

Preparation of Oxopentachlororhenate(VI) and Oxotetrachlororhenate(V). The Crystal and Molecular Structure of $\text{AsPh}_4\text{ReOCl}_4$

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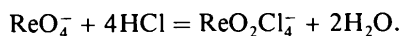
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From a suspension of $\text{AsPh}_4\text{ReO}_4$ or PPh_4ReO_4 in various solutions such as ethanol, methanol, acetone, chloroform, water, benzene, formic acid and others, the red compounds containing oxopentachlororhenate(VI) anions were obtained on reaction with gaseous HCl. $\text{AsPh}_4\text{ReOCl}_5$ and $\text{PPh}_4\text{ReOCl}_5$ crystallize in the space group $P4/n$, with similar axial lengths. From solutions of these complexes in ethanol the yellow complexes $\text{AsPh}_4\text{ReOCl}_4$ or $\text{PPh}_4\text{ReOCl}_4$ could be obtained. The crystal structure of $\text{AsPh}_4\text{ReOCl}_4$ has been determined by single-crystal diffractometry. The structure was solved by the heavy-atom technique and refined by the block-diagonal least-squares method to an $R = 0.059$ for 1134 reflexions. In the square-pyramidal $[\text{ReOCl}_4]^-$ anion the Re and O atoms lie on a fourfold axis, with Re–O and Re–Cl 1.63 (3) and 2.344 (4) Å respectively. The AsPh_4^+ cation has $\bar{4}$ (S_4) crystallographic symmetry, with As–C 1.91 (1) Å and two independent C–As–C angles of 107.2 (5) and 110.6 (5)°. [Crystal data for $\text{AsPh}_4\text{ReOCl}_4$: space group $P4/n$, $a = 13.117$ (6), $c = 7.358$ (4) Å.]

Introduction

The dissolution of perrhenate ions (ReO_4^-) in concentrated hydrochloric acid saturated with hydrogen chloride produced a yellow solution which turned brown-red with increase in HCl concentration. This reaction was studied for the first time by Jeźowska-Trzebiatowska (1951) and described as:



Grove, Johnson & Wilkinson (1969) reported the precipitation of a pale-yellow solid of stoichiometry $\text{Cs}_2(\text{ReO}_3\text{Cl}_3)$ from similar solutions. Sergiyenko, Porai-Koshits, Khodashova, Babeshkina & Butman (1975) have obtained another complex compound of formula bpyReO_3Cl , and have determined its crystal structure. A similar oxo-compound of formula $\text{phenReO}_3\text{Cl}$ was recently obtained by us and its crystal structure will be published. Moreover, Yatirajam & Singh (1975) reported that by the action of hydrogen chloride on perrhenate in acetic acid the oxo-complexes of rhenium(VI) could be obtained as the reduction products. Therefore, we decided to reinvestigate the interaction of HCl with ReO_4^- ions. This paper is the first of this series.

Experimental

The PPh_4ReO_4 and $\text{AsPh}_4\text{ReO}_4$ salts were obtained from the reaction between NH_4ReO_4 and phosphonium or arsonium chloride.

The $\text{AsPh}_4\text{ReO}_4$ or PPh_4ReO_4 salts were suspended in different liquids: acetone, ethanol, methanol,

chloroform, carbon tetrachloride, water, acetic or formic acid, and a slow stream of dry hydrogen chloride was bubbled through. The initial yellow colour of the solutions changed to dark red. After some time, red crystals were precipitated from the solutions as tetragonal needles. The crystals were removed by filtration. Both (arsonium and phosphonium) red complexes were quite stable if obtained from acetone or chloroform mixtures. The crystals were identical with those obtained by Brisdon & Edwards (1968) and Yatirajam & Singh (1975). Weissenberg photographs showed systematic absences for $hk0$ reflexions for $h + k = 2n + 1$, uniquely indicating the $P4/n$ space group. Preliminary X-ray analysis showed that the two compounds are isomorphous. In the ReOCl_5^- anions the Re, O and Cl (*trans* to O) atoms lie on a fourfold axis. The AsPh_4^+ and PPh_4^+ cations have $\bar{4}$ crystallographic symmetry. The structure was solved to $R = 0.051$ and $R = 0.084$ for the phosphonium and arsonium salts respectively. The detailed data will be reported later.

If the rhenium(VI) red oxo-complexes so obtained were stood in an ethanol reaction mixture in air for a few days, yellow crystals crystallized as tetragonal needles for the phosphonium salt and as tetragonal plates for the arsonium salt. Both compounds crystallize in the same $P4/n$ space group but are not isomorphous. The crystal data are summarized in Table 1.

A crystal of $\text{AsPh}_4\text{ReOCl}_4$ of approximate size $0.11 \times 0.08 \times 0.06$ mm was selected. It was mounted on a Syntex $P2_1$ automatic four-circle diffractometer and intensity data to $\theta = 73^\circ$ were measured. $\text{Cu } K\alpha$ radiation with a graphite monochromator was used. The intensities of reflexions were measured by the $2\theta-\omega$ scan technique. After each group of 40 reflexions the inten-

sity of a standard reflexion was measured and no significant change in intensity was observed. 1278 independent reflexions were measured, of which 144 were judged to be 'unobserved' as the net count of each was less than $1.96\sigma(I)$. Reflexion intensities were corrected for Lorentz and polarization effects but not for absorption or extinction.

Structure determination and refinement

All calculations were performed with the Syntex *XTL* structure determination system (NOVA 1200 computer and additional external disc memory). Neutral-atom scattering factors used were those listed in *International Tables for X-ray Crystallography* (1974).

A three-dimensional Patterson synthesis gave a straightforward solution for the Re and As positions, and least-squares refinement gave $R = 0.25$. Refinement with all other non-hydrogen atoms reduced R to 0.078. A few cycles of anisotropic refinement of all non-H atoms then gave $R = 0.061$. Five H atoms were placed in geometrically calculated positions with a distance of 1.0 Å. Further refinement reduced R to 0.056. A final three-dimensional difference synthesis was

essentially flat. The final atomic coordinates, temperature factors and their estimated standard deviations are listed in Table 2.*

Description of the structure and discussion

The crystals of the investigated compound are composed of $(\text{Ph}_4\text{As})^+$ cations and $[\text{ReOCl}_4]^-$ complex anions. The more important interatomic distances and bond angles in the two ions are listed in Table 3.

Both the Re and O atoms lie on fourfold rotation axes, and the square-pyramidal coordination about the metal is completed by four Cl atoms which constitute the base of the pyramid. The complex anion therefore possesses $4mm$ (C_{4v}) symmetry. The Re atom is not located in the Cl plane perpendicular to the fourfold axis of the anion but on the axis 0.407 Å distant from the Cl plane on the side toward the O atom.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32221 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Crystal data*

	$\text{AsPh}_4\text{ReOCl}_4$	$\text{PPh}_4\text{ReOCl}_4$	$\text{AsPh}_4\text{ReOCl}_5$	$\text{PPh}_4\text{ReOCl}_5$
a (Å)	13.117 (6)	12.702 (3)	13.210 (6)	13.116 (9)
c (Å)	7.358 (4)	7.707 (1)	7.411 (3)	7.412 (4)
V (Å ³)	1266.0	1243.5	1293.2	1275.1
M_r	727.4	683.4	762.8	718.8
D_c (g cm ⁻³)	1.91	1.83	1.96	1.87
D_o (g cm ⁻³)	1.92		1.96	1.86
μ (cm ⁻¹)	147.2	139.3	153.8	145.7
(Cu $K\alpha$, $\lambda = 1.5418$ Å)				

Table 2. *The final atom parameters with standard deviations in parentheses*

Coordinates are in terms of an alternative unit cell in space group $P4/n$ with origin on $\bar{1}$ at $\frac{1}{4}, \frac{3}{4}, 0$ from $\bar{4}$. The hydrogen atom positions are unrefined, and these atoms have the same numbers as the parent carbon atoms (all $B = 4.5$ Å²). Anisotropic temperature factors are expressed as $\exp[-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	$\frac{1}{4}$	$\frac{1}{4}$	0.1965 (2)	3.21 (3)	3.21	2.43 (4)	0	0	0
O	$\frac{1}{4}$	$\frac{3}{4}$	0.4177 (32)	5.5 (8)	5.5	4.9 (12)	0	0	0
Cl	0.1901 (3)	0.0845 (3)	0.1412 (6)	4.8 (2)	3.0 (2)	4.6 (2)	-0.8 (2)	0.0 (2)	-0.7 (2)
As	$\frac{1}{4}$	$\frac{3}{4}$	0	2.50 (6)	2.50	3.09 (11)	0	0	0
C(1)	0.1413 (9)	0.7060 (9)	0.1540 (14)	2.0 (5)	2.9 (6)	1.8 (5)	-0.1 (4)	0.2 (4)	0.3 (4)
C(2)	0.1057 (11)	0.7755 (11)	0.2853 (20)	3.8 (7)	3.2 (6)	3.8 (7)	0.2 (5)	0.0 (6)	-0.6 (6)
C(3)	0.0289 (11)	0.7457 (12)	0.3994 (19)	3.8 (7)	4.7 (8)	2.6 (6)	0.9 (6)	1.0 (6)	0.1 (6)
C(4)	-0.0102 (11)	0.6488 (12)	0.3892 (19)	3.0 (6)	5.1 (8)	2.6 (6)	0.2 (6)	0.2 (5)	0.7 (6)
C(5)	0.0250 (11)	0.5809 (12)	0.2700 (21)	3.2 (6)	3.8 (7)	4.6 (7)	-0.9 (5)	0.0 (6)	1.1 (6)
C(6)	0.1024 (10)	0.6093 (11)	0.1453 (17)	3.2 (6)	3.5 (6)	2.4 (6)	0.3 (5)	-0.1 (5)	0.1 (5)
	x	y	z		x	y	z		
H(2)	0.1365	0.8467	0.2919		H(5)	-0.0049	0.5095	0.2665	
H(3)	0.0007	0.7948	0.4948		H(6)	0.1286	0.5593	0.0512	
H(4)	-0.0670	0.6269	0.4761						

Table 3. *Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses*

$[\text{ReOCl}_4]^-$ anion			
Re—O	1.627 (24)	Re—Cl	2.344 (4)
O—Re—Cl	100.0 (5)		
$(\text{Ph}_4\text{As})^+$ cation			
As—C(1)	1.910 (11)	C(4)—C(5)	1.333 (21)
C(1)—C(2)	1.408 (18)	C(5)—C(6)	1.419 (19)
C(2)—C(3)	1.369 (20)	C(6)—C(1)	1.368 (18)
C(3)—C(4)	1.373 (21)	Mean C—C	1.378
C(1)—As—C(1)	107.2 (5) (×2)	C(1)—As—C(1)	110.6 (5) (×4)
As—C(1)—C(2)	117.3 (9)	As—C(1)—C(6)	122.0 (9)
C(2)—C(1)—C(6)	120.6 (12)	C(1)—C(2)—C(3)	118.7 (13)
C(2)—C(3)—C(4)	120.4 (14)	C(3)—C(4)—C(5)	121.7 (14)
C(4)—C(5)—C(6)	119.8 (14)	C(5)—C(6)—C(1)	118.7 (12)

Reports of crystal structures of five-coordinate compounds of Re are restricted to ReOCl_4 (Edwards, 1972), $\text{ReNCl}_2(\text{PPh}_3)_2$ (Doedens & Ibers, 1967) and $\text{ReN}(\text{dtc})_2$ (Fletcher, Rowbottom, Skapski & Wilkinson, 1970). Comparison of the bond and angle values in the oxotetrachlororhenate(V) ion $[\text{ReOCl}_4]^-$ and rhenium(VI) oxide tetrachloride $[\text{ReOCl}_4]$ is informative. As may be seen (Table 4), the Re—O distances are similar. This is reflected in the IR spectra: the Re—O stretching frequency was found at 1033 cm^{-1} (Brisdon & Edwards, 1968) and at 1040 cm^{-1} (Guest & Lock, 1971) in ReOCl_4 and at 1067 cm^{-1} in $\text{AsPh}_4\text{ReOCl}_4$ (this work). However, the difference of 0.08 Å in the Re—Cl bonding lengths and of 5° in the O—Re—Cl bonding angles is definitely significant. Molecular-orbital analysis of ReOCl_4 by Al-Mowali & Porte (1975) showed that the unpaired electron is in the antibonding orbital. The extra electron in ReOCl_4^- probably goes into the same antibonding orbital, which is a mixture of Re and Cl orbitals, and hence the Re—Cl bond lengths increase.

The Re—O triple bond of 1.63 Å in the investigated compound may be compared with 1.67 Å found in the ReOCl_5^{2-} anion (Głowiak & Jeżowska-Trzebiatowska, 1976), (see Table 4). The longer Re—O distance (by 0.04 Å) in K_2ReOCl_5 gives rise to an IR absorption at a lower frequency, 989 cm^{-1} (Jeżowska-Trzebiatowska Hanuza & Bałuka, 1971), than we observed, 1067 cm^{-1} , for $\text{AsPh}_4\text{ReOCl}_4$. The Re—Cl distances in the ReOCl_4^- ions are 0.05 Å shorter than the average of equivalent distances in ReOCl_5^{2-} ions. These differences are consistent with a shortening of bonds on going from six to five coordination. A very similar situation was found for a pair of OsNCl_4^- and OsNCl_5^{2-} ions by Phillips & Skapski (1975b).

In the $(\text{AsPh}_4)^+$ cation the As atom lies on a fourfold rotation-inversion axis, and the As—C distances of

Table 4. *Comparison of bond distances (Å) and angles (°) in $[\text{ReOCl}_4]^-$ with those in ReOCl_4 and $[\text{ReOCl}_5]^{2-}$*

	O—Re	Cl—Re	O—Re—Cl	Reference
$[\text{ReOCl}_4]^-$	1.63	2.34	100.0	This paper
ReOCl_4	1.63	2.26	105.0	Edwards (1972)
$[\text{ReOCl}_5]^{2-}$	1.67	2.39	95.5	Głowiak & Jeżowska-Trzebiatowska (1976)

$1.91(1)\text{ Å}$ are not exceptional. Its tetrahedral geometry is a little distorted with four C—As—C angles of 110.6° and two of 107.2° . A least-squares calculation showed that the phenyl ring is quite planar. The As atom lies 0.05 Å out of these phenyl-ring planes. The structure of the $(\text{AsPh}_4)^+$ cation is quite similar to those observed in $\text{Ph}_4\text{AsOsNCl}_4$ (Phillips & Skapski, 1975a) and in $\text{Ph}_4\text{AsAuCl}_4$ (Jones, Guy & Sheldrick, 1975).

References

- AL-MOWALI, A. H. & PORTE, A. L. (1975). *J. Chem. Soc. Dalton*, pp. 50–55.
- BRISDON, B. J. & EDWARDS, D. A. (1968). *Inorg. Chem.* **7**, 1898–1903.
- DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 204–210.
- EDWARDS, A. J. (1972). *J. Chem. Soc. Dalton*, pp. 582–584.
- FLETCHER, S. R., ROWBOTTOM, J. F., SKAPSKI, A. C. & WILKINSON, G. (1970). *Chem. Commun.* pp. 1572–1573.
- GŁOWIAK, T. & JEŻOWSKA-TRZEBIATOWSKA, B. (1976). Unpublished.
- GROVE, D. E., JOHNSON, N. P. & WILKINSON, G. (1969). *Inorg. Chem.* **8**, 1196.
- GUEST, A. & LOCK, C. J. L. (1971). *Canad. J. Chem.* **49**, 603–610.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JEŻOWSKA-TRZEBIATOWSKA, B. (1951). *Trav. Soc. Sci. Wrocław, Ser. B*, No. 36, pp. 1–51.
- JEŻOWSKA-TRZEBIATOWSKA, B., HANUZA, J. & BAŁUKA, M. (1971). *Spectrochim. Acta*, **27A**, 1753–1772.
- JONES, P. G., GUY, J. J. & SHELDRIK, G. M. (1975). *Acta Cryst.* **B31**, 2687–2688.
- PHILLIPS, F. L. & SKAPSKI, A. C. (1975a). *J. Cryst. Mol. Struct.* **5**, 83–92.
- PHILLIPS, F. L. & SKAPSKI, A. C. (1975b). *Acta Cryst.* **B31**, 2667–2670.
- SERGIYENKO, W. S., PORAI-KOSHITS, KHODASHOVA, T. S., BABESHKINA, G. K. & BUTMAN, L. A. (1975). *Koord. Khim.* **1**, 1282–1283.
- YATIRAJAM, V. & SINGH, H. (1975). *J. Inorg. Nucl. Chem.* **37**, 2006–2008.