 (3)
S_3	0.016 (9)	C_4	−0.11 (3)
S_4	0.016 (8)		

TABLE VI

CALCULATED VALUES FOR THE DIHEDRAL ANGLES BETWEEN THE CHELATE AND PHENYL RINGS

Chelate ring[a]	Phenyl ring	Dihedral angle, deg
1	1	50.4
1	6	55.0
2	2	62.3
2	5	46.4
3	3	38.2
3	4	65.2

[a] The chelate rings are numbered according to the order given in Table V.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Chemical and Structural Studies of Rhenium(V) Oxyhalide Complexes. III. The Crystal and Molecular Structure of Tetraphenylarsonium Oxotetrabromoacetonitrilerhenate(V)[1]

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The crystal and molecular structure of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ has been investigated by X-ray diffraction. The anion is shown to consist of a square-pyramidal (C_{4v}) $ReBr_4O$ group, with a molecule of acetonitrile weakly bonded to the rhenium atom at a distance Re–N of 2.31 A. The Re–O distance of 1.73 A is indicative of considerable multiple bond character. The structure of the cation is discussed in terms of idealized S_4 symmetry. Various features of the molecular geometry of the $[ReBr_4O(CH_3CN)]^-$ ion are compared with the structural results of other related complexes reported in the literature.

Introduction

Recently, we have reported the preparation and characterization of several new rhenium(V) oxyhalide complexes.[3-5] From rhenium(III) bromide in concentrated aqueous HBr, compounds containing either the $[ReBr_4O]^-$ or $[ReBr_4O(H_2O)]^-$ anions are obtained.[4] A complete X-ray structure investigation of

(1) Supported by the U. S. Atomic Energy Commission.

(2) National Science Foundation Predoctoral Fellow, 1962–1965.

(3) F. A. Cotton and S. J. Lippard, *Chem. Commun.* (London), 245 (1965).

(4) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965).

(5) F. A. Cotton and S. J. Lippard, *ibid.*, **5**, 9 (1966).

$[(C_2H_5)_4N][ReBr_4O(H_2O)]$ revealed the presence of a square-pyramidal ($ReBr_4O$) grouping as the basic structural unit, with another, weakly coordinated ligand (H_2O) attached to its base.[4] The reduction of potassium perrhenate in a medium consisting of zinc, methanol, HX, and H_2SO_4, followed by treatment with an appropriate cation–solvent system, was also shown to produce compounds containing either the $[ReX_4O]^-$ or the $[ReX_4OL]^-$ anion, where X is chlorine or bromine and L is water or acetonitrile.[5] One of these compounds, *viz.*, $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$, was examined by single crystal X-ray diffraction techniques, the results of which are reported herein.

Experimental Procedures and Results

Single Crystal X-Ray Work.—The compound was prepared as described previously.[5] Because of its greater stability to hydrolytic decomposition, $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ was chosen for the X-ray investigation, rather than one of the more sensitive $M[ReX_4O]$ complexes. Despite this precaution, however, occasional diffuse spots of an impurity appeared on both oscillation and equiinclination photographs, in addition to the ordered lattice rows of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$. Fortunately, the orthogonal lattice of the impurity and the triclinic lattice of the complex were easily distinguished on the Weissenberg films. In the rare cases where reflections from the two different lattices coincided, the questionable reflection was not read. Of the 1100 reflections observed, less than 15 were excluded for this reason. As an additional precaution, to ensure against the possibility of serious crystal decomposition during the course of the measurements, two sets of zero-level Weissenberg films for each crystal mounting (*vide infra*) were taken and read, one before and one after all other data were recorded. The discrepancies did not exceed normal experimental uncertainties.

In order to minimize absorption errors, the crystals used in this study were reduced in size. Before being mounted, each crystal was partially dissolved in a small pool of acetonitrile on the microscopic stage. The average diameter of the crystals obtained in this manner was ~0.1 mm, resulting in a maximum value of 1.7 for μt ($\mu = 166\ \text{cm}^{-1}$), which is close to the optimum value of 2.0.[6] Absorption corrections were not applied.

Precession camera photographs using filtered molybdenum radiation were obtained for the determination of the unit cell parameters and space group. The density was measured by flotation in a mixture of CH_3I and C_2H_5I.

Intensity data were taken on the Weissenberg camera using copper radiation filtered through nickel. The intensities of nearly 1100 *observable* reflections were estimated visually from Weissenberg photographs using the multiple film technique. Each spot was compared to a scale prepared from timed exposures of one reflection from the same crystal. Levels of *h0l*–*h6l* and *0kl*–*4kl* from two separate crystals were read. About 600 reflections occurred in both sets of data and, from these, all data were initially placed on a common scale.[7] A separate scale factor for use in the least-squares refinement was then assigned to reflections of the type *hkl* which were read from the compacted half of the *0kl*–*4kl* Weissenberg films. Reflections $h\bar{k}l$, $hk\bar{l}$, and $h\bar{k}\bar{l}$ were read from the extended sides of the films.

The raw data were corrected for Lorentz-polarization effects by DFSET-4[8] from which $|F_o|$ and $|F_o|^2$ were then generated.[7] Prewitt's program, SFLSQ-3,[9] was used in the subsequent structure factor calculation and least-squares refinement, and MIFR-2[10] was used to compute Patterson and Fourier syntheses. All molecular geometry calculations, including bond angles, lengths, and best planes, were performed with the aid of MGEOM.[11] Equal weights were used in the least-squares process. Scattering factors for rhenium were those of Thomas and Umeda for Re(0),[12] modified for the real part of anomalous dispersion by adding −5.0 electrons according to Templeton.[13] The imaginary part of the dispersion correction is small and was ignored. Bromine, arsenic, carbon, nitrogen, and oxygen form factors were taken from the International Tables,[14] with the real part of the anomalous dispersion correction being applied to Br and As.[13]

Unit Cell and Space Group.—The $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ complex crystallizes in the triclinic system with $a = 8.47 \pm 0.02$ A, $b = 12.90 \pm 0.03$ A, $c = 13.82 \pm 0.03$ A, $\alpha = 104.7 \pm 0.3°$, $\beta = 98.8 \pm 0.3°$, $\gamma = 90.1 \pm 0.3°$. The cell volume ($V = 1443\ \text{A}^3$) and density ($2.05 < \rho < 2.20$ g/cc) require two formula weights per unit cell. The calculated density is 2.18 g/cc, in good agreement with that observed. The probable space group $P\bar{1}$ was adopted and appears to be a justifiable choice in view of the successful refinement of the structure. All atoms occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[15]

Determination of the Structure.—From the *0kl* and *k0l* data, the [100] and [010] Patterson projections were computed, revealing the location of the rhenium, bromine, and arsenic atoms. The presence of a monomeric ($ReBr_4$) grouping containing a C_4 symmetry axis was immediately apparent. When all the data were available, a three-dimensional Patterson function was generated, confirming the result of the projections. A Fourier synthesis was then performed based on structure factors whose signs were calculated using the following trial positions: for Re, $x = 0.271$, $y = 0.167$, $z = 0.255$; for Br_1, $x = 0.287$, $y = 0.021$, $z = 0.0933$; for Br_2, $x = 0.258$, $y = 0.0333$, $z = 0.339$; for Br_3, $x = 0.256$, $y = 0.312$, $z = 0.339$; for Br_4, $x = 0.287$, $y = 0.300$, $z = 0.152$; for As, $x = 0.463$; $y = 0.693$; $z = 0.275$.

From the Fourier map, the heavy atom parameters were relocated. In addition, the oxygen atom, the nitrogen and carbon atoms of the acetonitrile, and 9 of the 24 carbon atoms of the tetraphenylarsonium ion appeared. All of these atoms were then used in a structure factor calculation to compute the signs for another Fourier map. This revealed more carbon atoms, but the resolution was poor. Therefore, two cycles of least-squares refinement of heavy atom positional and isotropic thermal parameters, keeping the original oxygen, nitrogen, and 11 carbon atom parameters fixed, and omitting other possible carbon atoms, were run, and a Fourier map was generated from the resulting structure factors. At this point the conventional residual ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.21 (observable reflections only).

From the Fourier map, the remaining carbon atoms could be located. Five more cycles of least-squares and Fourier refinement of all atomic positional and thermal parameters reduced R to 0.110. Occasionally, a carbon atom positional or thermal parameter refined to an unrealistic value, at which time it was removed from the calculation of structure factors and relocated in the next Fourier synthesis. After the last cycle, a difference map was computed which revealed rather large anisotropic thermal motion of the heavy atoms, especially in the direction normal to the square of four bromine atoms, as would be expected. Thus, anisotropic thermal parameters were assigned to all atoms and the least-squares refinement continued.

After two more cycles of refinement of all atomic positions and

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(6) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, p 178 ff.

(7) A short FORTRAN II program for the IBM 7094 computer was written to help perform this operation.

(8) The program DFSET-4 was kindly made available to us by Professor M. J. Buerger's research group at MIT.

(9) C. T. Prewitt, MIT (1962), SFLSQ-3, a full-matrix crystallographic least-squares refinement program for the IBM 709/7090 computer.

(10) MIFR-2 is an updated version of the Sly–Shoemaker–Van den Hende Fourier program, ERFR-2: W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090," ERFR-2 (1962).

(11) J. S. Wood, "MGEOM—Molecular Geometry Program for the IBM 709/7090/7094 Computer," MIT (1964).

(12) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(13) D. H. Templeton in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p 215.

(14) Reference 13, Vol. III, p 218 ff.

(15) Reference 13, Vol. I.

Table I

List of Observed and Calculated Structure Factors for $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$

K	L	FOBS	FCAL
* * H = 0 * *			
0	2	159.	-219.
0	3	41.	47.
0	4	15.	-8.
0	5	46.	-55.
0	6	71.	-80.
0	7	62.	57.
0	8	76.	80.
0	9	42.	-41.
0	10	40.	-40.
0	11	42.	36.
0	12	37.	32.
1	1	105.	-114.
-1	2	43.	-46.
1	2	65.	-62.
-1	3	32.	-33.
1	3	23.	-9.
-1	4	51.	-57.
1	4	69.	75.
-1	5	33.	-35.
1	5	78.	-86.
-1	6	16.	-13.
1	6	53.	-55.
-1	7	120.	-121.
-1	8	42.	45.
-1	9	69.	68.
-1	10	20.	-19.
1	10	31.	-30.
-2	1	214.	182.
2	1	80.	-86.
-2	2	103.	111.
2	2	94.	101.
2	3	224.	221.
-2	3	49.	-57.
2	4	176.	-172.
2	5	145.	-148.
-2	5	65.	67.
2	6	93.	93.
-2	7	151.	-169.
2	7	34.	-27.
-2	8	49.	-55.
2	8	18.	-28.
2	9	22.	24.
-2	9	124.	131.
2	10	53.	60.
-3	1	40.	43.
3	1	11.	-14.
-3	2	35.	36.
3	2	151.	154.
-3	3	30.	48.
3	3	34.	-25.
-3	4	144.	-152.
3	4	211.	-218.
-3	5	18.	22.
3	5	15.	13.
-3	6	64.	59.
-3	8	68.	-82.
-3	10	24.	29.
3	10	45.	50.
4	0	17.	12.
-4	1	24.	-25.
4	1	87.	78.
-4	2	48.	46.
4	2	40.	44.
-4	3	283.	253.
4	3	167.	-168.
-4	4	133.	-126.
4	4	36.	-31.
-4	5	204.	-196.
4	5	96.	91.
4	6	16.	-9.
-4	6	57.	48.
-4	7	36.	38.
4	7	51.	-57.
-4	8	43.	-54.
-4	9	30.	-31.
4	9	51.	55.
-4	10	53.	57.
-5	1	21.	-31.
5	1	70.	81.
-5	2	40.	-18.
5	2	40.	-34.
-5	3	101.	109.
-5	-3	74.	-70.
5	3	69.	-70.
-5	5	153.	-150.
-5	4	120.	114.
5	5	38.	40.
-5	6	32.	-29.
5	6	25.	-27.
5	7	86.	-77.
-5	8	27.	-24.
5	9	35.	40.
5	8	42.	47.
6	0	171.	186.
-6	1	72.	78.
6	1	62.	-60.
-6	2	140.	-127.
6	2	68.	-72.
-6	3	29.	-32.
-6	4	183.	165.
6	4	30.	-33.
6	5	29.	-19.
-6	6	95.	-88.
6	6	46.	-46.
-6	7	31.	23.
6	7	38.	44.
6	8	40.	50.
-6	9	33.	-36.
-6	10	62.	-58.
7	0	74.	81.
-7	1	128.	141.
7	1	102.	-112.
-7	2	30.	-33.
7	2	18.	-23.
7	4	21.	24.
7	7	44.	54.
8	0	120.	-139.
-8	1	86.	109.
-8	2	94.	103.
8	2	54.	56.
-8	3	33.	-39.
8	4	39.	-46.
9	0	41.	-47.
-9	2	36.	41.
9	2	36.	60.
-9	3	34.	-35.
9	4	57.	-75.
* * H = 1 * *			
0	0	102.	-101.
0	1	236.	-228.
0	-2	111.	106.
0	2	76.	84.
0	-2	98.	106.
0	3	49.	-56.
0	-3	26.	26.
0	4	39.	-44.
0	-4	34.	-39.
0	5	26.	19.
0	-5	91.	97.
0	6	53.	50.
0	-6	35.	35.
0	7	49.	55.
0	-7	167.	-162.
0	8	42.	-51.
0	-9	70.	74.
0	10	27.	34.
0	-11	61.	-64.
0	11	16.	12.
-1	0	219.	215.
-1	1	69.	-71.
-1	-1	36.	39.
1	1	149.	-144.
-1	2	154.	-147.
-1	-2	217.	-201.
1	-2	62.	70.
1	2	167.	170.
1	-3	29.	-40.
1	3	61.	54.
-1	3	24.	21.
-1	-3	9.	11.
-1	4	105.	-95.
-1	-4	126.	117.
1	4	177.	-149.
-1	5	11.	-13.
-1	-5	28.	28.
1	5	50.	-41.
-1	6	73.	-71.
-1	-6	61.	-52.
1	-6	67.	69.
1	6	115.	95.
-1	7	74.	75.
-1	-7	16.	-8.
1	-7	90.	-95.
-1	8	103.	108.
-1	-8	30.	-25.
1	-8	81.	-89.
-1	9	56.	-55.
1	-9	36.	34.
-1	10	29.	-31.
-1	11	21.	23.
-2	0	169.	176.
2	0	74.	-68.
-2	1	47.	47.
-2	-1	16.	16.
2	-1	201.	-196.
2	1	144.	106.
-2	2	203.	-212.
-2	-2	188.	-178.
2	-2	126.	128.
2	2	22.	-13.
-2	3	93.	98.
-2	-3	119.	110.
2	-3	74.	69.
2	3	178.	-167.
-2	-4	237.	229.
2	4	60.	-58.
-2	-5	100.	-92.
2	-5	59.	-82.
-2	5	60.	-65.
2	5	106.	103.
-2	6	44.	-50.
-2	-6	91.	-87.
2	-6	66.	84.
2	-7	118.	126.
-2	8	135.	145.
2	-8	157.	-171.
-2	-9	39.	-38.
2	-9	72.	-72.
-2	10	42.	-51.
-3	0	46.	39.
3	0	24.	-19.
-3	-1	90.	78.
-3	2	13.	8.
-3	-2	9.	9.
3	-2	77.	76.
3	2	26.	21.
-3	3	138.	-131.
-3	-3	204.	194.
-3	4	7.	-10.
-3	-4	58.	-53.
3	4	26.	24.
-3	5	119.	119.
-3	-5	132.	-128.
3	-5	140.	-130.
3	5	177.	174.
3	-6	14.	-8.
-3	7	100.	-97.
-3	-7	21.	-18.
3	-7	95.	-91.
-3	9	90.	89.
-3	-9	20.	-18.
3	-9	56.	-53.
-3	11	22.	-24.
-4	0	65.	70.
4	0	71.	-60.
-4	-1	26.	-30.
4	1	69.	-59.
-4	-2	169.	163.
4	-2	139.	-149.
-4	2	61.	57.
4	2	90.	-78.
-4	3	204.	-204.
-4	-3	105.	102.
4	-3	55.	60.
-4	4	168.	-168.
-4	-4	156.	-150.
-4	5	133.	134.
-4	-5	43.	-48.
4	-5	68.	-74.
4	5	29.	-24.
-4	6	56.	54.
-4	-6	70.	70.
4	-6	109.	-121.
-4	7	83.	-76.
-4	-7	33.	33.
-4	8	30.	24.
-4	-8	94.	-93.
4	-8	39.	44.
-4	9	49.	47.
4	-9	26.	-25.
-4	10	5.	0.
4	-10	72.	-72.
-5	0	24.	-18.
5	0	64.	50.
-5	-1	14.	2.
-5	1	20.	14.
5	1	31.	-34.
-5	2	21.	17.
-5	-2	64.	56.
5	-2	82.	-82.
-5	2	27.	17.
5	2	75.	-69.
-5	3	79.	90.
-5	-3	43.	-34.
5	-3	113.	-107.
5	3	78.	72.
-5	4	111.	-108.
-5	-4	14.	-20.
-5	5	133.	-132.
5	-5	106.	117.
5	5	33.	-34.
-5	6	108.	101.
-5	-6	31.	22.
5	-6	92.	-88.
-5	-7	41.	-33.
5	-7	14.	20.
-5	8	18.	13.
5	-8	59.	-59.
-5	-8	15.	-21.
-5	-9	25.	20.
5	-9	36.	-37.
-5	10	33.	29.
6	0	102.	-83.
-6	-1	152.	150.
-6	1	154.	-152.
6	1	110.	-102.
-6	2	52.	54.
6	2	32.	30.
-6	-3	22.	-14.
6	-3	94.	-92.
-6	3	138.	131.
6	3	37.	-35.
-6	4	57.	-53.
-6	-5	52.	53.
6	-5	132.	121.
-6	5	118.	-121.
-6	6	40.	39.
-6	-6	29.	-28.
6	-6	62.	51.
-6	7	28.	13.
-6	-7	110.	-107.
6	-7	29.	-24.
-6	8	64.	-59.
-6	-8	25.	29.
6	-8	18.	-17.
-6	9	7.	19.
6	-9	26.	19.
-6	10	52.	48.
-7	0	138.	139.
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-4	-4	54.	-61.
-4	4	33.	-34.
-4	-5	50.	-50.
-4	5	101.	108.
-4	7	49.	-62.
-4	-7	31.	31.
-4	8	33.	28.
-5	-1	51.	-43.
-5	1	68.	68.
-5	-2	47.	50.
-5	-3	50.	50.
-5	3	6.	-14.
-5	-4	29.	-23.
-5	4	58.	-56.
-5	-5	51.	-54.
-5	-6	46.	41.
-5	6	34.	35.
-5	7	25.	-22.
-6	0	43.	-46.
-6	1	73.	-68.
-6	-1	49.	48.
-6	-2	57.	56.
-6	2	64.	62.
-6	3	47.	48.
-6	4	51.	-49.
-6	-4	38.	-36.
-6	5	55.	-59.
-6	6	64.	61.
* * H = 6 * *			
0	0	41.	-47.
0	1	51.	39.
0	-1	53.	-62.
0	-2	37.	-36.
0	-3	94.	85.
0	3	66.	-75.
0	-4	13.	21.
0	4	42.	41.
0	5	35.	45.
0	-5	71.	-75.
0	-6	30.	38.
0	6	31.	-31.
0	-7	41.	45.
0	7	30.	-30.
0	-8	27.	-31.
0	8	14.	20.
-1	0	43.	-52.
-1	1	42.	-54.
-1	2	36.	59.
-1	-2	35.	29.
-1	-3	14.	21.
-1	3	6.	-10.
-1	5	48.	53.
-2	0	63.	-63.
-2	-1	47.	44.
-2	1	24.	-35.
-2	-2	52.	51.
-2	2	58.	62.
-2	-3	91.	-94.
-2	4	95.	-102.
-2	-4	10.	-17.
-2	-5	67.	66.
-2	-6	51.	46.
-2	-7	23.	-27.
-3	-1	38.	36.
-3	1	31.	-34.
-3	-2	57.	-48.
-3	-3	17.	-17.
-3	3	39.	38.
-3	-4	45.	44.
-3	4	28.	21.
-3	-5	29.	25.
-3	5	46.	-44.
-3	-6	33.	30.
-3	6	7.	-12.
-3	7	47.	44.
-4	0	49.	53.
-4	-1	34.	34.
-4	1	94.	-108.
-4	2	26.	-30.
-4	-2	27.	-29.
-4	-3	27.	27.
-4	3	44.	45.
-4	-4	60.	65.
-4	4	47.	50.
-4	-6	48.	-52.
-4	5	46.	-54.
-5	0	31.	34.
-5	-1	31.	-37.
-5	2	44.	-45.
-5	3	31.	-36.
-5	5	49.	44.
-6	0	14.	-25.
-6	-1	45.	-43.
-6	1	59.	64.
-6	-3	60.	59.
-6	3	80.	-71.
* * H = 7 * *			
0	0	28.	24.
0	-1	33.	28.
0	-2	32.	-41.
0	2	35.	-40.
0	-3	59.	-72.
0	-4	55.	65.
-1	-1	50.	-55.
-1	1	68.	72.
-1	-2	19.	-22.
-1	3	43.	-55.
-1	-3	35.	41.
-1	4	47.	52.
-1	5	24.	26.
-1	6	43.	-46.

heavy atom thermal parameters, the residual fell to 0.082. A final difference Fourier showed no peaks of electron density greater than would be expected for individual hydrogen atoms. Table I contains the final list of calculated and observed structure factors. The atomic positional and isotropic temperature parameters, along with their standard deviations (σ values) as computed in the final least-squares refinement cycle, are given in Table II. Table III contains the final rhenium, bromine, and arsenic atom anisotropic temperature factors and their standard deviations. The orthogonal coordinates of all the atoms are listed in Table IV.

Discussion of the Structure

Packing Considerations.—The crystal structure of tetraphenylarsonium oxotetrabromoacetonitrilerhenate(V) is composed of discrete $[(C_6H_5)_4As]^+$ and $[ReBr_4O(CH_3CN)]^-$ molecule ions. The nearest nonbonded contact distance between atoms of two neighboring anions in the same unit cell is well over 6 A, with the phenyl groups of the cation interposed. Between unit cells, the anions stack head-to-tail approximately

TABLE II

FINAL POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR TETRAPHENYLARSONIUM OXOTETRABROMOACETONITRILERHENATE(V)[a,b]

Atom	*x/a*	*y/b*	*z/c*	*B*
Re	0.2876 (6)	0.1711 (1)	0.2559 (10)	4.02 (7)
Br_1	0.2567 (4)	0.0267 (5)	0.0960 (4)	7.00 (2)
Br_2	0.2281 (8)	0.0413 (6)	0.3472 (7)	6.2 (2)
Br_3	0.2335 (3)	0.3169 (1)	0.4055 (1)	5.7 (2)
Br_4	0.2693 (1)	0.3071 (6)	0.1553 (3)	6.8 (2)
O	0.493 (8)	0.156 (5)	0.278 (4)	10 (2)
N	0.015 (7)	0.181 (5)	0.215 (4)	7 (2)
C_{CN}	−0.128 (8)	0.183 (5)	0.180 (5)	5 (2)
C_{CH_3}	−0.297 (10)	0.185 (7)	0.134 (6)	9 (2)
As	0.4773 (3)	0.6915 (3)	0.2759 (2)	3.3 (2)
C_{A_1}	0.605 (1)	0.569 (3)	0.308 (4)	3 (1)
C_{A_2}	0.756 (4)	0.553 (1)	0.277 (2)	4 (1)
C_{A_3}	0.865 (4)	0.477 (3)	0.307 (2)	5 (2)
C_{A_4}	0.789 (1)	0.398 (6)	0.358 (4)	5 (2)
C_{A_5}	0.649 (3)	0.424 (4)	0.386 (7)	9 (2)
C_{A_6}	0.539 (8)	0.507 (6)	0.353 (5)	5 (1)
C_{B_1}	0.336 (7)	0.646 (5)	0.155 (4)	3 (1)
C_{B_2}	0.355 (7)	0.549 (5)	0.094 (4)	3 (1)
C_{B_3}	0.254 (10)	0.523 (7)	0.003 (6)	7 (2)
C_{B_4}	0.127 (13)	0.586 (9)	−0.029 (8)	13 (3)
C_{B_5}	0.102 (9)	0.688 (6)	0.044 (5)	6 (2)
C_{B_6}	0.203 (9)	0.719 (6)	0.141 (5)	6 (2)
C_{C_1}	0.613 (8)	0.782 (6)	0.254 (5)	4 (1)
C_{C_2}	0.606 (11)	0.818 (7)	0.150 (6)	6 (2)
C_{C_3}	0.732 (12)	0.882 (7)	0.148 (6)	5 (2)
C_{C_4}	0.843 (9)	0.912 (6)	0.220 (5)	5 (2)
C_{C_5}	0.857 (8)	0.890 (6)	0.313 (5)	3 (1)
C_{C_6}	0.748 (11)	0.817 (8)	0.338 (7)	6 (2)
C_{D_1}	0.339 (9)	0.743 (6)	0.383 (5)	4 (1)
C_{D_2}	0.397 (8)	0.833 (6)	0.464 (5)	4 (1)
C_{D_3}	0.320 (9)	0.885 (6)	0.543 (5)	5 (2)
C_{D_4}	0.183 (12)	0.840 (8)	0.526 (6)	9 (2)
C_{D_5}	0.120 (9)	0.753 (7)	0.460 (6)	4 (1)
C_{D_6}	0.208 (8)	0.698 (5)	0.376 (4)	4 (1)

[a] Standard deviations, in parentheses beside each atom, occur in the last significant figure for each parameter. [b] The numbering system used refers to that of Figures 2 and 3.

TABLE III

FINAL ANISOTROPIC THERMAL COEFFICIENTS (×10^4) FOR THE HEAVY ATOMS IN $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$[a,b]

Atom[c]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	130 (11)	66 (6)	74 (4)	24 (80)	10 (5)	30 (4)
Br_1	311 (40)	98 (17)	94 (13)	34 (22)	50 (18)	14 (12)
Br_2	199 (33)	79 (16)	111 (13)	−2 (7)	5 (3)	50 (12)
Br_3	171 (30)	78 (16)	94 (12)	−5 (18)	13 (15)	10 (11)
Br_4	200 (33)	98 (17)	126 (14)	−12 (20)	−8 (16)	69 (13)
As	199 (26)	47 (15)	57 (10)	7 (17)	6 (12)	21 (10)

[a] Standard deviations are in parentheses beside each value. [b] Anisotropic temperature factors 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] See Figure 2 for numbering scheme.

TABLE IV

ORTHOGONAL COORDINATES OF ALL ATOMS IN CRYSTALLINE $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$[a]

Atom	*X* coord	*Y* coord	*Z* coord
Re	1.891	1.310	3.379
Br_1	1.970	0.006	1.267
Br_2	1.193	−0.683	4.583
Br_3	1.115	2.668	5.352
Br_4	1.950	3.417	2.049
O	3.58	1.04	3.66
N	−0.34	1.58	2.84
C_{CN}	−1.46	1.75	2.37
C_{CH_3}	−2.78	1.95	1.77
As	3.494	7.953	3.639
C_{A_1}	4.51	6.26	4.06
C_{A_2}	5.83	6.16	3.65
C_{A_3}	6.69	5.07	4.05
C_{A_4}	5.96	3.87	4.72
C_{A_5}	4.73	4.12	5.09
C_{A_6}	3.87	5.30	4.65
C_{B_1}	2.53	7.78	2.04
C_{B_2}	2.81	6.74	1.24
C_{B_3}	2.13	6.72	0.04
C_{B_4}	1.12	7.64	−0.38
C_{B_5}	0.78	8.72	0.58
C_{B_6}	1.44	8.78	1.86
C_{C_1}	4.68	9.19	3.34
C_{C_2}	4.81	10.00	1.98
C_{C_3}	5.88	10.83	1.95
C_{C_4}	6.68	10.97	2.90
C_{C_5}	6.62	10.37	4.12
C_{C_6}	5.65	9.35	4.46
C_{D_1}	2.13	8.24	5.04
C_{D_2}	2.47	9.13	6.12
C_{D_3}	1.67	9.52	7.15
C_{D_4}	0.55	9.01	6.93
C_{D_5}	0.14	8.12	6.06
C_{D_6}	1.04	7.69	4.96

[a] Numbers given are in angstrom units and refer to the orthogonal system of coordinates used in the program MGEOM,[11] in which the orthogonal *Y* axis is taken to be coincident with the cell *y* axis, and the orthogonal *Z* axis normal to the *xy* plane.

along the *a* axis, with none of the intervening volume being occupied by the tetraphenylarsonium ion. In this direction, the closest nonbonded approach is about 3.2 A and occurs between the oxygen atom of one $[ReBr_4O(CH_3CN)]^-$ group and the methyl carbon atom of another. This value is close to the calculated one of 3.4 A, using Pauling's estimates for the van der Waal's radii of the oxygen atom and the methyl group.[16] These features are better revealed in Figure 1, which contains a projection of the full unit cell, converted for simplicity to an orthogonal coordinate system (Table IV), onto the [100] plane.

The $[ReBr_4O(CH_3CN)]^-$ Ion.—The dimensions of the ion are summarized in Table V and a sketch which shows the numbering scheme appears in Figure 2. In the triclinic space group $P\bar{1}$, the $[ReBr_4O(CH_3CN)]^-$ ion has no crystallographically required symmetry. An inspection of Table V, however, reveals that within the limits of the significance of the data, the $ReBr_4O$ group of the anion has the identical C_{4v} symmetry found for the same structural unit in $[(C_2H_5)_4N][ReBr_4O(H_2O)]$.[4] At the base of this $ReBr_4O$ group, a molecule of acetonitrile is coordinated to the rhenium atom through its nitrogen atom with a Re–N bond distance of 2.31 A. Again we may compare this result to the observed geometry of the oxotetrabromoaquorhenate(V) anion, where a molecule of water is attached to the rhenium atom at a distance of 2.32 A.[4] This close correspondence between the dimensions of the $[ReBr_4O(H_2O)]^-$ and $[ReBr_4O(CH_3CN)]^-$ ions may be cited as further evidence for the chemical and

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[16] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Table 7-20, p 260. As pointed out by a referee, the short observed O–C distance may be an artifact of the large thermal parameters of the oxygen and carbon atoms (Table II).

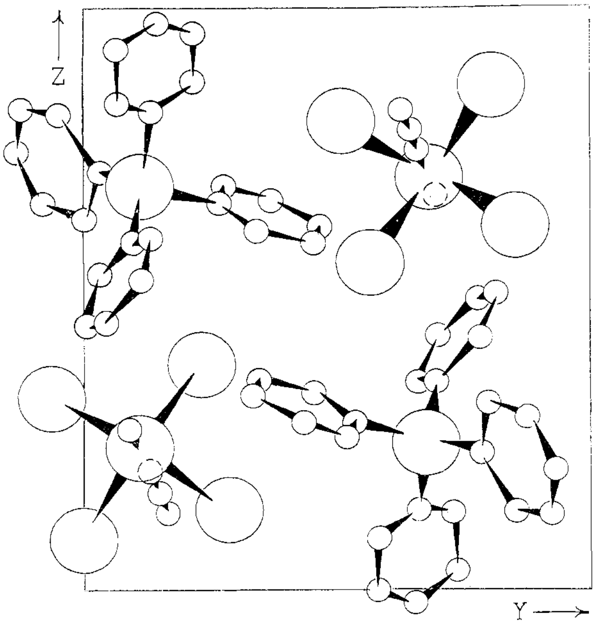

Figure 1.—Full unit cell of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$, converted to orthogonal coordinates (*cf.* Table IV) and projected onto the [100] plane of the new coordinate system.

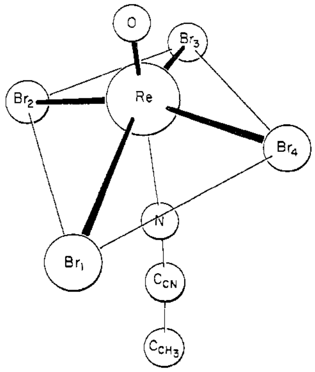

Figure 2.—Sketch of the $[ReBr_4O(CH_3CN)]^-$ ion showing the atom labeling scheme.

structural identity of the rhenium(V) oxyhalide complexes prepared from Re_3Br_9 and $KReO_4$, respectively (*cf.* ref 3–5).

The discrepancy between the shortest (2.43 A) and longest (2.51 A) Re–Br lengths in the $[ReBr_4O(CH_3CN)]^-$ ion is only slightly more than the sum of the standard deviations (0.06 A) and is therefore not significant. A similar comment can be made for the Br–Re–O and Br–Re–Br bond angles. For the purposes of discussion, we shall use distances and angles which have been averaged according to C_{4v} symmetry. Accordingly, we find the Re–Br bond length of 2.48 A to be comparable to that found in the Re_3Br_9 (2.45 and 2.54 A),[17] $[ReBr_6]^{-2}$ (2.51 A),[17] and $[ReBr_4O(H_2O)]^-$ (2.51 A)[4] groups, whose structures have been previously investigated by us. Apparently, within experimental error, the distance between bromine and rhenium atoms is independent of the oxidation state of the latter, at least for Re(III), Re(IV), and Re(V) complexes. Taking an average Re–Br distance of 2.49 A, and using a value of 1.11 A for the "tetrahedral covalent radius" of the bromine atom,[18] we conclude that the covalent radius of the rhenium atom in the bromorhenates is 1.38 A.

TABLE V

DIMENSIONS OF THE $[ReBr_4O(CH_3CN)]^-$ GROUP IN $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$[a]

Bond or angle[b]	Length, A, or angle, deg	Std dev[c]
$Re-Br_1$	2.48	0.03
$Re-Br_2$	2.43	0.03
$Re-Br_3$	2.51	0.03
$Re-Br_4$	2.49	0.03
Re–O	1.73	0.06
Re–N	2.31	0.06
$N-C_{CN}$	1.22	0.08
$C_{CN}-C_{CH_3}$	1.46	0.10
$Br_1-Re-Br_2$	90.0	0.3
$Br_2-Re-Br_3$	88.0	0.4
$Br_3-Re-Br_4$	88.2	0.4
$Br_4-Re-Br_1$	89.4	0.4
$Br_1-Re-Br_3$	163.6	0.3
$Br_2-Re-Br_4$	164.6	0.4
Br_1-Re-O	92	4
Br_2-Re-O	94	4
Br_3-Re-O	104	4
Br_4-Re-O	102	4
N–Re–O	176	3
$C_{CN}-N-Re$	170	4
$C_{CH_3}-C_{CN}-N$	179	6

[a] Equation of best molecular plane through Br_1, Br_2, Br_3, Br_4 and distances of atoms from this plane in A: $0.976X - 0.044Y + 0.230Z - 2.219 = 0$; Re, 0.342; Br_1, −0.010; Br_2, 0.027; Br_3, −0.018; Br_4, 0.002. [b] See Figure 2 for numbering scheme. [c] Standard deviations take into account errors in measurement of cell constants.

The short Re–O bond distance in the $[ReBr_4O(CH_3CN)]^-$ anion, 1.73 ± 0.06 A, supports our previous conclusion, based on infrared spectral and magnetic studies,[5] that there is strong π bonding between rhenium and oxygen atoms.

Using Pauling's value for the single-bond radius of tetrahedral covalent oxygen (0.66 A)[18] and the value (1.38 A) just calculated for rhenium, we get a theoretical Re–O single bond length of 2.04 A. For the typical rhenium–oxygen double bond[19] distance, we may take the value of 1.86 A found in the $[Re_2OCl_{10}]^{-2}$ ion.[20] Thus, it appears likely that some triple bond character occurs in the $M[ReX_4OL]$ and $M[ReX_4O]$ compounds, for which suitable orbitals are available (*cf.* Discussion, ref 5).

The compound *trans*-$ReCl_3O[P(C_2H_5)_2(C_6H_5)]_2$ was recently investigated[21] by X-ray diffraction and a rough value of 1.60 A for the Re–O bond length was found. The Re–O stretching frequency in this compound falls at 978 cm^{-1},[22] whereas the corresponding band occurs

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(17) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 59 (1965).

(18) L. Pauling, ref 16, Table 7-13, p 246.

(19) The assignment of a bond order of 2 to the Re–O bonds in $[Re_2OCl_{10}]^{2-}$ is based on a simple MO analysis in which (taking the Z axis to coincide with Re–O–Re) the d_{xz} and d_{yz} orbitals of each Re together with the p_x and p_y orbitals of O form two bonding, two nonbonding, and two antibonding π MO's. The bonding π MO's and the nonbonding π MO's are each occupied by two electron pairs, thus giving a π bond order of one to be added to the underlying σ bond order of one.

(20) J. C. Morrow, *Acta Cryst.*, **15**, 851 (1962).

(21) H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 4368 (1963).

(22) J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

at 1000 cm^{-1} in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$.[5] Since in general one would expect a 1.60 A Re–O bond to absorb at a higher energy than a 1.72 A Re–O bond, it seems unlikely that the value reported by Ehrlich and Owston is reliable. Nevertheless, these authors do observe distortions away from true octahedral symmetry,[22] which strongly suggests extensive π bonding between the rhenium and oxygen atoms. In the $[ReBr_4O(CH_3CN)]^-$ ion, an analogous distortion exists which also may be ascribed to π bonding. Here, the rhenium atom lies 0.34 A above the "best plane" through the four bromine atoms (see Figure 2 and Table V).

Turning now to the dimensions of the CH_3CN group in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$, we find our results to be comparable to the values reported for other transition metal–methyl cyanide complexes. Recently, Willett and Rundle[23] have reported the crystal structures of $Cu_2Cl_4(CH_3CN)_2$ and $Cu_3Cl_6(CH_3CN)_2$, which contain acetonitrile coordinated to copper through the nitrogen atom. Corresponding to the values in Table V of 1.22 ± 0.08 A for the N–C_{CN} and 1.46 ± 0.1 A for the C_{CN}–C_{CH_3} bond distances, and 179 ± 6° for the C_{CH_3}–C_{CN}–N bond angle, these authors find average values of 1.16 A, 1.47 A, and 178°, respectively. Furthermore, as recently noted by Walton,[24] the M–N–C angle in these copper–methyl cyanide complexes was the first known example of a nonlinear metal-to-acetonitrile linkage, a phenomenon ascribed by Willett and Rundle[23] to the partial use of sp^2 hybrid orbitals by the nitrogen atom. In Table V, we note that the Re–N–C_{CN} angle of 170 ± 4° appears to be nonlinear, but because of the inherent errors in locating the light atom positions, this result may not be significant.

One important difference between the geometry of the copper and rhenium complexes does exist, however, namely the length of the metal–nitrogen bond. In the two copper complexes, the Cu–N bond lengths were found to be 1.96 and 1.97 A,[23] whereas we find a Re–N distance of 2.31 A (Table V). Even allowing for differences in the covalent radii of the copper (1.28 A)[25] and rhenium (1.38 A, *vide supra*) atoms, this disparity is significant. Presumably the longer Re–N bond length reflects the weakness of the metal-to-acetonitrile bond in the $[ReBr_4O(CH_3CN)]^-$ ion *vs.* the corresponding bond in the copper complexes. This conclusion is consistent with our previous finding[4] that the Re–OH_2 bond in the $[ReBr_4O(H_2O)]^-$ ion is unusually weak. Thus, as before,[4] we prefer to describe the $[ReBr_4OL]^-$ ions as containing a square-pyramidal ($ReBr_4O$) grouping as the basic structural unit, with a weakly coordinated solvent molecule attached to its base, rather than as a distorted octahedron.

TABLE VI

DIMENSIONS OF THE $[(C_6H_5)_4As]^+$ GROUP IN $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$[a,b]

Bond	Length, A	Angle	Deg	Angle	Deg
As–C_{A_1}	2.01 (0.05)	C_{A_1}–As–C_{B_1}	111 (2)	C_{B_1}–As–C_{C_1}	105 (3)
As–C_{B_1}	1.87 (0.06)	C_{A_1}–As–C_{C_1}	107 (3)	C_{B_1}–As–C_{D_1}	106 (3)
As–C_{C_1}	1.74 (0.07)	C_{A_1}–As–C_{D_1}	109 (3)	C_{C_1}–As–C_{D_1}	118 (4)
As–C_{D_1}	1.98 (0.08)				

Best Plane Equation through Ring A

$$0.218X + 0.416Y + 0.883Z - 7.140 = 0$$

Distances of Carbon Atoms from Plane (A)

C_{A_1}, 0.01; C_{A_2}, −0.07; C_{A_3}, 0.04; C_{A_4}, −0.04; C_{A_5}, 0.07; C_{A_6}, −0.01

Bond	Length, A	Angle	Deg
C_{A_1}–C_{A_2}	1.38 (0.07)	As–C_{A_1}–C_{A_2}	118 (3)
C_{A_2}–C_{A_3}	1.43 (0.09)	C_{A_1}–C_{A_2}–C_{A_3}	123 (5)
C_{A_3}–C_{A_4}	1.54 (0.08)	C_{A_2}–C_{A_3}–C_{A_4}	112 (2)
C_{A_4}–C_{A_5}	1.35 (0.10)	C_{A_3}–C_{A_4}–C_{A_5}	120 (4)
C_{A_5}–C_{A_6}	1.53 (0.11)	C_{A_4}–C_{A_5}–C_{A_6}	118 (6)
C_{A_6}–C_{A_1}	1.26 (0.09)	C_{A_5}–C_{A_6}–C_{A_1}	120 (6)
		C_{A_6}–C_{A_1}–As	118 (4)

Best Plane Equation through Ring B

$$-0.685X - 0.580Y + 0.442Z + 5.332 = 0$$

Distances of Carbon Atoms from Plane (A)

C_{B_1}, 0.03; C_{B_2}, 0.02; C_{B_3}, 0.02; C_{B_4}, −0.04; C_{B_5}, 0.00; C_{B_6}, 0.06

Bond	Length, A	Angle	Deg
C_{B_1}–C_{B_2}	1.33 (0.08)	As–C_{B_1}–C_{B_2}	120 (5)
C_{B_2}–C_{B_3}	1.42 (0.09)	C_{B_1}–C_{B_2}–C_{B_3}	119 (6)
C_{B_3}–C_{B_4}	1.44 (0.12)	C_{B_2}–C_{B_3}–C_{B_4}	122 (7)
C_{B_4}–C_{B_5}	1.51 (0.12)	C_{B_3}–C_{B_4}–C_{B_5}	117 (7)
C_{B_5}–C_{B_6}	1.47 (0.09)	C_{B_4}–C_{B_5}–C_{B_6}	123 (6)
C_{B_6}–C_{B_1}	1.53 (0.09)	C_{B_5}–C_{B_6}–C_{B_1}	111 (6)
		C_{B_6}–C_{B_1}–As	112 (5)

Best Plane Equation through Ring C

$$-0.578X + 0.722Y + 0.380Z - 5.213 = 0$$

Distances of Carbon Atoms from Plane (A)

C_{C_1}, 0.00; C_{C_2}, 0.01; C_{C_3}, 0.01; C_{C_4}, −0.03; C_{C_5}, 0.02; C_{C_6}, −0.01

Bond	Length, A	Angle	Deg
C_{C_1}–C_{C_2}	1.61 (0.09)	As–C_{C_1}–C_{C_2}	127 (5)
C_{C_2}–C_{C_3}	1.37 (0.11)	C_{C_1}–C_{C_2}–C_{C_3}	115 (7)
C_{C_3}–C_{C_4}	1.22 (0.10)	C_{C_2}–C_{C_3}–C_{C_4}	124 (8)
C_{C_4}–C_{C_5}	1.34 (0.09)	C_{C_3}–C_{C_4}–C_{C_5}	126 (8)
C_{C_5}–C_{C_6}	1.41 (0.10)	C_{C_4}–C_{C_5}–C_{C_6}	124 (6)
C_{C_6}–C_{C_1}	1.51 (0.10)	C_{C_5}–C_{C_6}–C_{C_1}	114 (6)
		C_{C_6}–C_{C_1}–As	117 (5)

Best Plane Equation through Ring D

$$0.319X - 0.759Y + 0.554Z + 2.853 = 0$$

Distances of Carbon Atoms from Plane (A)

C_{D_1}, −0.02; C_{D_2}, 0.01; C_{D_3}, 0.01; C_{D_4}, −0.04; C_{D_5}, 0.03; C_{D_6}, 0.01

Bond	Length, A	Angle	Deg
C_{D_1}–C_{D_2}	1.44 (0.10)	As–C_{D_1}–C_{D_2}	121 (5)
C_{D_2}–C_{D_3}	1.34 (0.09)	C_{D_1}–C_{D_2}–C_{D_3}	130 (6)
C_{D_3}–C_{D_4}	1.23 (0.11)	C_{D_2}–C_{D_3}–C_{D_4}	109 (7)
C_{D_4}–C_{D_5}	1.33 (0.12)	C_{D_3}–C_{D_4}–C_{D_5}	130 (8)
C_{D_5}–C_{D_6}	1.47 (0.09)	C_{D_4}–C_{D_5}–C_{D_6}	119 (7)
C_{D_6}–C_{D_1}	1.24 (0.10)	C_{D_5}–C_{D_6}–C_{D_1}	116 (6)
		C_{D_6}–C_{D_1}–As	123 (5)

[a] Numbers given in parentheses refer to the standard deviation in the last significant figure listed. [b] See Figure 3 for numbering scheme.

The $[(C_6H_5)_4As]^+$ Ion.—Table VI summarizes the dimensions of the tetraphenylarsonium cation as it appears in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$. The numbering system used refers to Figure 3, where a projection view of the cation is shown. The standard deviations in bond angles (2–8°) and bond lengths (0.1 A) are large. This is to be expected since the carbon atoms contribute very little to each structure factor compared to the contributions of the Re, Br, and As atoms.

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(23) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).
(24) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).
(25) L. Pauling, ref 16, p 262.

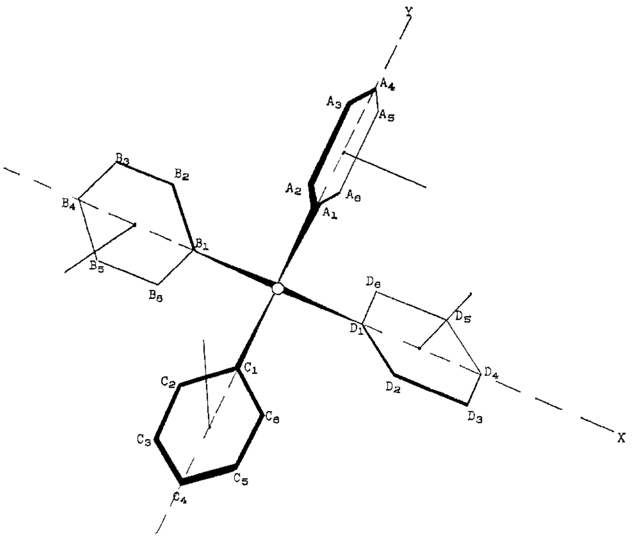

Figure 3.—Projected view of the tetraphenylarsonium cation as it occurs in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$. (---------) represents best planes *X* and *Y* as discussed in text and in Table VII. Normal lines to each of the four phenyl groups are shown.

Nevertheless, the results compare favorably with those previously obtained by other workers, as will be shown.

From Table VI we see that the angles between the arsenic atom and the four nearest carbon atoms are close to the expected value of 109° 28′. The mean As–C bond length is 1.90 A, in good agreement with the value of 1.95 A found by Mooney.[26] The mean C–C bond length within the phenyl rings is 1.45 ± 0.05 A, again close to the value (1.39 A) reported by Mooney.[26] Also included in the table are the equations of the best molecular planes through the four crystallographically independent benzene rings and the distances of the carbon atoms from their respective planes. In no case does this distance exceed 0.07 A, a feature which may be taken as a measure of the accuracy of the structure.

The tetraphenylarsonium ion in $[(C_6H_5)_4As]I$ has approximately full D_{2d} symmetry, with the planes of each of the four phenyl rings being perpendicular to one or the other of two mirror planes whose line of intersection coincides with the crystallographically required S_4 axis.[26] If the benzene rings of the cation are each tipped about their own $As–C_1–C_4$ axis (Figure 3) through the same constant angle ($0° < \phi < 90°$), however, the symmetry of the ion is lowered to S_4. An example of this is the tetraphenylarsonium ion in $[(C_6H_5)_4As][FeCl_4]$, where $\phi = 28°$.[27] In our compound, the crystallographically required point symmetry is C_1. For the sake of discussion, however, we can consider the ion in terms of idealized S_4 symmetry as follows.

Let us assume that the two molecular planes passing through the arsenic atom, one containing carbon atoms C_{A_1}, C_{A_4}, C_{C_1}, and C_{C_4} and the other containing C_{B_1}, C_{B_4}, C_{D_1}, and C_{D_4}, are mutually perpendicular (Figure 3). (A calculation of the best molecular planes (*X* and *Y*) containing these two sets of atoms shows that, in reality, they intersect at an angle of 85.6° (Table VII).) Now, we can easily compute the angle (ϕ) through which each of our four benzene rings must be rotated to make it orthogonal to the *X* or *Y* plane passing through it. From Table VII, we see that three of the four phenyl groups have been rotated through approximately the same ϕ angle, 37 ± 3°. The fourth ring (ring A), however, has been rotated by 72°. The failure of A to assume the ϕ value of 37° common to B, C, and D may be understood from packing considerations. For, if ring A were to have a ϕ value of 37°, it would sterically interfere with the $[ReBr_4O(CH_3CN)]^-$ ions between which it is situated in the unit cell. Some feeling for this steric interaction may be obtained by examining Figure 1, and it is quite clear from a molecular model that the spatial requirements of the $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ lattice are incompatible with a ϕ value of 37° for ring A. In summary, then, the symmetry of the tetraphenylarsonium ion may be related to an idealized S_4 symmetry by the single parameter ϕ (37 ± 3°), except for ring A, whose orientation has been distorted by an additional intermolecular packing interaction in the crystal lattice.

Table VII

Relationship of the Tetraphenylarsonium Ion in $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ to Idealized S_4 Symmetry[a]

Best Plane (*X*) through C_{A_1}, C_{A_4}, As, C_{C_1}, C_{C_4}

$$-0.029X + 0.245Y + 0.969Z - 5.364 = 0$$

Best Plane (*Y*) through C_{B_1}, C_{B_4}, As, C_{D_1}, C_{D_4}

$$-0.144X - 0.976Y + 0.163Z + 7.656 = 0$$

Angle of Intersection between *X* and *Y* = 85.6°

Angles of Rotation (ϕ) of Phenyl Groups

Phenyl ring	Intersecting plane	ϕ,[b] deg
A	*X*	+72
B	*Y*	−41
C	*X*	+32
D	*Y*	−37

[a] See Figure 3 for atom labeling scheme and text for full discussion. [b] The signs of the angles are taken as plus if, when viewed down the $C_4–C_1–As$ axis, the phenyl group must be rotated in a clockwise direction to bring its perpendicular to the intersecting plane and as minus if in a counterclockwise direction. For idealized S_4 symmetry, $\phi_A = \phi_C = -\phi_B = -\phi_D$.

Anisotropic Thermal Motion.—From the values of the anisotropic temperature factor coefficients, β_{ij}, given in Table III, it is apparent that the motions of the heavy atoms have considerable anisotropic character. In particular, since the plane of the four bromine atoms corresponds roughly to the plane of the *b* and *c* crystallographic axes, the large β_{11} coefficients for the heavy atoms indicate thermal motion in a direction normal to this plane. While it is difficult to assign any chemical significance to the motion, it seems reasonable in view of the head-to-tail packing arrangement of the anions described earlier.

Relation to Other Oxotetrahalometallates

The anionic rhenium(V) oxyhalide complexes reported in this and the previous papers[3–5] of this series

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[26] R. C. L. Mooney, *J. Am. Chem. Soc.*, **62**, 2995 (1940).

[27] B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

bear a marked resemblance to certain molybdenum and tungsten compounds which we wish to discuss briefly at this time. Recently, complexes of general formula $M[MoOX_4]$, $M[MoOX_5]$, and $M[WOX_5]$ were prepared[28] and characterized, where M is a univalent cation and X is Cl or Br. From the chemical and physical properties reported for these compounds,[28] it is apparent that they are structurally very similar to the rhenium analogs described by us. In fact, X-ray studies by Rogers and Scane[29] have verified that in salts containing the $(MoOBr_4)$ moiety, the basic structural unit is the square-pyramidal $(MoOX_4)$ group, with perhaps a sixth ligand (H_2O) bonded weakly to the molybdenum atom at the base. Moreover, a comparison of the (orthorhombic) unit cell parameters and space groups of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$[4] and $[(C_2H_5)_4N][MoOBr_4(H_2O)]$[29] shows that they are in fact isomorphous and, in all probability, isostructural.

Thus, the oxotetrahalo complexes and their derivatives of Mo(V) and W(V) are quite similar to the series of Re(V) compounds reported by us, both in their chemical and structural properties. In view of the arguments presented[3,5] for the existence of strong $O \rightarrow M$ π bonding in the rhenium compounds, it seems likely that this feature also occurs in the molybdenum and tungsten complexes. The degree of $O \rightarrow M$ π bonding (and, presumably, the *stability* of the complex) ostensibly depends upon two factors: first, incomplete occupancy of the $d\pi$ orbitals of the metal atom so that these orbitals are able to receive electrons from oxygen atoms, and, second, the high oxidation state of the metal atom, so that the resulting complex does not have too great a negative charge to stabilize, which it might perhaps do by delocalization back through the π orbitals onto the electronegative oxygen atom. In view of these two criteria, it seems possible that square-pyramidal tetrahalometallate complexes of Nb(V), Ta(V), Tc(V), Ru(VI), and Os(VI) might be prepared under the appropriate conditions.

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(28) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

(29) D. Rogers, Department of Chemistry, Imperial College, London, private communication, Oct. 1965.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

The Crystal and Molecular Structure of Dimeric Bis(acetylacetonato)aquocobalt(II) and the Preparation of Some Other New Hydrates[1a]

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The preparation of $[Co(AA)_2H_2O]_2$ and other hydrated derivatives of $Co(AA)_2$ is discussed (AA = the acetylacetonate anion). The structure of the former, determined by single-crystal X-ray techniques, is that of a centrosymmetric dimer, corresponding to the center of the $[Co(AA)_2]_4$ structure with the missing bridge bonds replaced by bonds to water molecules. A second, triclinic, crystal form of the dihydrate, $Co(AA)_2(H_2O)_2$, has been isolated as well as a new compound which may be either $[Co(AA)_2]_2H_2O$ or $[Co(AA)_2]_3H_2O$.

Introduction

The solution chemistry of bis(acetylacetonato)cobalt(II), $Co(AA)_2$, is rather complex. The tendency of the cobalt to achieve six-coordination is pronounced and appears to be the most important single structural principle governing the behavior of these systems. In donor solvents, the bis(acetylacetonate) reacts with two donor molecules, D, to form the octahedral complex, $Co(AA)_2D_2$.[2,3] In noncoordinating solvents, spectroscopic[4a] studies have shown that $Co(AA)_2$ exists as a tetrahedral monomer in very dilute solution; both spectroscopic[4a] and cryoscopic[4b] evidence indicate that in more concentrated solutions octahedral coordination is achieved through polymerization. Polymerization has also been shown to occur in the solid $[Co(AA)_2]_4$ formed by sublimation.[5] If a small amount of some neutral donor ligand, D, is introduced into a solution of polymer in a noncoordinating solvent, complex equilibria are established and the following types of compounds can be obtained from such solutions: $[Co(AA)_2]_4$, $[Co(AA)_2]_2D$, $[Co(AA)_2D]_2$, and $Co(AA)_2D_2$, where D may be water, pyridine,[6] or cyclohexylamine.[7]

While attempts to crystallize consistently an anhy-

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(1) (a) Supported by a grant from the National Science Foundation; (b) National Institutes of Health Predoctoral Fellow, 1962–1964.

(2) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

(3) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(4) (a) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964); (b) D. P. Graddon, *Nature*, **195**, 891 (1962).

(5) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965). It is to be emphasized that tetramers were found in the solid, whereas the solutions were reported to contain either dimers[4a] or trimers.[4b] This point will be discussed in a later paper in this series.

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(7) J. A. Bertrand, F. A. Cotton, and W. J. Hart, *Inorg. Chem.*, **3**, 1007 (1964).