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Structure of Cesium *fac*-Trichlorotrioxorhenate(VII), $Cs_2[ReCl_3O_3]$

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Abstract. $M_r = 606{\cdot}4$, orthorhombic, *Pnam*, $a = 10{\cdot}499\,(9)$, $b = 12{\cdot}57\,(1)$, $c = 7{\cdot}000\,(6)$ Å, $V = 923{\cdot}8$ Å^3, $Z = 4$, $D_x = 4{\cdot}36$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 22{\cdot}6$ mm^{-1}, $F(000) = 1040$, $T = 296\,(2)$ K. Final $R = 0{\cdot}066$ for 1378 non-zero reflexions. The $[ReCl_3O_3]^{2-}$ anion has crystallographic point symmetry m (C_s) but approximates closely to $3m$ (C_{3v}) symmetry. The average bond lengths and bond angles are: Re—Cl 2·50 (1), Re—O 1·70 (2) Å, Cl—Re—Cl 81·5 (3), O—Re—O 103·1 (9)°.

Introduction. The dissolution of ReO_4^- ions in concentrated hydrochloric acid saturated with hydrogen chloride produced at first a yellow solution which turned brown-red with increase in HCl concentration. When tetraphenylphosphonium (or arsonium) chloride is added to the red solution the oxopentachlororhenate(VI) salts are precipitated (Yatirajam & Singh, 1975; Lis & Jeżowska-Trzebiatowska, 1977). From the yellow solution the $[ReCl_3O_3]^{2-}$ ion was obtained as the cesium salt by Grove, Johnson & Wilkinson (1969) and Jeżowska-Trzebiatowska, Hanuza & Bałuka (1971). Later, it was reported that other yellow complexes may be isolated depending on HCl concentration, complexing agent used, and the kind of cation. The detailed X-ray data were given for $Re(bpy)ClO_3$ (Sergiyenko, Khodashova, Porai-Koshits & Butman, 1977) and $(H_2phen)[ReCl_2(H_2O)O_3]Cl$ (Lis, 1979). The X-ray analysis showed the *fac*-trioxo structure which had been suggested on the basis of theoretical considerations and IR spectra. In this paper the crystal structure of $Cs_2[ReCl_3O_3]$ is presented.

Experimental. Preparation described by Grove *et al.* (1969) gave crystals too small for X-ray studies, therefore a new method of preparation was employed: the equimolar mixture of $CsReO_4$ and CsCl in concentrated HCl was left in a desiccator over P_2O_5. After some weeks yellow well formed crystals appeared. They were extremely unstable in air giving a yellow crystalline powder. Density not measured. Weissenberg photographs showed space group to be *Pnam* or $Pna2_1$. Specimen ~0·35 × 0·40 × 0·45 mm cut from a large crystal and sealed in a capillary. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation. Lattice parameters from 15 reflexions in 2θ range 15–30°. 2θ–ω scan technique. After each group of 40 reflexions intensities of two standard reflexions measured, no significant change observed. 2308 intensities (*hkl* to 16,20,11) measured below $2\theta = 70°$. Empirical absorption corrections made from φ-scan data. Re atoms found from Patterson synthesis and centrosymmetric (*Pnam*) space group assumed; all other atoms from difference syntheses. Full-matrix least-squares refinement on F of all anisotropic thermal parameters and a scale factor. $R = 0{\cdot}066$, $R_w = 0{\cdot}085$ for 1378 reflexions with $I > 2\sigma(I)$. Ratio of max. LS shift to error no greater than 0·00. On final difference synthesis two highest peaks 2·4 and 2·0 e Å^{-3} around Re atom, two further peaks 1·5 and 1·8 e Å^{-3} around Cs(2). No correction for secondary extinction. All calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for all atoms.

Discussion. Final atomic parameters are in Table 1 and principal bond distances and angles in Table 2.* The structure is built up from complex $[ReCl_3O_3]^{2-}$ anions and Cs^+ cations. Since the Re atoms are situated on a mirror plane the anions as a whole also possess m (C_s) symmetry. However, the anions approximate closely to $3m$ (C_{3v}) symmetry as is shown by the interatomic distances and bond angles (Table 2). The C_{3v} symmetry

Table 1. *Final atom coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	y	z	B_{eq}(Å^2)
Re	0·1865 (2)	0·0669 (1)	$\frac{1}{4}$	1·15
Cs(1)	0·1554 (3)	0·4107 (2)	$\frac{1}{4}$	2·43
Cs(2)	0·4667 (2)	0·6820 (2)	$\frac{1}{4}$	1·61
Cl(1)	0·3768 (8)	−0·0548 (6)	$\frac{1}{4}$	2·31
Cl(2)	0·3214 (6)	0·1678 (5)	0·0193 (8)	2·42
O(1)	0·0874 (22)	0·1737 (17)	$\frac{1}{4}$	2·7
O(2)	0·1352 (16)	−0·0068 (13)	0·0607 (24)	2·9

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38557 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Bond lengths* (Å) *and bond angles* (°) *in the title compound*

Atoms marked with a prime are related to those at *x*,*y*,*z* by a mirror plane at *x*,*y*,$\frac{1}{4}$.

Re–O(1)	1·698 (21)	Re–O(2)	1·704 (17)
Re–Cl(1)	2·517 (8)	Re–Cl(2)	2·494 (5)
O(1)–Re–O(2)	103·7 (9)	O(2)–Re–O(2′)	102·1 (8)
Cl(1)–Re–Cl(2)	81·9 (2)	Cl(2)–Re–Cl(2′)	80·7 (2)
O(1)–Re–Cl(1)	165·2 (7)	O(1)–Re–Cl(2)	86·9 (7)
O(2)–Re–Cl(1)	85·4 (6)	O(2)–Re–Cl(2)	87·3 (6)
O(2)–Re–Cl(2′)	163·6 (6)		

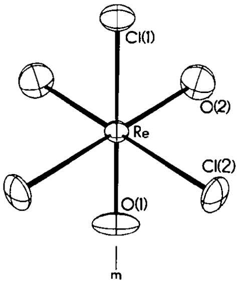

Fig. 1. The $[ReCl_3O_3]^{2-}$ anion viewed along the idealized threefold axis.

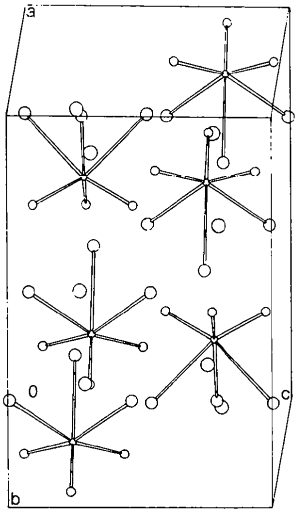

Fig. 2. The packing of the crystal.

is also visualized in Fig. 1 which shows an *ORTEP* (Johnson, 1976) projection along the idealized threefold axis.

The Re–O distances [average value 1·70 (2) Å] are similar to those found in Re(bpy)ClO_3 (Sergiyenko *et al.*, 1977) and in (H_2phen)[$ReCl_2(H_2O)O_3$]Cl (Lis, 1979). Also the Re–Cl bond lengths [average value 2·50 (1) Å] are similar. In the *fac*-trioxo compound the Re–Cl distances are determined by the presence of oxygen in *trans* positions. This is the so-called structural *trans* effect, already observed in complexes with 'short' *M*–O bonds. This effect results in an increase of 0·1–0·25 Å in the Re–Cl distances compared to other complexes of Re^{III}–Re^{VI}. This effect for *fac*-trioxo complexes was discussed by Sergiyenko *et al.* (1977).

Both different Cs^+ cations lie on the mirror plane and have different environments. Cs(1) has six neighbors at 3·25–3·55 Å, and Cs(2) has nine neighbors at 3·12–3·57 Å, which form rather irregular shapes. The packing of the crystal is shown in Fig. 2.

An attempt to obtain other salts of six-coordinated Re^{VII} complexes with simple cations such as Rb^+, K^+ and others gave no result.

References

GROVE, D. E., JOHNSON, N. P. & WILKINSON, G. (1969). *Inorg. Chem.* **8**, 1196.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JEŻOWSKA-TRZEBIATOWSKA, B., HANUZA, J. & BAŁUKA, M. (1971). *Spectrochim. Acta Part A*, **27**, 1753–1772.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

LIS, T. (1979). *Acta Cryst.* **B35**, 1230–1232.

LIS, T. & JEŻOWSKA-TRZEBIATOWSKA, B. (1977). *Acta Cryst.* **B33**, 1248–1250.

SERGIYENKO, W. S., KHODASHOVA, T. S., PORAI-KOSHITS, M. A. & BUTMAN, L. A. (1977). *Koord. Khim.* **3**, 1060–1068.

Syntex (1976). *XTL/XTLE Structure Determination System.* Cupertino: Syntex Analytical Instruments.

YATIRAJAM, V. & SINGH, H. (1975). *J. Inorg. Nucl. Chem.* **37**, 2006–2008.