Acta Cryst. (1987). C**43**, 1710–1711

Structure of Chlorotrioxo(1,10-phenanthroline)rhenium(VII)

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(*Received* 9 *June* 1986; *accepted* 27 *April* 1987)

Abstract. [$ReClO_3(C_{12}H_8N_2)$], $M_r = 449{\cdot}9$, monoclinic, $C2/m$, $a = 16{\cdot}676\,(9)$, $b = 11{\cdot}570\,(6)$, $c = 7{\cdot}563\,(5)$ Å, $\beta = 123{\cdot}33\,(4)°$, $V = 1219$ Å^3, $Z = 4$, $D_m = 2{\cdot}44$, $D_x = 2{\cdot}45$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = $10{\cdot}77$ mm^{-1}, $F(000) = 840$, $T = 295\,(2)$ K. Final $R = 0{\cdot}049$ for 1389 non-zero reflexions. The structure consists of discrete partially disordered molecules. In the approximately octahedral molecules, which have crystallographic point symmetry m (C_s), three O atoms are *fac*.

Introduction. X-ray investigations in the last two decades have indicated that heptavalent rhenium, in addition to the most important perrhenate ions, is capable of forming more complicated oxo complexes with coordination numbers six and five (Weber, Dehnicke, Müller & Fenske, 1984; Johnson, Brody, Ansell & Zentz, 1984, and references therein). Some of these oxo compounds are relatively stable. As was reported earlier (Lis, 1979), in the reactions of the ReO_4^- ions with 1,10-phenanthroline in hydrochloric acid, two kinds of yellow crystals may be obtained (in which Re atoms have octahedral environments) depending on the HCl concentration. In this paper the full structure of the second of them, $ReClO_3$(phen), is presented.

Experimental. Irregularly shaped yellow crystals of the title compound were obtained as reported earlier (Lis, 1979). They are quite stable in air. D_m measured by flotation in 1,2-dibromoethane/$CHBr_3$. Preliminary examination by rotation and Weissenberg photographs showed space group to be $C2/m$, Cm or $C2$. A crystal ~$0{\cdot}25 \times 0{\cdot}15 \times 0{\cdot}05$ mm was selected. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflexions in range $13 < 2\theta < 21°$) and intensity measurements; 2θ–ω scan technique. 2834 reflexions measured below $2\theta = 55°$ (h 0→21, k −15→15, l −9→8); after every 50 reflexions three standards measured, variation 3%. Most calculations performed on a NOVA 1200 computer with locally modified *XTL/XTLE* programs (Syntex, 1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for all non-H atoms. Re atoms found from Patterson synthesis and centrosymmetric ($C2/m$) space group assumed by analogy to Re(bpy)ClO_3 crystals (Sergiyenko, Khodashova, Porai-Koshits & Butman, 1977); all other non-H atoms from difference synthesis; H atoms placed in calculated positions [d(C—H) = 1·0 Å]. An absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) applied on isotropically refined data; min. and max. absorption corrections 0·680 and 1·387; the symmetry-related reflexions were averaged after *DIFABS*; $R_{\rm int} = [\sum w(F - \langle F \rangle)^2/\sum wF^2]^{1/2} = 0{\cdot}025$. Full-matrix refinement based on F (Re, Cl, O, N and C anisotropic) for 1389 reflexions with $I \geq 1{\cdot}96\sigma(I)$, $w = 1/\sigma^2(F_o)$, gave $R = 0{\cdot}065$ and $wR = 0{\cdot}052$. A difference synthesis computed at this stage contained one peak 0·6 Å from an Re atom (similar to the peak density for O atoms on the earlier difference map), indicating the possibility of partial disorder of the Re atom. This peak was replaced by the second Re atom and the structure was again refined with 90% and 10% occupancy factors for both Re atoms. Further refinement reduced R to 0·049 and wR to 0·041; max. Δ/σ 0·01. On final difference synthesis two highest peaks 1·8 e Å^{-3} were near Re and Re$^{\rm i}$ atoms; smaller peaks were around other atoms.

The final atomic parameters are listed in Table 1.*

Discussion. The crystal structure is composed of isolated partially disordered molecules located on mirror planes. The atom-numbering scheme of the molecule with higher occupancy factor is shown in Fig. 1 and the principal interatomic distances and angles are given in Table 2. The atoms which surround the Re atom are at the apices of a distorted octahedron and the three O atoms are *fac*, as in all d^0 trioxo complexes. Because of the disorder the molecular parameters are not as precise as might otherwise be expected and the interatomic distances and bond angles are probably subject to more uncertainty than indicated by the standard deviations.

The shift from Re to Re$^{\rm i}$ (0·48 Å) is essentially a shift away from O(1) and towards Cl (Table 2). Other

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44007 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/091710-02$01.50

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

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

	x	y	z	B_{eq}/B_{iso}(Å^2)
Re*	0·15749 (5)	0	0·2351 (2)	2·17 (4)
Re^{i}*	0·1777 (5)	0	0·3107 (11)	1·89 (14)
Cl	0·2829 (3)	0	0·6222 (5)	2·95 (21)
O(1)	0·1104 (6)	0	−0·0381 (12)	2·1 (6)
O(2)	0·1080 (5)	0·1193 (5)	0·2735 (11)	3·6 (5)
N	0·2733 (5)	0·1154 (5)	0·2583 (11)	2·2 (5)
C(1)	0·2752 (7)	0·2295 (7)	0·2762 (14)	2·7 (7)
C(2)	0·3428 (7)	0·2955 (7)	0·2662 (15)	2·9 (6)
C(3)	0·4094 (7)	0·2440 (8)	0·2406 (16)	2·9 (6)
C(4)	0·4108 (6)	0·1224 (7)	0·2288 (14)	2·6 (6)
C(5)	0·3405 (6)	0·0615 (6)	0·2409 (13)	2·2 (6)
C(6)	0·4793 (6)	0·0579 (8)	0·2144 (15)	3·0 (7)
H(1)	0·228	0·269	0·299	5
H(2)	0·342	0·382	0·276	5
H(3)	0·457	0·291	0·230	5
H(6)	0·528	0·101	0·203	5

* The occupancy factors of Re and Re^{i} are 90% and 10% respectively.

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*, 0, *z*.

[Re—Re^{i}	0·48 (1)]		
Re—Cl	2·494 (3)	[Re^{i}—Cl	2·02 (1)]
Re—O(1)	1·761 (7)	[Re^{i}—O(1)	2·23 (1)]
Re—O(2)	1·714 (7)	[Re^{i}—O(2)	1·73 (1)]
Re—N	2·274 (8)	[Re^{i}—N	2·27 (2)]
N—C(1)	1·326 (9)	N—C(5)	1·350 (13)
C(1)—C(2)	1·398 (16)	C(2)—C(3)	1·364 (17)
C(3)—C(4)	1·412 (12)	C(4)—C(5)	1·413 (14)
C(4)—C(6)	1·418 (15)	C(5)—C(5′)	1·422 (10)
C(6)—C(6′)	1·341 (12)		
Cl—Re—O(1)	157·4 (3)	Cl—Re—O(2)	88·4 (3)
Cl—Re—N	77·3 (2)	O(1)—Re—O(2)	104·7 (4)
O(1)—Re—N	84·5 (3)	O(2)—Re—N	89·0 (3)
O(2)—Re—O(2′)	107·3 (4)	O(2)—Re—N′	158·1 (3)
N—Re—N′	71·9 (3)	Re—N—C(1)	124·3 (6)
Re—N—C(5)	115·9 (6)	C(1)—N—C(5)	119·7 (8)
N—C(1)—C(2)	120·9 (9)	C(1)—C(2)—C(3)	120·9 (10)
C(2)—C(3)—C(4)	119·1 (10)	C(3)—C(4)—C(5)	116·8 (9)
C(3)—C(4)—C(6)	124·8 (9)	C(5)—C(4)—C(6)	118·4 (9)
N—C(5)—C(4)	122·6 (8)	N—C(5)—C(5′)	117·5 (8)
C(4)—C(5)—C(5′)	119·9 (8)	C(4)—C(6)—C(6′)	121·7 (9)

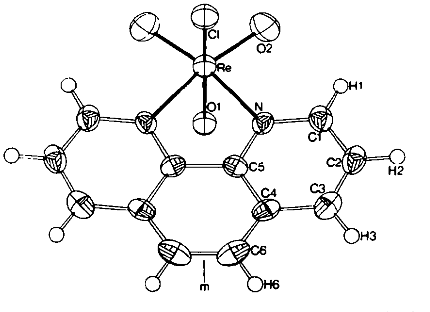

Fig. 1. Molecular structure of $ReClO_3$(phen). Unlabelled atoms are related to labelled atoms by the mirror plane. The Re^{i} atom is omitted for clarity.

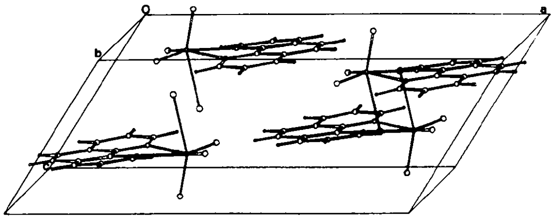

Fig. 2. Crystal packing of the molecules with higher occupancy factor.

Re–ligand and Re^{i}–ligand distances remain more or less the same. In fact, the Re^{i}—O(1) distance is similar to the Re—Cl distance and *vice versa*. It might thus be suggested that the molecule is disordered by 'reflexion' in the plane O(2), N, O(2′) and N′. Alternatively, it could be said that the molecule occupies two alternative sites, in which the positions of these four atoms are more or less constant. {It is to be noted that a similar kind of disorder was found in (H_2phen)[$ReCl_2$(H_2O)O_3]Cl crystals (Lis, 1979)}. In such a kind of disorder the carbon atoms from phenanthroline ligands for both sites also have similar positions and the Re and Re^{i} atoms are displaced from the plane of 1,10-phenanthroline by a similar distance [0·35 (1) and 0·13 (1) Å] but in opposite directions.

The observed disorder may also be interpreted as the result of specific packing of the crystal. (The packing is shown in Fig. 2.) The almost planar parts of the molecules are parallel to the (001) plane and the Re—O(1) and Re—Cl bonds are perpendicular to this plane. There are no unusually short distances between non-bonded atoms and the molecules are held together by van der Waals forces only. The replacement of the Re—Cl group by an Re—O(1) group (with very similar positions of all other atoms) probably gives in this case only a very small energetic effect.

All the Re–ligand distances are similar to these found in other *fac*-trioxorhenate(VII) complexes (Sergiyenko *et al.*, 1977; Lis, 1983). The molecular dimensions of the bidentate phenanthroline group are acceptable and similar to those found in other complexes of this ligand (Weakley, 1978).

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