$z=0$, placés devant les faces latérales du prisme formé par les six premiers.

L'atome d'uranium $U_{(3a)}$ est heptacoordiné; il est entouré de deux atomes de soufre $[S'_{(3a)}$ et $S'_{(4a)}]$ de cote $z=-\frac{1}{2}$, de leurs homologues en $z=\frac{1}{2}$, et de trois autres atomes de soufre $[S_{(2a)}, S_{(5b)}, S_{(6a)}]$ situés dans le plan $z=0$, l'ensemble formant un polyèdre que l'on peut considérer comme dérivant de l'octaèdre par dédoublement de l'un des sommets (coordination 7-octaédrique), ou du prisme à bases triangulaires par addition d'un atome de soufre devant l'une des faces latérales (coordination 7-prismatique).

Les deux sites occupés par le scandium sont au centre d'octaèdres presque réguliers d'atomes non-métalliques.

Les atomes de soufre $S_{(1a)}$, $S_{(3a)}$, $S_{(4a)}$ et $S_{(6a)}$ sont pentacoordinés. Leur environnement comprend: deux sites métalliques dans le plan $z=-\frac{1}{2}$, leurs homologues dans le plan $z=\frac{1}{2}$, et un autre site métallique en $z=0$. Ces cinq sites réalisent une pyramide dont la base rectangulaire est parallèle à **c**.

L'atome de soufre $S_{(5a)}$ est également pentacoordiné, mais les atomes métalliques qui sont ses proches voisins réalisent un type de polyèdre nettement différent de celui qui vient d'être décrit. En effet, $S_{(5a)}$ est entouré de trois atomes d'uranium de cote $z=0$, d'un atome de scandium en $z=-\frac{1}{2}$ et de l'homologue de celui-ci en $z=\frac{1}{2}$.

$S_{(2a)}$ est à l'intérieur d'un tétraèdre irrégulier dont trois sommets sont occupés par l'uranium et le quatrième par le scandium.

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trans-Oxoaqua-*cis*-dichloro-*cis*-bis(thiourea)rhenium(V) Chloride, [ReO(H₂O)Cl₂tu₂]Cl

BY T. LIS

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

Abstract. $C_2H_{10}N_4O_2S_2Cl_3Re$, triclinic, $P\bar{1}$, $a=6\cdot344$ (5), $b=8\cdot785$ (6), $c=12\cdot838$ (8) Å, $\alpha=100\cdot16$ (5), $\beta=109\cdot55$ (5), $\gamma=105\cdot31$ (5)°, M.W. 478·8, $V=622\cdot1$ Å³, $Z=2$, $D_m=2\cdot5$, $D_x=2\cdot56$ g cm⁻³, μ(Cu $K\alpha$, $\lambda=1\cdot5418$ Å)$=273\cdot4$ cm⁻¹. The structure consists of discrete $[ReO(H_2O)Cl_2tu_2]^+$ cations and Cl^- anions. The mean bond lengths are Re–O 1·654 (10), Re–H₂O 2·23 (1), Re–S 2·35 (1), Re–Cl 2·40 (1) Å. The structure was refined to an R of 0·041 for 1573 diffractometer data.

Introduction. In the system Re^{VII}–HCl–Sn^{II}–$CS(NH_2)_2$ a number of Re^V thiourea complexes and at the same time a number of Re^{IV} thiourea complexes are formed depending on the $SnCl_2$ concentration (Ryabchikov & Lazarev, 1955; Ryabchikov, 1962; Evteev, 1964; Borisova, Gerlit, Spivakov & Kalinichenko, 1966; Borisova & Kariakin, 1967; Kotiegov, Fadeeva & Kukushkin, 1973; Borisova, 1969; Borisova, Plastinina & Ermakov, 1974). Many of these complexes are particularly interesting from the structural point of view, since it seems that coordination around the metal atoms can be determined from the X-ray data only. Very scarce structural data are available for $ReSn[CS(NH_2)_2]_4Cl_4 \cdot H_2O$ (Kuznetsov, Novitskaia, Koz'min & Borisova, 1973).

It is interesting to note that in the system Re^{VII}–HCl–thiourea a number of thiourea complexes of Re^V can also be obtained. From a mixture of $KReO_4$ and $CS(NH_2)_2$, in various volumes of concentrated HCl, the orange, green or blue (two kinds) compounds crystallized after few days. Kotiegov *et al.* (1974) have proposed the $(ReOCl_3tu_2) \cdot 2H_2O$ and $(ReOCl_3tu) \cdot H_2O$ formulae for blue complexes. The X-ray analysis reported in this paper has established that one of the blue complexes has the formula $[ReO(H_2O)Cl_2tu_2]Cl$. The crystal structure of the green compound with the formula $ReO(H_2O)Cl_3tu$ will be reported later.

The compound investigated was obtained by dissolving 0·1 g $KReO_4$ and 0·1 g $CS(NH_2)_2$ in 3 ml of concentrated HCl. On standing, well-formed blue needles were obtained. Weissenberg photographs showed that the crystals are triclinic. An irregularly shaped crystal of approximate size $0\cdot07 \times 0\cdot06 \times 0\cdot04$ mm was selected for the data collection. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with 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 15 reflexions the intensity of a standard reflexion was measured and no significant change in in-

Table 1. *The final atom parameters with standard deviations in parentheses*

Positional parameters are given as fractions of cell edges $\times 10^4$ ($\times 10^5$ for rhenium). Anisotropic temperature factors are expressed as $\exp\left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	19119 (11)	28939 (8)	25137 (5)	1·99 (3)	2·08 (3)	2·08 (3)	0·64 (2)	0·67 (2)	0·51 (2)
S(1)	3899 (7)	1763 (5)	1506 (3)	3·0 (2)	3·8 (2)	2·0 (2)	2·1 (2)	1·5 (2)	1·2 (2)
S(2)	3234 (6)	1777 (4)	4031 (3)	2·6 (2)	1·6 (2)	1·8 (2)	0·8 (2)	1·1 (2)	0·9 (2)
Cl(1)	1544 (7)	4891 (4)	1483 (3)	2·9 (2)	2·6 (2)	1·7 (2)	0·9 (2)	0·3 (2)	1·2 (2)
Cl(2)	954 (6)	4524 (4)	3884 (3)	2·2 (2)	2·2 (2)	2·0 (2)	1·0 (2)	0·9 (2)	0·2 (2)
Cl(3)	2075 (6)	2272 (4)	7139 (3)	2·3 (2)	2·3 (2)	3·4 (2)	0·6 (2)	1·5 (2)	1·4 (2)
O	−802 (15)	1517 (11)	1760 (8)	1·0 (4)	1·6 (4)	3·3 (5)	−0·4 (3)	0·1 (3)	−0·3 (4)
H₂O	5491 (16)	4857 (11)	3512 (8)	1·6 (4)	2·5 (4)	2·0 (4)	−0·2 (3)	0·3 (3)	0·9 (4)
C(1)	3476 (29)	2327 (19)	215 (14)	3·8 (8)	3·1 (7)	3·3 (8)	1·6 (6)	2·2 (7)	0·8 (6)
C(2)	4731 (23)	450 (17)	3708 (11)	1·9 (6)	2·4 (7)	1·6 (6)	1·0 (5)	0·5 (5)	0·9 (5)
N(1)	1276 (23)	1986 (18)	−573 (11)	2·5 (6)	4·5 (7)	2·4 (6)	0·5 (5)	0·1 (5)	0·2 (5)
N(2)	5329 (28)	3048 (25)	14 (15)	3·9 (8)	9·8 (13)	5·2 (9)	1·3 (8)	2·5 (7)	4·1 (9)
N(3)	7003 (21)	1030 (15)	3848 (12)	2·0 (6)	2·9 (6)	4·7 (7)	0·4 (5)	1·6 (5)	1·6 (5)
N(4)	3501 (21)	−1191 (14)	3345 (11)	2·2 (5)	1·8 (5)	3·4 (6)	0·6 (4)	0·6 (5)	0·8 (5)

tensity was observed. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. Of 1688 reflexions accessible below $2\theta = 115°$, 1573 with $I > 1·92\sigma(I)$ 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).

The heavy-atom method was employed for the 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 and S atoms. Difference Fourier syntheses, after preliminary refinements of the heavy atoms, showed the positions of all the remaining non-H atoms. Full-matrix least-squares refinement with isotropic thermal parameters reduced R from 0·10 to 0·060. Several cycles of full-matrix refinement with anisotropic thermal parameters yielded the final values $R = 0·041$ and $R_w = 0·050$, where $R = \sum ||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. A difference synthesis computed towards the end of the refinement contained the highest two peaks (around the Re atom) about $\frac{1}{4}$ the peak density for N atoms on earlier difference Fourier maps, but H atoms were not resolvable. Scattering factors for Re, Cl⁻, O, N and C atoms used were those listed in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for all atoms. The final atomic coordinates, temperature factors and their estimated standard deviations are listed in Table 1.*

Discussion. Crystals of [ReO(H₂O)Cl₂tu₂]Cl are composed of complex [ReO(H₂O)Cl₂tu₂]⁺ cations and Cl⁻ anions. The arrangement of the molecules in projection

* A list of structure factors has been deposited ·with the British Library Lending Division as Supplementary Publication No. SUP 31810 (32 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

on the (100) plane is shown in Fig. 1. The bond lengths and angles in the complex cation are given in Table 2. Table 3 gives details of various least-squares planes.

The ligands which surround the rhenium atom are at the apices of a distorted octahedron and the oxo O atom and water molecule are *trans* as had been ex-

Table 2. *Bond lengths (Å) and angles (°) in the [ReO(H₂O)Cl₂tu₂]⁺ cation*

Re—O	1·654 (10)	Re—H₂O	2·231 (10)
Re—S(1)	2·356 (5)	Re—S(2)	2·340 (4)
Re—Cl(1)	2·390 (4)	Re—Cl(2)	2·408 (4)
S(1)–C(1)	1·768 (17)	S(2)–C(2)	1·764 (16)
C(1)–N(1)	1·337 (23)	C(2)–N(3)	1·333 (21)
C(1)–N(2)	1·311 (28)	C(2)–N(4)	1·352 (19)
O——Re——H₂O	176·9 (4)	O——Re——S(1)	98·1 (4)
O——Re——S(2)	100·1 (4)	O——Re——Cl(1)	97·8 (4)
O——Re——Cl(2)	97·1 (4)	H₂O–Re——S(1)	83·8 (3)
H₂O–Re——S(2)	82·2 (3)	H₂O–Re——Cl(1)	79·6 (3)
H₂O–Re——Cl(2)	81·1 (3)	S(1)–Re——S(2)	92·9 (2)
S(1)–Re——Cl(1)	93·5 (2)	S(1)–Re——Cl(2)	164·6 (2)
S(2)–Re——Cl(1)	159·9 (2)	S(2)–Re——Cl(2)	82·3 (2)
Re—S(1)—C(1)	110·8 (6)	Re—S(2)–C(2)	110·8 (5)
S(1)–C(1)–N(1)	120·5 (13)	S(2)–C(2)–N(3)	121·6 (12)
S(1)–C(1)–N(2)	119·8 (15)	S(2)–C(2)–N(4)	117·3 (11)
N(1)–C(1)–N(2)	119·6 (17)	N(3)–C(2)–N(4)	121·0 (14)
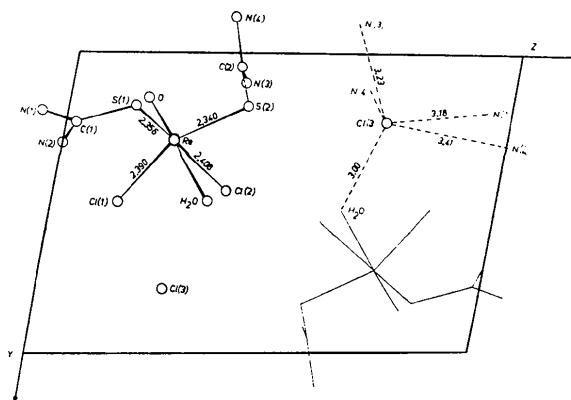
Fig. 1. The crystal structure of [ReO(H₂O)Cl₂tu₂]Cl; projection on the (100) plane.

Table 3. *Planarity of groups of atoms in the structure and distances from least-squares planes*

The equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space.

P	Q	R	S	Deviations (Å) of atoms from plane			
−0·8921	−0·4376	−0·1120	−2·4290	Cl(1)	−0·027 (4)	Cl(2)	0·029 (4)
				S(1)	0·026 (4)	S(2)	−0·029 (4)
				Not defining plane: Re 0·348			
−0·1900	−0·9302	−0·3141	−0·8466	S(1)	0·002 (4)	C(1)	−0·008 (16)
				N(1)	0·003 (15)	N(2)	0·003 (21)
−0·5822	−0·0811	−0·8090	−3·3973	S(2)	−0·002 (4)	C(2)	0·008 (14)
				N(3)	−0·003 (13)	N(4)	−0·003 (13)

pected. The rhenium atom does not lie in the 'best plane' defined by the two S and two Cl atoms but is displaced in the direction of the O atom by 0·35 Å. This distortion is also indicated by the means of the O–Re–Cl and O–Re–S apical angles, 97·5 and 99·1° respectively. The short Re–O bond length of 1·654 (10) Å is indicative of a triple bond. There are several reported measurements of Re^V–O 'triple bond' distances: 1·663 (11) in K_2ReOCl_5 (Głowiak, 1967; Głowiak & Jeżowska-Trzebiatowska, 1976), 1·689 (16) in $(enH_2)ReOCl_5$ (Głowiak & Jeżowska-Trzebiatowska, 1976), 1·73 (6) in $(Ph_4As)[ReOBr_4(CH_3CN)]$ (Cotton & Lippard, 1966), 1·60 in $ReOCl_3(PEt_2Ph)_2$ (Ehrlich & Owston, 1963), and 1·71 (4) Å in $(Et_4N)[ReOBr_4(H_2O)]$ (Cotton & Lippard, 1965). It is noteworthy that in all these compounds the single-bonded ligands are in *trans* positions relative to the oxo O atoms. The value of 2·23 (1) Å for the Re–aqua bond distance is quite satisfactory. The value of 2·32 Å found in $(Et_4N)[ReOBr_4H_2O]$ (Cotton & Lippard, 1965) for the Re–H_2O distance is rather large for the coordinated water.

Although there are no other Re–S(thiourea) distances to compare with the average Re–S(thiourea) 2·35 (1) Å, the distance is comparable to that observed for Re–S(diethyl dithiocarbamate) 2·39 (1) Å in $ReN(S_2CNEt_2)_2$ (Fletcher, Rowbottom, Skapski & Wilkinson, 1970) and is probably representative of a Re–S single bond. The two thiourea molecules are tilted with respect to the Re–S bonds by 110·8 (6)° Re–S–C angles, which are close to the tetrahedral value and to those observed in other thiourea and ethylene-thiourea complexes. The thiourea molecules are quite planar (Table 3). Mean values for S–C, 1·76 (2), and N–C, 1·34 (2) Å, agree with those found in the free ligand and other metal thiourea complexes (Baggio, Manzanares & Baggio, 1975; Baggio, Baggio & de Perazzo, 1975).

The average Re–Cl bond length, 2·40 (1) Å, is typical of distances in other rhenium(V) complexes: (K_2ReOCl_5) 2·39 (Głowiak & Jeżowska-Trzebiatowska, 1976; $[(enH_2)ReOCl_5]$ 2·39 Å (Głowiak & Jeżowska-Trzebiatowska, 1976).

The packing of the Cl^- ions in the unit cell is shown in Fig. 1. The anions are surrounded by six atoms at distances 3·0–3·41 Å forming an irregular shape [H_2O, N(1), N(2), N(3) and two N(4) atoms from two different molecules].

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