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The Crystal Structure of Bis(tetraphenylarsonium) Tri-μ-chloro-octachlorotrirhenate(III), $[(C_6H_5)_4As]_2Re_3Cl_{11}$

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Received February 7, 1966

A three-dimensional crystal structure analysis of the compound of composition $[(C_6H_5)_4As]_2Re_3Cl_{11}$ establishes that it contains the trinuclear anion $(Re_3Cl_{11})^{2-}$. This anion has the same general structural features as $(Re_3Cl_{12})^{3-}$, but one terminal chlorine atom in the plane of the Re_3 triangle is missing and there is an accompanying shortening (to 2.435 A) of the two Re–Re bonds involving the deficient rhenium atom. The remaining Re–Re bond has a length of 2.483 A. There is evidence that a water molecule is associated with the deficient rhenium atom. In each of the two crystallographically independent tetraphenylarsonium cations, S_4 symmetry is destroyed by varying degrees of rotation of the phenyl rings. The anions are effectively shielded by the bulky cations.

Introduction

The solution of the crystal structure of $Cs_3Re_3Cl_{12}$[1,2] established that the structure of the $(Re_3Cl_{12})^{3-}$ anion is based on a tightly bound triangular group of rhenium atoms. This structural feature has since been shown[3-6] to be common to all known tervalent rhenium species of the general formula $(Re_3X_{9+n})^{n-}$ where X is Cl or Br. Following our structure analysis of $Cs_3Re_3Cl_{12}$ we directed our attention to the compound $[(C_6H_5)_4As]_2Re_3Cl_{11}$ reported by Fergusson,[7] who had predicted a polymeric structure for the anion on the basis of its composition. Preliminary results of our crystal structure analysis of this compound insofar as the anion is concerned have already been reported.[8] We now present a full account of this analysis following a complete refinement. The results are of structural interest both for the anion and the cations.

Experimental Section

The crystals used were prepared[7] by adding tetraphenylarsonium chloride to a solution of rhenium trichloride in ethyl alcohol saturated with hydrogen chloride.

Crystal Data.—$[(C_6H_5)_4As]_2Re_3Cl_{11}$, formula weight 1714, triclinic, space group $P\bar{1}$ (suggested by the Patterson function and confirmed by the structure analysis), $a = 12.01$ A, $b = 26.22$ A, $c = 9.87$ A, $\alpha = 88.5°$, $\beta = 66.2°$, $\gamma = 105.4°$ (assuming $\lambda = 1.5405$, 1.5443 A for Cu $K\alpha_1,\alpha_2$ radiation), $U = 2712$ A^3, $D_m = 1.95$ g cm^{-3} (by density balance), $Z = 2$, $D_x = 2.10$ g cm^{-3}, linear absorption coefficient = 189 cm^{-1} for Cu $K\alpha$ radiation.

Unit cell parameters were derived from reciprocal lattice parameters, five of which were obtained from two NaCl calibrated zero-level Weissenberg photographs and the sixth from precession photographs. Standard errors in the parameters for the direct unit cell are on the average 0.2% of the corresponding identity period and 0.3° for angles.

The single crystal specimen used for all X-ray data collection was roughly spherical with mean radius 0.06 mm. Reciprocal lattice levels ($hk0$–5) were recorded using the equiinclination Weissenberg method with Cu $K\alpha$ radiation and the relative intensities of 2575 independent reflections within these levels were measured by visual estimation. Nearly all of these were within the range $\sin\theta/\lambda < 0.4$. An additional 611 were recorded as unobserved. Preliminary correlation between levels was achieved using the intensities of ($0kl$), ($1kl$), and ($h0l$) reflections recorded on the Buerger precession camera using Mo $K\alpha$ radiation. Absorption corrections were made to the Weissenberg data only, assuming the crystal to be a sphere of radius 0.06 mm ($\mu R = 1.1$).

Structure Determination and Refinement

The starting point for the solution of the structure was the projection on (001) of the sharpened Patterson function. The fact that there were only six independent vector peaks of greatest height, with the next in order being approximately half this height, confirmed that the cell possessed a center of symmetry. The six most prominent peaks were thus of double weight and the three of these close to the origin, representing vectors between bonded atoms, indicated that there was indeed a Re_3 triangle which was reasonably well resolved in this projection. Single Re–Re vectors were located by trial and error, two of the three being incompletely resolved from double-weight vectors. Trial x and y coordinates for the three rhenium atoms were thus established.

Following a structure factor calculation based on the rhenium atoms alone, the two arsenic atoms were located from a difference electron density projection and all five atomic positions were adjusted following a second difference map. The Patterson projection on (100) was then examined, and it led to the assignment of z coordinates for the rhenium atoms. Thence a three-dimensional structure factor calculation for about 1000 low-order reflections followed by a difference map established the z coordinates of the arsenic atoms. Six subsequent difference cycles led to the location of eleven chlorine atoms and to the partial refinement of all 16 atoms considered so far. The R factor was 0.29 for all 2558 observed reflections being considered.

The positions and isotropic thermal parameters of the 16 heavy atoms and also several film scale factors were refined by one cycle of least squares using the

(1) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).
(2) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1166 (1963).
(3) F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1402 (1964).
(4) F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1094 (1964).
(5) M. Elder and B. R. Penfold, *Nature*, **205**, 276 (1965); *Inorg. Chem.*, **5**, 1763 (1966).
(6) F. A. Cotton and S. J. Lippard, *ibid.*, **4**, 59 (1965).
(7) J. E. Fergusson, Ph.D. Thesis, University of London, 1960.
(8) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

FORTRAN program ORFLS of Busing, Martin, and Levy.[9] A subsequent difference map enabled us to locate 30 of the 48 carbon atoms and a further full-matrix least-squares cycle was performed, R falling to 0.22. After this stage, because we no longer had access to an IBM 7090 computer, all subsequent least-squares refinement made use of the block diagonal approximation in a program written by Mair.[10] The weighting scheme chosen was such that $\sqrt{w} = kF_o/50$ for $kF_o < 50$, $\sqrt{w} = 50/kF_o$ for $kF_o > 50$.

All carbon atoms were eventually located from difference maps. In some cases, where resolution was poor, a choice between alternative positions had to be made on the basis of the known geometry of a phenyl ring. That all final assignments were satisfactory was confirmed by the fact that, during the course of seven least-squares cycles, the dimensions of the rings steadily improved, and, finally, all bond lengths and angles are, within estimated limits of error, those expected in phenyl rings.

During the refinement, all atoms were assigned individual isotropic thermal parameters. Those for carbon atoms were held constant but all others were allowed to vary. The parameters for the bridging chlorine atoms Cl(7), Cl(8), and Cl(9) were observed to be diverging. After the fourth cycle, these parameters were reduced to the average value of the eight remaining chlorine atoms and were then converted into sets of six anisotropic parameters which converged satisfactorily in subsequent cycles.

A complete list of atomic parameters is given in Table I. The equivalent isotropic thermal parameters listed for Cl(7,8,9) do not agree well, and those for Cl(7) and Cl(8) are unusually high. It is not surprising, however, that errors both in position and vibration amplitude should be highest for these bridging atoms, being, as they are, relatively light atoms each bonded to two very heavy atoms. Structure factors for observed reflections are listed in Table II. Atomic scattering factors[11] used were, for Re and As, from the Thomas–Fermi–Dirac statistical model with corrections for anomalous dispersion (the actual value being $f = \sqrt{\{(f_o + \Delta f')^2 + (\Delta f'')^2\}}$) and for C and Cl from the self-consistent field model.

From preliminary structure factor calculations it was clear that intensity estimates of a number of the strongest reflections were seriously low. Empirical corrections for these reflections (72 in all) were calculated in the following manner. From F_c, values for calculated intensities I_c prior to Lorentz-polarization corrections were derived. Corrections to the original measurements were then made as a linear function of I_c. These reflections were not included in the refinement process, nor were they used in the evaluation of the electron density difference maps. For all 2503

(9) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-squares Program," Oak Ridge National Laboratory, 1962.

(10) G. A. Mair, "Structure Factor and Least Squares Programs for the IBM 1620," Pure Chemistry Division, N.R.C., Ottawa, 1963.

(11) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

TABLE I

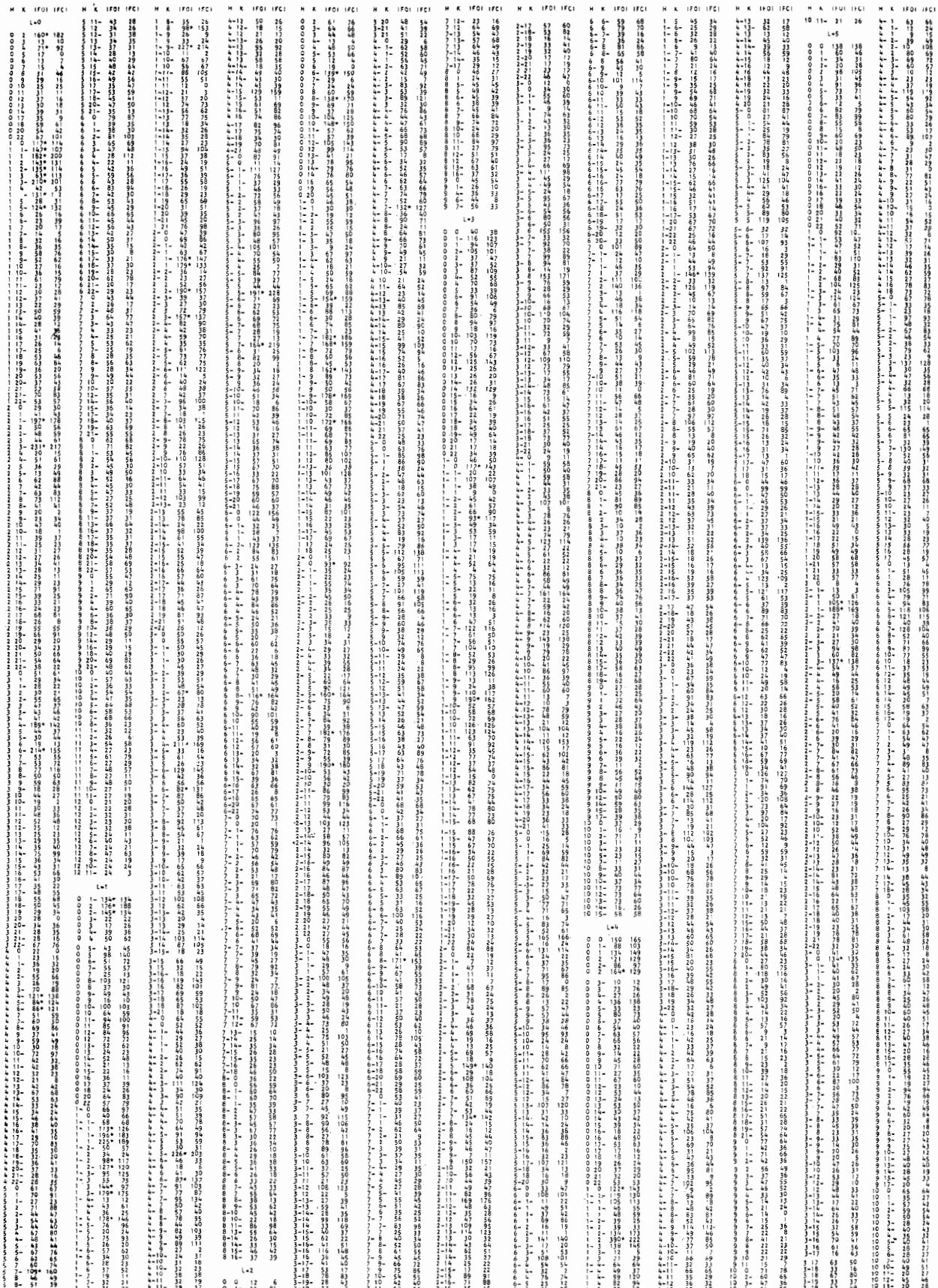
ATOMIC PARAMETERS FOR $[(C_6H_5)_4As]_2Re_3Cl_{11}$

	x	y	z	B, A^2	
Re(1)	0.6007	0.2036	0.4976	1.87	
Re(2)	0.7327	0.2979	0.4605	2.21	
Re(3)	0.6125	0.2463	0.7100	2.12	
Cl(1)	0.759	0.1609	0.457	4.2	
Cl(2)	0.418	0.2132	0.502	4.0	
Cl(3)	0.926	0.2836	0.404	2.5	
Cl(4)	0.585	0.3370	0.453	3.0	
Cl(5)	0.765	0.2192	0.744	3.0	
Cl(6)	0.435	0.2764	0.793	3.7	
Cl(7)	0.712	0.2612	0.252	7.6	
Cl(8)	0.732	0.3318	0.689	6.6	
Cl(9)	0.489	0.1614	0.740	3.6	
Cl(10)	0.524	0.1232	0.378	4.2	
Cl(11)	0.880	0.3863	0.295	4.6	
		Cation 1			
As(1)	0.3237	0.4252	−0.0903	2.5	
C(1)[a]	0.35	0.385	0.05		
C(2)	0.50	0.399	0.01		
C(3)	0.49	0.362	0.13		Ring 1
C(4)	0.41	0.326	0.22		
C(5)	0.29	0.309	0.26		
C(6)	0.25	0.346	0.17		
C(7)[a]	0.24	0.478	0.03		
C(8)	0.21	0.468	0.20		
C(9)	0.15	0.520	0.24		Ring 2
C(10)	0.13	0.552	0.13		
C(11)	0.15	0.538	0.00		
C(12)	0.20	0.497	−0.05		
C(13)[a]	0.22	0.372	−0.18		
C(14)	0.07	0.367	−0.09		
C(15)	0.02	0.332	−0.16		Ring 3
C(16)	0.06	0.305	−0.30		
C(17)	0.18	0.332	−0.37		
C(18)	0.26	0.354	−0.29		
C(19)[a]	0.48	0.472	−0.26		
C(20)	0.55	0.436	−0.34		
C(21)	0.67	0.467	−0.46		Ring 4
C(22)	0.72	0.530	−0.50		
C(23)	0.61	0.560	−0.42		
C(24)	0.51	0.529	−0.28		
		Cation 2			
As(2)	0.0064	0.0796	−0.2913	2.0	
C(25)[a]	−0.17	0.038	−0.27		
C(26)	−0.21	0.007	−0.12		
C(27)	−0.35	−0.035	−0.06		Ring 5
C(28)	−0.41	−0.014	−0.20		
C(29)	−0.33	0.014	−0.34		
C(30)	−0.20	0.049	−0.39		
C(31)[a]	0.10	0.032	−0.27		
C(32)	0.25	0.072	−0.33		
C(33)	0.30	0.039	−0.33		Ring 6
C(34)	0.26	−0.036	−0.26		
C(35)	0.11	−0.076	−0.20		
C(36)	0.04	−0.024	−0.27		
C(37)[a]	−0.01	0.134	−0.17		
C(38)	−0.13	0.127	−0.06		
C(39)	−0.12	0.166	0.02		Ring 7
C(40)	−0.01	0.196	0.04		
C(41)	0.13	0.204	−0.12		
C(42)	0.09	0.164	−0.15		
C(43)[a]	0.08	0.122	−0.49		
C(44)	0.18	0.095	−0.58		
C(45)	0.24	0.137	−0.75		Ring 8
C(46)	0.18	0.165	−0.80		
C(47)	0.11	0.179	−0.68		
C(48)	0.03	0.154	−0.52		
"O"	0.54	0.239	0.98		

[a] Carbon atom bonded to an arsenic atom.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]



[a] There is a scale factor of 0.5, making $F(000) = 806$. An asterisk indicates a F_o value after empirical correction.

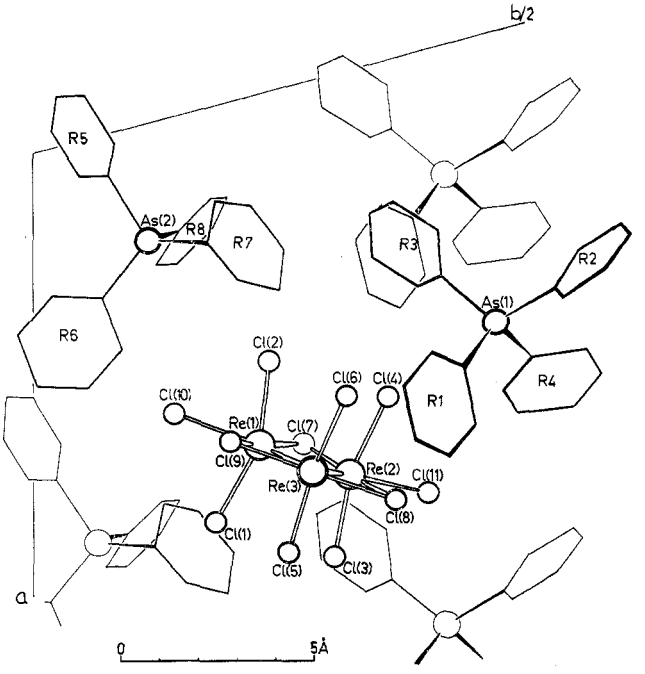


Figure 1.—The crystal structure of $[(C_6H_5)_4As]_2Re_3Cl_{11}$ viewed perpendicular to (001) showing the environment of the anion. Equivalent cations containing As(2) are related by the cell translation a–c, and those containing As(1) are related by translations a and c, respectively. The shapes of phenyl rings are somewhat idealized. The water molecule, which is not shown, would lie almost directly above Re(3).

remaining observed reflections, $R = 0.18$, this relatively high value reflecting the quality of the photographic data as a whole.

After all carbon positions had been assigned, the only significant peaks which remained in subsequent difference maps were, first, those associated directly with the very heavy rhenium atoms and, second, a pair of peaks close to the position where the missing terminal chlorine atom would have been. The placing of an oxygen atom on the larger of these two peaks eliminated the peak entirely. The possibility of the existence of a water molecule in this position is considered in detail below.

Discussion

The crystal structure consists of discrete $(Re_3Cl_{11})^{2-}$ anions well separated from each other by the bulky $(C_6H_5)_4As^+$ cations. A view of the structure, projected on (001), is shown in Figure 1.

The $(Re_3Cl_{11})^{2-}$ Anion.—The anion is based on the same framework as exists in $(Re_3Cl_{12})^{3-}$,[1,2] Re_3Cl_9,[3] and $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$.[4] This framework consists of a triangle of bonded rhenium atoms bridged in the plane of the triangle by three chlorine atoms and with an additional pair of chlorine atoms projecting above and below this plane attached to each rhenium. In the case of $(Re_3Cl_{11})^{2-}$, two of the three rhenium atoms are each bonded to another chlorine atom in the plane of the Re_3 triangle. A drawing of the anion to illustrate these points is shown in Figure 2, and bond lengths and angles, with their estimated standard deviations, are listed in Table III. (The standard deviations are as given directly by the least-squares refinement. These values are confirmed as being realistic estimates by an examination of the internal consistency within sets of chemically equivalent bond lengths and angles.) Mean values are given in Table IV with those of $(Re_3Cl_{12})^{3-}$ and $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$ for comparison. Although no symmetry is required of the anion by the space group, it does have effective symmetry C_{2v} within limits of error, there being a plane of symmetry containing the Re_3 triangle and the bridging chlorine atoms and another containing atoms Re(3) and Cl(5,6,7). Two other groups of atoms, Re-

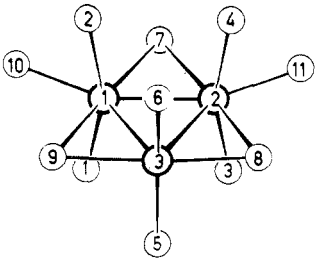


Figure 2.—An idealized drawing of the $(Re_3Cl_{11})^{2-}$ anion. Thick circles represent Re and thin circles Cl atoms. Atom numbering as in Table I.

TABLE III
INTERATOMIC DISTANCES AND BOND ANGLES IN THE $(Re_3Cl_{11})^{2-}$ ION, WITH THEIR STANDARD DEVIATIONS[a]

Bond	Length, A	σ, A	Angle	Value, deg	σ, deg
Re(1)–Re(2)	2.483	0.007	Re(1)Re(2)Re(3)	59.5	0.25
Re(2)–Re(3)	2.431	0.009	Re(2)Re(3)Re(1)	61.3	0.25
Re(3)–Re(1)	2.438	0.007	Re(3)Re(1)Re(2)	59.2	0.25
Re(1)–Cl(7)	2.47	0.06	Cl(1)Re(1)Cl(10)	79.1	0.9
Re(2)–Cl(7)	2.37	0.05	Cl(2)Re(1)Cl(10)	77.2	1.0
Re(2)–Cl(8)	2.45	0.05	Cl(1)Re(1)Cl(9)	91.3	1.5
Re(3)–Cl(8)	2.27	0.05	Cl(1)Re(1)Cl(7)	95.6	1.5
Re(3)–Cl(9)	2.26	0.06	Cl(2)Re(1)Cl(9)	88.9	1.6
Re(1)–Cl(9)	2.29	0.06	Cl(2)Re(1)Cl(7)	87.1	1.6
Re(1)–Cl(1)	2.36	0.03	Cl(9)Re(1)Re(3)	57.1	1.0
Re(1)–Cl(2)	2.26	0.03	Cl(7)Re(1)Re(2)	57.2	0.9
Re(1)–Cl(10)	2.58	0.03	Cl(7)Re(1)Cl(10)	90.8	1.2
Re(2)–Cl(3)	2.30	0.03	Cl(9)Re(1)Cl(10)	96.0	1.3
Re(2)–Cl(4)	2.29	0.03	Cl(3)Re(2)Cl(11)	80.7	1.0
Re(2)–Cl(11)	2.55	0.06	Cl(4)Re(2)Cl(11)	79.7	1.1
Re(3)–Cl(5)	2.27	0.03	Cl(3)Re(2)Cl(7)	93.7	1.5
Re(3)–Cl(6)	2.31	0.04	Cl(3)Re(2)Cl(8)	90.5	1.5
			Cl(4)Re(2)Cl(7)	83.2	1.3
Cl(1)---Cl(10)	3.15		Cl(4)Re(2)Cl(8)	93.9	1.3
Cl(2)---Cl(10)	3.03		Cl(7)Re(2)Re(1)	61.1	1.3
Cl(3)---Cl(11)	3.14		Cl(8)Re(2)Re(3)	55.6	1.3
Cl(4)---Cl(11)	3.10		Cl(7)Re(2)Cl(11)	90.8	1.5
Cl(1)---Cl(3)	3.21		Cl(8)Re(2)Cl(11)	93.2	1.5
Cl(1)---Cl(5)	3.27		Cl(5)Re(3)Cl(6)	152.5	1.2
Cl(3)---Cl(5)	3.25		Cl(8)Re(3)Cl(9)	177.9	2.0
Cl(2)---Cl(4)	3.24		Cl(5)Re(3)Cl(9)	92.8	1.3
Cl(2)---Cl(6)	3.41		Cl(5)Re(3)Cl(8)	87.5	1.4
Cl(4)---Cl(6)	3.22		Cl(6)Re(3)Cl(8)	87.9	1.6
			Cl(6)Re(3)Cl(9)	90.9	1.5
			Cl(8)Re(3)Re(2)	62.6	1.3
			Cl(9)Re(3)Re(1)	58.1	1.2
			Re(1)Cl(7)Re(2)	61.7	1.1
			Re(2)Cl(8)Re(3)	61.8	0.9
			Re(1)Cl(9)Re(3)	64.8	1.4

[a] Standard deviations are as given directly by the least-squares refinement. Internal consistency of chemically equivalent bonds indicates that these are realistic values.

(1), Cl(1,2,8,10) and Re(2), Cl(3,4,9,11), are planar within limits of error.

The most striking dimensional feature of the anion, when compared with the two other complexes in Table IV, is the inequality of the Re–Re bonds. Re(1)–Re(2) is the same length as the three equal bonds of the other complexes, but Re(1)–Re(3) and Re(2)–Re(3), the two bonds involving the chlorine-deficient rhenium atom, are significantly (6σ) shorter. Similar bond shortening has been observed in the $(Re_3Br_{11})^{2-}$ anion,[5] and its significance in terms of bonding has been discussed.[12] Differences among the three types of Re–Cl bond parallel those observed in $(Re_3Cl_{12})^{3-}$ and $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$, but the differences in absolute magnitudes among the three species cannot be considered significant in view of the large uncertainties in chlorine positions.

TABLE IV

MEAN DISTANCES, IN A, AND ANGLES, IN DEGREES, IN $(Re_3Cl_{11})^{2-}$ COMPARED WITH THOSE OF $(Re_3Cl_{12})^{3-}$ AND $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$[a,b]

	$(Re_3Cl_{11})^{2-}$	$(Re_3Cl_{12})^{3-}$	$Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$
Re–Re	2.483 (0.008) 2.435[c]	2.48 (0.01)	2.49 (0.004)
Re–Cl_b	2.35 (0.03)	2.39 (0.03)	2.38 (0.02)
Re–Cl_t	2.30 (0.02) 2.29[c] (0.04)	2.36 (0.03)	2.31 (0.02)
Re–$Cl_{t'}$	2.56 (0.04)	2.52	
Cl_t---$Cl_{t'}$	3.10	3.09	
Cl_t---Cl_b	3.29	3.37	3.32
Cl_t---Cl_t	3.25	3.28	3.24
$ReCl_bRe$	63	62	63
Cl_tReCl_t	158, 153[c]	158	159

[a] Cl_b = bridging chlorine; Cl_t = terminal off-plane chlorine; $Cl_{t'}$ = terminal in-plane chlorine. [b] Figures in parentheses are standard deviations. [c] Dimension associated with the chlorine-deficient rhenium atom.

The Evidence for a Water Molecule.—In order to establish whether the larger of the two residual electron density peaks in the neighborhood of Re(3) could be the oxygen of a water molecule, the environment of this peak was analyzed. It lies in the plane of the Re_3 triangle on a line which bisects both the angles Cl(5)-Re(3)Cl(6) and Cl(8)Re(3)Cl(9), *i.e.*, in a position corresponding to the two terminal in-plane chlorine atoms. Its closest neighbors are Re(3) at 2.4 A and Cl(5) and Cl(6), both at 2.9 A, all these distances having a standard deviation of about 0.1 A. The Cl(5)"O"-Cl(6) angle is 100°. The nearest carbon atom is 3.6 A away.

The distance of 2.4 A agrees, within limits of error, with the value of 2.32 A found for the Re–H_2O bond in $[ReBr_4O(H_2O)]^-$ by Cotton and Lippard,[13] but it is significantly longer than 1.72 A, the value found for the Re–O bond in the same structure. There would appear to be two possibilities. (1) A water molecule is hydrogen bonded to Cl(5) and Cl(6), has its lone pairs directed away from Re(3), and therefore makes a close nonbonded approach to Re(3). (2) There is a weak electrostatic bond between Re(3) and the water molecule *via* the two lone pairs of the oxygen atom. The hydrogen atoms would then not be directed so as to form O–H---Cl hydrogen bonds. Infrared spectral evidence[14] for the existence of a water molecule is negative but inconclusive. The weight of the crystallographic evidence is in favor of a water molecule being present, and this would be in line with the finding of Robinson and Fergusson[15] that neutral ligands such as triphenylphosphine may be attached to $(Re_3Cl_{11})^{2-}$ anions.

The $(C_6H_5)_4As^+$ Cations.—The mean standard deviations in C–C bond lengths and C–C–C bond angles are 0.18 A and 8°, respectively, and we have therefore established no more than the general orientation of each phenyl ring. Individual values range from 1.10 to 1.97 A for bond lengths and from 91 to 145° for angles and are not worth listing in detail. The eight individual As–C bonds range in length from 1.84 to 2.05 A, and the mean value is 1.97 A (σ = 0.05 A). This may be compared with the values of 1.95 A found by Mooney[16] in $(C_6H_5)_4AsI$, 1.97 A found by Hedberg, Hughes, and Waser[17] in $(C_6H_5As)_6$, and 1.90 A found in both $[(C_6H_5)_4As]ReBr_4O(CH_3CN)]$ by Cotton and Lippard[18] and in an azapentadienide salt by Palenik.[19] The twelve C–As–C angles range in magnitude from 100 to 118°, the mean value being the expected 109° (σ = 2°).

It is of interest to examine the general symmetry of the cations as entities. The tetraphenylarsonium ion possesses approximate D_{2d} symmetry in $(C_6H_5)_4AsI$[16] with the planes of each of the four phenyl rings being perpendicular to a mirror plane of the tetrahedral grouping C_4As. For $[(C_6H_5)_4As]FeCl_4$, however, Zaslow and Rundle[20] found the most probable symmetry to be S_4, each phenyl ring being rotated about the appropriate As–C bond by a constant amount (28°) relative to D_{2d} symmetry. In $[(C_6H_5)_4AsReBr_4O(CH_3CN)]$[17] the cation symmetry is further reduced because of unequal rotation of the phenyl rings, which is also apparently the case in the azapentadienide salt of Palenik.[19]

We have carried out an analysis of the symmetry of each of the two independent cations in $[(C_6H_5)_4As]_2Re_3Cl_{11}$ along the same lines as that described by Cotton and Lippard.[17] Because of the large uncertainties associated with the angles between planes of carbon atoms the results are not of quantitative significance, but it is clear from a qualitative study of the results, as also from a model of the crystal structure,

(12) J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965).
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that the cations depart significantly from S_4 symmetry. Zaslow and Rundle[20] had commented that the versatility of form of the tetraphenylarsonium cation helps to account for its effectiveness as a precipitating agent. Our results serve to reinforce this statement and help to explain the effectiveness of this large cation in precipitating trinuclear halogeno anions of Re(III) which have fewer than 12 halogen atoms.[15]

Ionic Packing.—The anions are well shielded from one another by the bulky cations as can be seen from Figure 1 and there are no interionic Cl---Cl contacts within 4.5 A. The closest Cl---C contacts made by individual chlorine atoms range from 3.2 A for Cl(10) to 3.8 A for Cl(7), which, considering the large errors in carbon positions, are reasonable van der Waals distances.

Acknowledgment.—We wish to thank Dr. J. E. Fergusson for supplying a sample of the compound and for many helpful discussions. Most of the computations were performed on the IBM 1620 of the Mobil Computer Laboratory, University of Canterbury, using, in part, programs from the Institute for Cancer Research, Philadelphia, Pa., and from the Pure Chemistry Division, National Research Council, Ottawa, Canada. This work was supported financially by the New Zealand University Grants Committee, which also awarded a Research Fellowship to W. T. R.

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The Crystal Structure of Bis(cesium) Tri-μ-bromo-octabromotrirhenate(III), $Cs_2Re_3Br_{11}$

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Received February 7, 1966

A three-dimensional crystal structure analysis of the compound of composition $Cs_2Re_3Br_{11}$ establishes that it contains the trinuclear anion $(Re_3Br_{11})^{2-}$ which possesses the same general structural features as other rhenium(III) species of the general formula $(Re_3X_{9+n})^{n-}$ where X is Br or Cl. As with the $(Re_3Cl_{11})^{2-}$ anion, Re–Re bond lengths are unequal, those involving the deficient Re atom being 2.43 A and the remaining Re–Re bond 2.49 A. A new feature is that the bonds which the deficient Re atom makes to its off-plane bromine atoms are greatly shortened to 2.38 A and are bent toward one another to make an angle of 133°.

Introduction

The existence of trinuclear Re(III) bromide species analogous to the chloride compounds already known[1-4] was first reported by Fergusson and Robinson[5] and independently by Cotton and Lippard.[6] The preparative and spectral properties of some of these compounds have been discussed by Robinson and Fergusson[7] and by Cotton, Lippard, and Mague.[8] It is as a part of our systematic studies of the structures of trinuclear Re(III) species that we have determined in detail the crystal structure of $Cs_2Re_3Br_{11}$, a preliminary account of which has already been given.[9] The crystal structure of one other compound containing the neutral Re_3Br_9 species has been reported by Cotton and Lippard.[10]

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Experimental Section

Small black needle-shaped crystals were prepared following the method of Fergusson and Robinson.[5] The crystals were completely stable in air.

Crystal Data.—$Cs_2Re_3Br_{11}$, formula weight 1704, orthorhombic, space group Pnma from systematic absences of X-ray reflections; $a = 9.53 \pm 0.01$ A, $b = 16.114 \pm 0.007$ A, $c = 13.744 \pm 0.007$ A ($\lambda = 1.5405$, 1.5443 for Cu $K\alpha_1,\alpha_2$ radiation), $U = 2109.5$ A^3, $D_x = 5.38$ g cm^{-3}, $Z = 4$, symmetry of anion C_s (=m). Linear absorption coefficients are 865 cm^{-1} for Cu $K\alpha$ and 459 cm^{-1} for Mo $K\alpha$ radiation.

Reciprocal lattice levels (0–6kl) were recorded by the equi-inclination Weissenberg method using Cu $K\alpha$ radiation, and levels (hk0–1), ($h0l$), and (hkk–$hk(k + 4)$) were recorded on the Buerger precession camera using Mo $K\alpha$ radiation. Intensities were estimated visually by comparison with a suitably calibrated scale. The Weissenberg data totalled 1713 independent reflections of which 323 were recorded as unobserved and given an estimated intensity one-third of the minimum observable intensity. These Weissenberg data were used for the structure refinement, supplemented by 178 precession reflections with $h > 6$, of which 30 were recorded as unobserved. The two crystals used were each mounted on a glass fiber and showed no signs of deterioration after prolonged exposure to the atmosphere and to X radiation. They were of a very similar size, needles of length about 0.5 mm and rectangular cross section 0.095 mm × 0.070 mm. Corrections for absorption were applied assuming a cylindrical crystal of radius 0.04 mm ($\mu R = 3.5$) for the Weissenberg data and assuming a spherical crystal of the same radius ($\mu R = 1.8$) for the precession data.