1,10-Phenanthrolinium Aquadichlorotrioxorhenate(VII) Chloride, (H2phen)[ReCl2(H2O)O3]Cl

By T. Lis

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Joliot-Curie 14, Poland

Abstract. $[C_{12}H_{10}N_2]^{2+}.[ReCl_2(H_2O)O_3]^-.Cl^-$, triclinic, $P\bar{1}$, $a = 7.703$ (5), $b = 8.961$ (7), $c = 15.281$ (20) Å, $\alpha = 115.02$ (5), $\beta = 98.82$ (5), $\gamma = 115.62$ (5)°, $M_r = 540.8$, $V = 785.5$ Å^3, $Z = 2$, $D_m = 2.2$, $D_x = 2.29$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71069$ Å) = 8.71 mm^{-1}. The structure consists of discrete diprotonated phenanthrolinium cations, Cl$^-$ anions and partially disordered [ReCl$_2$(H$_2$O)O$_3$]$^-$ anions. In the octahedral complex anions the multiply bonded O atoms are *cis*. The structure was refined to an R of 0.047 for 1323 diffractometer data.

Introduction. In the course of our study of the interactions of hydrogen chloride with perrhenate ions we have recently obtained a new octahedral complex of Re^{VII} with 1,10-phenanthroline: ReClO$_3$(phen) (Lis & Jeżowska-Trzebiatowska, 1977). The irregularly shaped yellow crystals of this compound were quite stable in air; preliminary X-ray data have shown that they crystallize in the same space group (and with similar cell parameters) as do crystals of Re(bpy)ClO$_3$ (Sergiyenko, Khodashova, Porai-Koshits & Butman, 1977), suggesting isomorphism of these compounds. If crystals of ReClO$_3$(phen) in concentrated HCl were left in a desiccator over P$_2$O$_5$ for some weeks, red or yellow platy crystals precipitated. The study of these yellow crystals, rather unstable in air, is reported in this work. The X-ray analysis has shown that this compound has the formula (H$_2$phen)[ReCl$_2$(H$_2$O)O$_3$]Cl.

An irregularly shaped crystal (approximately 0.12 to 0.20 mm on edge) was chosen and coated with paraffin oil to prevent crystal decomposition, since it was observed that decomposition occurs if the material is submitted to prolonged exposure to the atmosphere. Weissenberg photographs showed that the crystals are triclinic. A Syntex $P2_1$ diffractometer and Mo $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities of the reflexions were measured by the 2θ–ω scan technique. After each group of 40 reflexions, the intensities of two standard reflexions were measured; no significant change in intensities was observed. The data were corrected for Lorentz and polarization effects. No absorption corrections were made because of the irregular shape of the crystal. Of 1626 reflexions in the range $6.0 \le 2\theta \le 42°$, 1323 with $I > 1.96\sigma(I)$ were used for the structure determination. All calculations were performed with the Syntex *XTL* structure-determination system (Nova 1200 computer and additional external disc memory). Neutral-atom scatter-

Table 1. *Final positional parameters with standard deviations in parentheses*

Positional parameters are given as fractions of cell edges ($\times 10^4$). The H-atom positions ($\times 10^3$) are unrefined.

	x	y	z
*Re	310 (9)	894 (15)	2580 (4)
*Re(i)	176 (21)	404 (53)	2769 (35)
Cl(1)	2343 (7)	−672 (7)	2217 (4)
Cl(2)	−379 (9)	−642 (8)	3602 (4)
Cl(3)	3186 (7)	−4847 (7)	964 (4)
O(1)	335 (18)	933 (19)	1423 (10)
O(2)	2476 (19)	3007 (17)	3653 (11)
O(3)	−1837 (20)	972 (21)	2678 (10)
H$_2$O	−2316 (19)	−2433 (22)	1309 (9)
N(1)	2917 (20)	−3610 (18)	3125 (10)
N(10)	−939 (19)	−6074 (19)	1247 (10)
C(2)	4753 (28)	−2542 (26)	3975 (14)
C(3)	4687 (28)	−1954 (26)	4970 (14)
C(4)	2829 (27)	−2481 (25)	5042 (14)
C(5)	−1081 (27)	−4224 (25)	4212 (14)
C(6)	−2824 (27)	−5383 (25)	3352 (14)
C(7)	−4719 (27)	−7248 (26)	1412 (14)
C(8)	−4657 (28)	−7832 (27)	461 (14)
C(9)	−2693 (27)	−7231 (25)	382 (13)
C(11)	−917 (23)	−5407 (21)	2266 (12)
C(12)	−2867 (24)	−6016 (23)	2350 (13)
C(13)	897 (25)	−3619 (23)	4168 (12)
C(14)	965 (23)	−4255 (21)	3153 (12)
H(1)	295	−399	240
H(10)	47	−562	119
H(2)	611	−218	389
H(3)	604	−115	564
H(4)	282	−201	578
H(5)	−114	−374	494
H(6)	−424	−585	342
H(7)	−616	−771	146
H(8)	−603	−872	−21
H(9)	−263	−769	−34

* The occupancy factors of Re and Re(i) are 0.81 (5) and 0.20 (5) respectively.

ing factors used are those listed in *International Tables for X-ray Crystallography* (1974).

The heavy-atom method was employed for phase determination. The Re—Re vectors were identified in a three-dimensional Patterson function. A three-dimensional electron-density map calculated with signs based on the Re structure showed the positions of the Cl atoms. Difference Fourier syntheses, after preliminary refinement of the heavy atoms, showed the positions of all remaining non-H atoms. Full-matrix least-squares refinement with isotropic thermal parameters reduced R to 0·09. A difference synthesis computed at this stage contained one peak 0·6 Å from a Re atom (similar to the peak density for Cl atoms on the earlier Fourier 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 varied occupancy factors for both Re atoms. Ten H atoms from the phenanthrolinium cation were placed in geometrically calculated positions (1·0 Å from the atoms to which they are attached). Further refinement with anisotropic temperature factors for Re, Cl, O and isotropic for N and C atoms reduced R to 0·047 and R_w to 0·046. A difference synthesis computed towards the end of the refinement was featureless and H atoms from the water molecule were not resolvable. The occupancy factors for the disordered Re atoms were 0·81 (5) and 0·20 (5) respectively. The final atomic coordinates and their estimated standard deviations are listed in Table 1.*
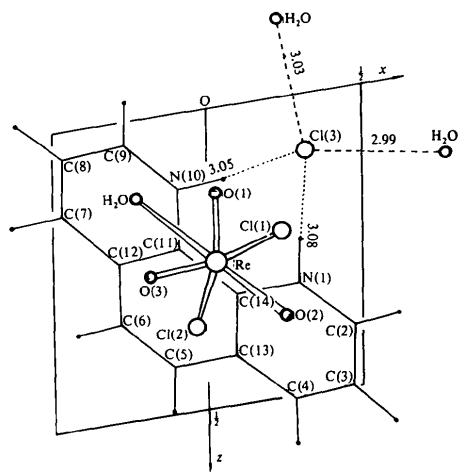
Fig. 1. The crystal structure of (H₂phen)[ReCl₂(H₂O)O₃]Cl: projection on the (010) plane.

Discussion. Crystals of (H₂phen)[ReCl₂(H₂O)O₃]Cl are composed of phenanthrolinium cations, complex [ReCl₂(H₂O)O₃]⁻ anions and Cl⁻ anions. The arrangement of the molecules in projection on the (010) plane is shown in Fig. 1. The more important interatomic distances and bond angles are listed in Table 2.

The ligands which surround the Re atom are at the apices of a distorted octahedron and the three oxo O atoms are *cis*, as expected. A similar *cis* arrangement of d^0 trioxo complexes has been found in all Mo^{VI} and Re^{VII} compounds which have been subjected to X-ray structural analysis. In Re^{VII} octahedral complexes with three oxo O atoms the C_{3v} configuration was suggested by Atovmyan & Porai-Koshits (1969), Grove, Johnson & Wilkinson (1969), Jeżowska-Trzebiatowska, Hanuza & Bałuka (1971), Gerlach & Ringel (1974) and Shustorovich, Porai-Koshits & Buslaev (1975), and C_{2v} symmetry by Kuhlmann & Sawodny (1977) on the basis of theoretical calculations, and spectroscopic and other data.

Since the [ReCl₂(H₂O)O₃]⁻ ions are partially disordered in the crystals under investigation, the interatomic distances and bond angles are probably subject to more uncertainty than indicated by the standard deviations. However, all interatomic distances, *i.e.* Re—Cl, Re—O, Re—H₂O, are similar to those found in compounds such as Re₂O₇.2H₂O (Beyer, Glemser &

Table 2. *Interatomic distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Re—Re(i)	0·60 (6)		
Re—Cl(1)	2·498 (11)	|Re(i)—Cl(1)|	2·36 (4)|
Re—Cl(2)	2·460 (12)	|Re(i)—Cl(2)|	1·87 (5)|
Re—O(1)	1·786 (16)	|Re(i)—O(1)|	2·31 (5)|
Re—O(2)	1·691 (16)	|Re(i)—O(2)|	1·85 (5)|
Re—O(3)	1·712 (19)	|Re(i)—O(3)|	1·83 (4)|
Re—H₂O	2·331 (18)	|Re(i)—H₂O|	2·19 (5)|
N(1)—C(2)	1·35 (3)	N(10)—C(9)	1·31 (3)
C(2)—C(3)	1·40 (3)	C(9)—C(8)	1·41 (4)
C(3)—C(4)	1·34 (4)	C(8)—C(7)	1·34 (3)
C(4)—C(13)	1·40 (3)	C(7)—C(12)	1·41 (3)
C(5)—C(13)	1·40 (4)	C(6)—C(12)	1·38 (3)
C(13)—C(14)	1·43 (3)	C(12)—C(11)	1·41 (3)
C(14)—N(1)	1·37 (3)	C(11)—N(10)	1·41 (2)
C(14)—C(11)	1·39 (3)	C(5)—C(6)	1·31 (3)
Cl(1)—Re—Cl(2)	80·4 (4)	Cl(1)—Re—O(1)	85·7 (7)
Cl(1)—Re—O(2)	90·8 (7)	Cl(1)—Re—O(3)	155·6 (8)
Cl(1)—Re—H₂O	76·8 (5)	Cl(2)—Re—O(1)	155·5 (8)
Cl(2)—Re—O(2)	90·9 (7)	Cl(2)—Re—O(3)	83·3 (7)
Cl(2)—Re—H₂O	75·7 (5)	O(1)—Re—O(2)	109·4 (9)
O(1)—Re—O(3)	102·6 (9)	O(1)—Re—H₂O	81·7 (8)
O(2)—Re—O(3)	107·5 (9)	O(2)—Re—H₂O	163·0 (9)
O(3)—Re—H₂O	81·7 (8)		
C(14)—N(1)—C(2)	124·9 (17)	C(11)—N(10)—C(9)	122·8 (17)
N(1)—C(2)—C(3)	117·8 (19)	N(10)—C(9)—C(8)	119·7 (19)
C(2)—C(3)—C(4)	119·4 (20)	C(9)—C(8)—C(7)	119·8 (21)
C(3)—C(4)—C(13)	123·7 (20)	C(8)—C(7)—C(12)	121·7 (20)
C(4)—C(13)—C(5)	125·2 (19)	C(7)—C(12)—C(6)	124·6 (19)
C(4)—C(13)—C(14)	116·7 (18)	C(7)—C(12)—C(11)	118·2 (18)
C(5)—C(13)—C(14)	118·1 (18)	C(6)—C(12)—C(11)	117·3 (18)
C(13)—C(5)—C(6)	121·4 (20)	C(12)—C(6)—C(5)	123·4 (20)
C(13)—C(14)—C(11)	118·5 (17)	C(12)—C(11)—C(14)	121·3 (17)
C(13)—C(14)—N(1)	117·3 (16)	C(12)—C(11)—N(10)	117·9 (16)
C(11)—C(14)—N(1)	124·2 (17)	C(14)—C(11)—N(10)	120·8 (16)

Krebs, 1968) and Re(bpy)ClO₃ (Sergiyenko, Khodashova, Porai-Koshits & Butman, 1977).

The shift from Re to Re(i) (0·60 Å) is essentially a shift away from O(1) and toward Cl(2). Other distances remain more or less the same. In fact, the Re(i)—Cl(2) distance is almost equal to the Re—O(1) distance, and vice versa. It might thus be suggested that the molecule is disordered by 'reflexion' in the plane of O(2), O(3), H₂O, and Cl(1). 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.

The phenanthrolinium cations have the normal structure. All interatomic distances and angles are similar to those found in $C_{12}H_8N_2.2HClO_4.H_2O$ (Thevenet, Rodier & Khodadad, 1978), where the phenanthroline groups also exist as diprotonated cations.

The packing of the Cl⁻ ions in the unit cell is shown in Fig. 1. The shortest contacts for Cl⁻ anions are with N(1) and N(10) [H(1) and H(10)] and two with H₂O molecules from two different complex anions. The values of these distances (2·99–3·08 Å) suggest that these are hydrogen bonds.

References

ATOVMYAN, L. O. & PORAI-KOSHITS, M. A. (1969). Zh. Strukt. Khim. 10, 853–858.

BEYER, H., GLEMSER, O. & KREBS, B. (1968). Angew. Chem. 80, 286–287.

GERLACH, U. & RINGEL, C. (1974). Z. Anorg. Allg. Chem. 408, 180–186.

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.

KUHLMANN, W. & SAWODNY, W. (1977). J. Fluorine Chem. 9, 341–357.

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.

SHUSTOROVICH, E. M., PORAI-KOSHITS, M. A. & BUSLAEV, YU. A. (1975). Coord. Chem. Rev. 17, 1–98.

THEVENET, G., RODIER, N. & KHODADAD, P. (1978). Acta Cryst. B34, 2594–2599.

Structure of Bis[μ-bis(salicylaldehyde)ethylenediimine]-dicobalt(III) Dichloride Chloroform Solvate*

BY B.-C. WANG,† BEN T. HUIE‡ AND WILLIAM P. SCHAEFER

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

Abstract. $[Co_2(C_{32}H_{28}N_4O_4)]^{2+}.2Cl^-.4CHCl_3$, FW 1198·89, Pbca, $a = 24.588$ (9), $b = 11.124$ (2), $c = 17.034$ (2) Å, $Z = 4$, $\rho_c = 1.71$, $\rho_o = 1.61$ Mg m⁻³, $F(000) = 2400$, $\lambda(Co\,K\alpha_1) = 1.78892$ Å, $\lambda(Co\,K\alpha_2) = 1.79278$ Å. The oxygen-carrying compound bis(salicylaldehyde)ethylenediiminecobalt(II) [Co(salen)] is oxidized by O₂ in chloroform solution to give a Co^III(salen) chloride dimer. Refinement by least squares of all 1845 data gave a final R index of 0·126. The dimers are formed across a center of symmetry by the Co atom coordinating to a salen O atom of the other half of the dimer. The Co—O bond is short [1·99 (1) Å] and the tricoordinated salen O atom causes the salen group to be slightly distorted.

Introduction. In the course of trying to obtain crystals of an oxygen adduct of bis(salicylaldehyde)ethylenediiminecobalt(II) [Co(salen)], we obtained brown crystals of a material which was inactive toward oxygen. An X-ray structural determination showed that the compound was an irreversibly oxidized Co(salen) dimer similar to those found for Co^II(salen) (DeIasi, Holt & Post, 1971), for Cu(salen) (Hall & Waters, 1960; Pachler & von Stackelberg, 1960) and for Fe(salen) chloride (Gerloch & Mabbs, 1967). It seemed useful to report our structure for comparison with these compounds, as well as to provide some bonding parameters for an unambiguous Co^III complex.

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