Table 5. *Hydrogen bonds* (Å) *in crystals of loperamide*

N(11)–O(35)	2·903	O(35)	$x, y, z - 1$
O(14)–O(19)	2·732	O(19)	$-0·5 + x, y, -0·5 - z$
O(14)–O(35)	2·965	O(35)	$-0·5 + x, y, 0·5 - z$
O(19)–O(14)	2·732	O(14)	$0·5 + x, y, -0·5 - z$

International Tables for X-ray Crystallography (1962). The final coordinates are given in Table 2.*

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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 32326 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The conformation of the molecule and the numbering scheme are shown in Fig. 1 and the bond distances and angles in Table 3. The torsion angles defining the conformation are given in Table 4.

The molecules are connected as indicated in the *Abstract* and in Table 5.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *World List of Crystallographic Computer Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

trans-(Oxoaqua)trichlorothiourearhenium(V), ReO(H₂O)Cl₃tu

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Abstract. $CH_6N_2O_2SCl_3Re$, orthorhombic, $Pca2_1$ (C_{2v}^5), $a = 11·032$ (8), $b = 7·083$ (5), $c = 11·166$ (8) Å, $M_r = 402·7$, $V = 872·5$ Å³, $Z = 4$, $D_m = 3·04$, $D_x = 3·06$ g cm⁻³, μ(Cu $K\alpha$, $\lambda = 1·5418$ Å) = 366·0 cm⁻¹. The molecule is somewhat distorted from true octahedral symmetry and the oxo O atom and water molecule are *trans*. The bond lengths are Re–O 1·71 (2), Re–H₂O 2·29 (2), Re–S 2·311 (7) and Re–Cl 2·347–2·425 Å. The structure was refined to an R of 0·051 for 901 diffractometer data.

Introduction. This investigation is a part of the study of coloured oxo-complexes of Re^V which can be obtained in the system Re^{VII}–HCl–thiourea. In the previous paper (Lis, 1976) the crystal structure of blue [ReO(H₂O)Cl₂tu₂]Cl was reported. The X-ray analysis presented here has shown that the green compound has the formula ReO(H₂O)Cl₃tu. The crystal structure of the orange compound of the formula ReOCl₃tu₂ will be reported later.

The title compound was obtained by dissolving 0·1 g NH₄ReO₄ (or KReO₄) and 0·1 g CS(NH₂)₂ in 10–20 ml of concentrated HCl. On standing, well formed green crystals were obtained. Weissenberg photographs showed that the crystals are orthorhombic: the sys-

tematic absences were: $h0l$ for $h = 2n + 1$, $0kl$ for $l = 2n + 1$: space group $Pca2_1$ (C_{2v}^5) or $Pcam$ (D_{2h}^{11}). An almost spherical crystal, of approximate radius 0·05 mm, was used for the data collection. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities of reflexions were measured by the $2\theta–\omega$ scan technique. The data were corrected for Lorentz and polarization effects and for absorption as for spherical crystals ($\mu r = 1·8$). Of 941 accessible reflexions below $2\theta = 146°$, 901 with $I > 1·96\sigma(I)$ were used for the structure determination. All calculations were performed on the NOVA 1200 computer with programs supplied by Syntex (Syntex XTL structure determination system). Neutral-atom scattering factors used were those tabulated by Cromer & Waber as given in *International Tables for X-ray Crystallography* (1974).

A three-dimensional Patterson map was computed, from which no clear basis for choice between the two possible space groups was available. The non-centrosymmetric one, $Pca2_1$, was tentatively assumed, in which all atoms occupy the fourfold general set of positions. The approximate coordinates of the Re atoms were easily determined from the Patterson map. With phases
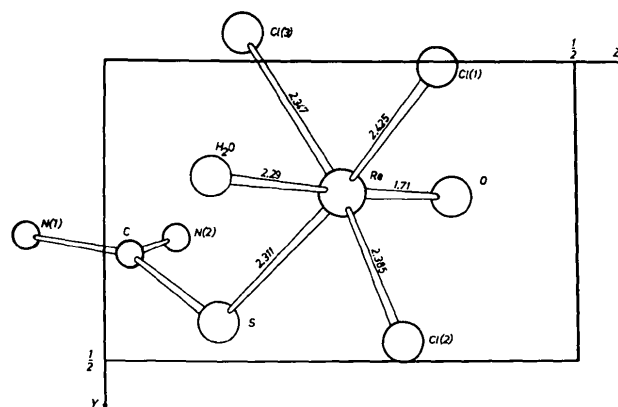
Table 1. *The final positional parameters* (×10⁴) *with standard deviations in parentheses*

	x	y	z
Re	1327 (1)	2205 (2)	2500 (fixed)
Cl(1)	2722 (6)	59 (9)	3481 (7)
Cl(2)	2619 (6)	4697 (9)	3156 (7)
Cl(3)	583 (6)	−441 (9)	1471 (7)
S	526 (7)	4390 (9)	1183 (7)
O	342 (18)	2318 (30)	3684 (18)
H₂O	2817 (19)	1973 (30)	1078 (18)
C	−561 (23)	3226 (35)	263 (25)
N(1)	−277 (25)	2855 (41)	−810 (26)
N(2)	−1687 (25)	2888 (45)	712 (27)

Fig. 1. The crystal structure of ReO(H₂O)Cl₃tu: projection on the (100) plane.

based on Re, a three-dimensional difference Fourier synthesis was then computed which revealed several peaks, some of which no doubt resulted from the false symmetry. Three large peaks were taken to be Cl atoms and a new difference Fourier map was computed with these as well as the Re atom to determine phases. All peaks on this map were used for determination of the remaining non-H atom positions of the ReO(H₂O)Cl₃tu formula, and R then dropped to 0·080. The observed density, measured by flotation in a mixture of CHBr₃ and CBr₄, is 3·04 (3) g cm⁻³, which agrees well with the calculated density of 3·06 g cm⁻³ assuming four molecules in the unit cell. Several cycles of full-matrix refinement with anisotropic thermal parameters yielded the final values $R = 0·051$ and $R_w = 0·064$. A difference map based on the final parameters was essentially flat and H atoms were not resolvable. The positional parameters and their estimated standard deviations derived from the least-squares refinement are presented in Table 1.*

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* ReO(H₂O)Cl₃tu *molecule*

Re—O	1·713 (19)	Re—H₂O	2·291 (20)
Re—S	2·311 (7)	Re—Cl(1)	2·425 (7)
Re—Cl(2)	2·385 (6)	Re—Cl(3)	2·347 (7)
S—C	1·781 (27)	C—N(1)	1·27 (4)
C—N(2)	1·36 (4)	C—N (average)	1·32
O—Re—H₂O	173·3 (9)	O—Re—S	102·6 (7)
O—Re—Cl(1)	94·8 (7)	O—Re—Cl(2)	96·2 (7)
O—Re—Cl(3)	101·1 (7)	H₂O—Re—S	83·2 (6)
H₂O—Re—Cl(1)	79·2 (6)	H₂O—Re—Cl(2)	80·6 (6)
H₂O—Re—Cl(3)	81·6 (6)	S—Re—Cl(1)	161·8 (3)
S—Re—Cl(2)	85·9 (3)	S—Re—Cl(3)	95·1 (3)
Cl(1)—Re—Cl(2)	86·9 (3)	Cl(1)—Re—Cl(3)	86·7 (3)
Cl(2)—Re—Cl(3)	162·0 (3)	Re—S—C	108·3 (9)
S—C—N(1)	118·4 (21)	S—C—N(2)	119·0 (21)
N(1)—C—N(2)	122·5 (27)		

Discussion. The crystals of the title compound consist of discrete molecules. The structure of the ReO(H₂O)Cl₃tu molecule viewed in projection along *a* is shown in Fig. 1 and the intramolecular bond lengths and angles are given in Table 2.

The coordination about Re is that of a distorted octahedron and the oxo O atom and the water molecule are *trans*. The Re—O distance of 1·71 (2) Å is similar to that obtained in other six-coordinated monooxo-complexes of Reᵛ. The Re atom does not lie in the 'best plane' defined by three Cl and one S atom, but is displaced in the direction of the O atom by 0·36 Å. This distortion is also indicated by the means of the O—Re—Cl and O—Re—S apical angles of 97·3 and 102·6° respectively. A similar situation was found in all monooxo-complexes of Reᵛ in which the short Re—O

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bonds are the triple bonds. The Re—H₂O bond length of 2·29 (2) Å lies between the corresponding value found in (Et₄N)(ReOBr₄H₂O), 2·32 Å (Cotton & Lippard, 1965), and in [ReO(H₂O)Cl₂tu₂]Cl, 2·23 Å (Lis, 1976), and suggests that this bond is rather weak. The Re—S distance, 2·311 (7) Å, is a little shorter than the corresponding distances in [ReO(H₂O)Cl₂tu₂]Cl [2·356 (5) and 2·340 (4) Å]. The thiourea molecule is planar and the S—C, C—N distances and Re—S—C angles agree with those found in [ReO(H₂O)Cl₂tu₂]Cl. The Re—Cl bond lengths lie in the 2·347–2·425 Å range. Similar values were earlier observed in other Reᵛ complexes. However, the difference of 0·08 Å suggests that the Cl atoms are not quite equivalent in the investigated compound.

The intermolecular distances appear to be normal. The shortest intermolecular contacts are H₂O—Cl(1) and H₂O—Cl(3) 3·26, N(1)—Cl(2) and N(2)—Cl(2) 3·3 Å.

In this and the previous investigation (Lis, 1976) it was found that the addition of thiourea to solutions of

perrhenate ions in hydrochloric acid results in the formation of many coloured Re^V complexes. The blue [ReO(H₂O)Cl₂tu₂]Cl (1) was obtained first, and green ReO(H₂O)Cl₃tu (2) and orange ReOCl₃tu₂ (3) were precipitated with increasing concentration of HCl. It was observed that thiourea was a reducing agent, and that the presence of strong reducing agents such as SnCl₂ is not necessary to obtain thiourearhenium(V) complexes from ReO₄⁻ ions. In (1) the Re—H₂O bond of 2·23 Å is quite strong and therefore the Cl⁻ ions replace thiourea molecules (with increasing concentration of HCl). However, in (2) this bond is lengthened to 2·29 Å and therefore the water molecule could be replaced by thiourea molecules. It is interesting to note that in (3)

thiourea molecules *trans* to O atoms are nitrogen-bonded with Re atoms.

On the basis of this and the previous investigations it seems that the coordination around the Re atoms in other thiourea complexes can be determined from the X-ray data only.

References

Cotton, F. A. & Lippard, S. J. (1965). *Inorg. Chem.* **4,** 1621–1629.

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

Lis, T. (1976). *Acta Cryst.* B32, 2707–2709.

Radioprotectant Sodium Fluoroacetate

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Abstract. (FCH₂.COO)⁻.Na⁺; $P2_1$; $a = 9\cdot32$ (1), $b = 5\cdot33$ (1), $c = 3\cdot65$ (2) Å, $\beta = 99\cdot4$ (5)°; $D_m = 1\cdot79$ (flotation); $D_c = 1\cdot86$ g cm⁻³; $Z = 2$. The Na⁺ ion is coordinated by five O atoms and a F atom which form a distorted octahedron. The average value of the Na···O distances in the octahedron is 2·46 (2) Å and the Na···F distance is 2·56 (2) Å. By including also a long Na···O distance of 2·98 (2) Å in the Na coordination, the polyhedron becomes seven-cornered with the F atom centring a face of the distorted trigonal prism formed by the O atoms. In the fluoroacetate ion, the F atom is *cis* to one of the carboxylate O atoms.

Introduction. A very tiny, transparent crystal of sodium fluoroacetate, about 0·2 × 0·2 × 0·3 mm, was obtained by slow evaporation from aqueous solution. Efforts to obtain larger crystals by the same and different procedures were not fruitful. Hence, the one tiny crystal was used for data collection. Intensity data from reciprocal levels *hkl*, $l = 0$ to 2, were recorded on multiple films by the equi-inclination Weissenberg method with Cu $K\alpha$ radiation. The diffraction pattern was generally weak. When the second-level data were recorded, the spot shape of the reflexions was beginning to change, indicating deterioration of the sample, and soon after the recording of that level, the specimen lost its crystallinity and acquired a chalky appearance. The

intensities of 207 observed reflexions were measured by comparison with a calibrated strip and were corrected for Lp and spot-shape effects.

The structure was solved by direct methods followed by Fourier methods. *MULTAN* (Germain, Main & Woolfson, 1971), as modified by S. Ramakumar and N. Murthy for the IBM 360/44 computer, was used with 84 E's greater than 1·0. From the E map corresponding to the best solution of *MULTAN*, the positions of the Na⁺ ion and the two acetate O atoms could be obtained. From a subsequent difference electron density map, the positions of the rest of the atoms in the structure were derived. The structure was refined by an iterative, block-diagonal structure-factor least-squares procedure. Anisotropic thermal parameters were employed and Cruickshank's weighting scheme with the constants $a = 2\cdot95$, $b = 0\cdot53$ and $c = 0\cdot030$ was used. When the least-squares refinement converged, R, defined as $\Sigma || F_o | - | F_c ||/\Sigma |F_o|$, for 207 observed reflexions was 0·127. The least-squares program used was originally written by R. Shiono and later modified by B. S. Reddy. The scattering factors were those of Cromer & Waber (1965).

Discussion. Sodium fluoroacetate is well known for its protective action against ionizing radiation (Bacq, Fischer & Herve, 1958). This analysis forms part of a