Fig. 2. View of the crystal structure of [NH(CH₃)₃][CuCl₃].2H₂O along **a**. The thermal ellipsoids correspond to the 20% probability surfaces.

bonds. The shorter coordinative bond at Cu(2) causes a lengthening of the Cu(2)—Cl(1) single bond to 2·3060 (5) Å, compared with a Cu(1)—Cl(2) bond length of 2·2770 (5) Å. The Cu—O bonds are longer than in $CuCl_2.2H_2O$ and increase the more the Cu atom deviates from the plane of the water molecule.

The Cl⁻ atom is involved in four hydrogen bonds with the $CuCl_2.2H_2O$ chains (see deposition footnote). These hydrogen bonds are of intermediate strength and interconnect the $CuCl_2.2H_2O$ chains along **b** (Fig. 2).

The cations are attached by very weak bifurcated hydrogen bonds to the $CuCl_2.2H_2O$ chains. The bonding along **c** consists of electrostatic interactions between the methyl H atoms and Cl atoms of the next $CuCl_3^-.2H_2O$ layers [shortest H···Cl contact: 2·85 (2) Å].

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The Structure of α,α'-Dithiobisformamidinium Chloride Pentachloro(thiourea)-rhenate(IV) (I) and Bis(α,α'-dithiobisformamidinium) Dichloride Hexachlororhenate(IV) Trihydrate (II)

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Abstract. (I) [(NH₂)₂CSSC(NH₂)₂]Cl[ReCl₅{SC-(NH₂)₂}], $M_r = 627·3$, orthorhombic, *Pbca*, $a = 11·082$ (7), $b = 15·850$ (13), $c = 19·864$ (14) Å, $V = 3489$ Å³, $Z = 8$, $D_m = 2·38$, $D_x = 2·39$ Mg m⁻³, $F(000) = 2376$, μ(Mo *K*α, $\lambda = 0·71069$ Å) $= 8·61$ mm⁻¹, room temperature, final $R = 0·035$ and $wR = 0·033$ for 2257 non-zero reflexions. (II) [(NH₂)₂CSSC(NH₂)₂]₂Cl₂[ReCl₆].3H₂O, $M_r = 828·4$, orthorhombic, *Amam* (D_{2h}^{17}), $a = 16·768$ (6), $b = 13·672$ (8), $c = 11·348$ (5) Å, $V = 2601·6$ Å³, $Z = 4$, $D_m = 2·10$, $D_x = 2·11$ Mg m⁻³, $F(000) = 1604$, μ(Mo *K*α) = 6·09 mm⁻¹, room temperature, final $R = 0·031$ and $wR = 0·027$ for 1988 non-zero reflexions. The dithiobisformamidinium cations have the normal configuration and dimensions with CSSC torsion angles of 94·4 (6) and 96·1 (4)° for (I) and (II) respectively.

The [ReCl₆]²⁻ anion has crystallographic point symmetry *mm* (C_{2v}) and the average Re—Cl distance is 2·361 (2) Å. The Re—Cl distances in the [ReCl₅{SC(NH₂)₂}]⁻ anion are in the range 2·331 (3)–2·373 (3) Å and the Re—S bond length is 2·399 (4) Å.

Introduction. This investigation was undertaken as a part of our study on crystal structures of complexes isolated in the reaction of thiourea with ReO₄⁻ and ReCl₆²⁻ anions in HCl solution.

Experimental. The yellow platy crystals of (I) were obtained as reported earlier (Lis, 1979). The compound (II) may be obtained if a solution of thiourea and K₂ReCl₆ in dilute HCl is exposed to air. After some days at the top of the solution yellow crystals are

formed as large needles. (It was noticed that the presence of $[ReCl_6]^{2-}$ and the access of air were essential.) D_m measured pycnometrically in 1,2-dibromoethane/$CHBr_3$ for (I) and 1,2-dibromoethane/CCl_4 for (II). Systematic absences on Weissenberg photographs uniquely indicated the space group for (I). For (II) two space groups, $Amam$ or $Ama2$, were possible. A parallelepiped $0.16 \times 0.03 \times 0.4$ mm for (I) and a cube 0.25 mm on edge for (II) were cut from large crystals. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters [15 reflexions, $15 < 2\theta < 24°$ for (I) and $14 < 2\theta < 23°$ for (II)] and intensity measurements at room temperature (temperature not measured); $2\theta-\omega$ scan technique for both crystals. 2888 intensities measured only for reflexions above background and below $\theta = 30°$ for (I) (h 0 to 15, k 0 to 22, l 0 to 27); 2752 intensities measured below $\theta = 35°$ for (II) (h 0 to 22, k 0 to 19, l 1 to 16). After each group of 50 reflexions two standards were measured, variation 5%. Most of the calculations performed on a NOVA 1200 computer with locally modified $XTL/XTLE$ (Syntex, 1976) programs. 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. Both structures solved by the heavy-atom method. The Re atoms were found from Patterson maps and the centrosymmetric space group $Amam$ was assumed in the case of (II); all other non-H atoms from difference maps. In each structure, refinement based on F (Re, Cl, S, C, N, O anisotropic, N-bonded H atoms included in geometrically calculated positions, O-bonded H atoms from difference map and not refined) for reflexions with $I > 3\sigma(I)$; $w = 1/\sigma^2(F_o)$; $(\Delta/\sigma)_{max} = 0.01$. For (I) an absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data, for (II) empirical absorption corrections from φ-scan data. No corrections for secondary extinction. For (I), $S = 1.59$, for (II), 1.65; $(\Delta\rho)_{max}$ in final difference syntheses 1.1 and 1.4 e Å^{-3} for (I) and (II), respectively. The final atomic parameters for (I) and (II) are given in Tables 1 and 2 respectively.*

Discussion. Crystals of (I) consist of dithiobisformamidinium dications, pentachloro(thiourea)rhenate(IV) monoanions and Cl^- anions. The selected bond lengths and angles for (I) are listed in Table 3. Crystals of (II) comprise dithiobisformamidinium dications, hexachlororhenate(IV) dianions, Cl^- anions and water molecules.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42237 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atom coordinates and equivalent isotropic thermal parameters of compound* (I)

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

	x	y	z	$B_{eq}(\text{Å}^2)$
Re	0.19762 (3)	0.15761 (3)	0.11403 (2)	2.22 (2)
Cl(1)	0.0498 (3)	0.1682 (2)	0.1985 (2)	3.26 (21)
Cl(2)	0.3173 (3)	0.2573 (2)	0.1695 (2)	3.35 (21)
Cl(3)	0.3415 (3)	0.1430 (2)	0.0292 (2)	3.72 (24)
Cl(4)	0.2892 (3)	0.0484 (2)	0.1746 (2)	3.71 (24)
Cl(5)	0.0734 (3)	0.0599 (2)	0.0559 (2)	3.82 (26)
Cl(6)	0.4031 (3)	0.4620 (3)	0.3522 (2)	4.24 (26)
S(1)	0.1150 (3)	0.3581 (2)	0.3808 (2)	3.48 (23)
S(2)	0.2573 (3)	0.2827 (3)	0.3560 (2)	3.20 (21)
S(3)	0.0911 (3)	0.2660 (3)	0.0543 (2)	4.55 (30)
C(1)	0.0600 (10)	0.3924 (7)	0.3027 (6)	3.0 (10)
C(2)	0.1930 (10)	0.1812 (7)	0.3543 (5)	2.7 (8)
C(3)	0.1803 (13)	0.3551 (8)	0.0366 (6)	4.2 (12)
N(1)	0.0979 (9)	0.3665 (6)	0.2449 (5)	3.7 (9)
N(2)	−0.0221 (10)	0.4510 (7)	0.3053 (5)	4.7 (10)
N(3)	0.0802 (8)	0.1650 (7)	0.3690 (4)	3.3 (8)
N(4)	0.2691 (9)	0.1210 (7)	0.3393 (5)	4.4 (10)
N(5)	0.2965 (10)	0.3474 (8)	0.0155 (5)	5.1 (10)
N(6)	0.1279 (10)	0.4288 (7)	0.0399 (6)	4.6 (10)

Table 2. *Final atom coordinates and equivalent isotropic thermal parameters of compound* (II)

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

	x	y	z	$B_{eq}(\text{Å}^2)$
Re	0.25	0.15494 (2)	0	1.50 (2)
Cl(1)	0.15003 (8)	0.27625 (9)	0	2.39 (8)
Cl(2)	0.15186 (8)	0.03092 (9)	0	2.80 (9)
Cl(3)	0.25	0.15566 (11)	0.20813 (10)	2.85 (9)
Cl(4)	0.08221 (9)	0.17509 (9)	0.5	2.96 (9)
S	0.05663 (6)	0.47478 (7)	0.18266 (8)	2.51 (6)
C	0.0522 (3)	0.3766 (3)	0.2845 (3)	2.3 (3)
N(1)	0.1201 (3)	0.3306 (3)	0.2991 (3)	2.9 (3)
N(2)	−0.0136 (3)	0.3516 (3)	0.3386 (3)	3.3 (3)
O(1)	0.25	0.4323 (4)	0.2050 (4)	3.4 (4)
O(2)	0.25	0.5489 (5)	0	4.4 (6)

Table 3. *Selected intramolecular distances* (Å) *and angles* (°) *in compound* (I)

C(1)–N(1)	1.290 (14)	C(1)–N(2)	1.301 (15)
C(2)–N(3)	1.309 (14)	C(2)–N(4)	1.308 (14)
C(3)–N(5)	1.360 (17)	C(3)–N(6)	1.306 (17)
C(3)–S(3)	1.758 (13)	S(3)–Re	2.399 (4)
Re–Cl(1)	2.350 (2)	Re–Cl(2)	2.338 (3)
Re–Cl(3)	2.331 (3)	Re–Cl(4)	2.340 (3)
Re–Cl(5)	2.373 (3)	Cl(1)–Re–Cl(2)	90.6 (1)
Cl(1)–Re–Cl(3)	178.1 (1)	Cl(1)–Re–Cl(4)	89.3 (1)
Cl(1)–Re–Cl(5)	89.4 (1)	Cl(1)–Re–S(3)	87.6 (2)
Cl(2)–Re–Cl(3)	91.1 (1)	Cl(2)–Re–Cl(4)	90.7 (1)
Cl(2)–Re–Cl(5)	178.2 (1)	Cl(2)–Re–S(3)	91.6 (2)
Cl(3)–Re–Cl(4)	90.1 (1)	Cl(3)–Re–Cl(5)	88.9 (1)
Cl(3)–Re–S(3)	92.9 (2)	Cl(4)–Re–Cl(5)	91.1 (1)
Cl(4)–Re–S(3)	176.2 (2)	Cl(5)–Re–S(3)	86.6 (2)
Re–S(3)–C(3)	113.4 (5)	S(3)–C(3)–N(5)	121.5 (10)
S(3)–C(3)–N(6)	117.2 (10)	N(5)–C(3)–N(6)	121.1 (12)
S(1)–C(1)–N(1)	125.1 (9)	S(2)–C(2)–N(3)	124.1 (8)
S(1)–C(1)–N(2)	115.5 (9)	S(2)–C(2)–N(4)	114.2 (8)
N(1)–C(1)–N(2)	119.3 (11)	N(3)–C(2)–N(4)	121.6 (10)

In both crystals the dithiobisformamidinium dications [*ORTEP* drawings (Johnson, 1976), atom-numbering scheme, and some of the bond distances and angles are shown on Fig. 1] have similar dimensions and conformation. In crystal (II) the dications possess crystallographically required twofold symmetry, which is not the case for (I). All bond lengths and angles are within the range of accepted values. The thiourea parts of the cations are planar. The CSSC torsion angles of 94·4 (6)° for (I) and 96·1 (4)° for (II) are similar and lie between extreme values found in other structures for this species (Jameson, Blazsò, Seferiadis & Oswald, 1982 and references therein). The intramolecular contacts between N and S atoms (Table 4) may be either dipole interactions, or (more likely) intramolecular hydrogen bonds (Jameson *et al.*, 1982). In (II) the SSCN torsion angles are, within experimental error, equal to 0 and 180°; in (I) the S(1)—S(2)—C—N torsion angles of −2·3 (8) and −179·9 (9)° and the S(2)—S(1)—C—N torsion angles of 6·0 (11) and

−171·1 (11)° are within the range found for the dithiobisformamidinium dication (for a short review, see Jameson *et al.*, 1982).

In the [ReCl₅(thiourea)]⁻ cation (the structure of which is shown in Fig. 2) the six atoms bonded to Re form a distorted octahedron. The Re—Cl distances range from 2·331 (3) to 2·373 (3) Å and are similar to those found in other rhenium(IV) complexes (Lis, 1980). The Re—S distance, 2·399 (4) Å, is longer than the corresponding distances in [ReO(H₂O)Cl₂tu₂]Cl [2·356 (5) and 2·340 (4) Å] and in ReO(H₂O)Cl₃tu [2·311 (7) Å] (Lis, 1977). The thiourea molecule is planar and forms one intramolecular hydrogen bond between N(5) and Cl(3) – see Fig. 2 and Table 4.

Table 4. *Geometry of the probable hydrogen bonds for compounds* (I) *and* (II)

X—H···Y	X···Y	H···Y	∠X—H···Y
Compound (I)			
N(1)—H(1)···Cl(6ⁱ)	3·266 (10)Å	2·36Å	150°
N(1)—H(11)···Cl(2)	3·340 (10)	2·46	146
N(1)—H(11)···S(2)	3·124 (10)	2·58	114
N(2)—H(2)···Cl(6ⁱ)	3·241 (10)	2·33	151
N(2)—H(21)···Cl(5ⁱⁱ)	3·303 (10)	2·34	162
N(3)—H(3)···Cl(6ⁱⁱⁱ)	3·241 (10)	2·36	147
N(3)—H(31)···Cl(2ⁱ)	3·348 (10)	2·62	130
N(3)—H(31)···S(1)	3·092 (10)	2·53	116
N(4)—H(4)···Cl(6ⁱⁱⁱ)	3·172 (10)	2·26	151
N(4)—H(41)···Cl(1ⁱᵛ)	3·286 (10)	2·29	176
N(5)—H(51)···Cl(3)	3·289 (12)	2·37	153
N(6)—H(6)···Cl(3ᵛ)	3·420 (11)	2·57	142
N(6)—H(61)···Cl(6ⁱ)	3·328 (11)	2·48	142

Symmetry code: (i) $x-\frac{1}{2},y,\frac{1}{2}-z$; (ii) $-x,\frac{1}{2}+y,\frac{1}{2}-z$; (iii) $\frac{1}{2}-x,y-\frac{1}{2},z$; (iv) $\frac{1}{2}+x,y,\frac{1}{2}-z$; (v) $\frac{1}{2}-x,\frac{1}{2}+y,z$.

X—H···Y	X···Y	H···Y	∠X—H···Y
Compound (II)			
N(1)—H(11)···Cl(4)	3·181 (3)	2·24	157
N(1)—H(12)···O(1)	2·796 (4)	1·85	158
N(2)—H(21)···Cl(4)	3·429 (4)	2·57	143
N(2)—H(22)···Sⁱ	3·048 (4)	2·48	116
O(1)—H(1)···O(2)	2·819 (5)	2·23	118
O(1)—H(10)···Cl(3ⁱⁱ)	3·209 (5)	2·43	151
O(2)—H(2)···Cl(4ⁱⁱⁱ)	3·301 (4)	2·33	168

Symmetry code: (i) $-x,1-y,z$; (ii) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; (iii) $x,\frac{1}{2}+y,\frac{1}{2}-z$.
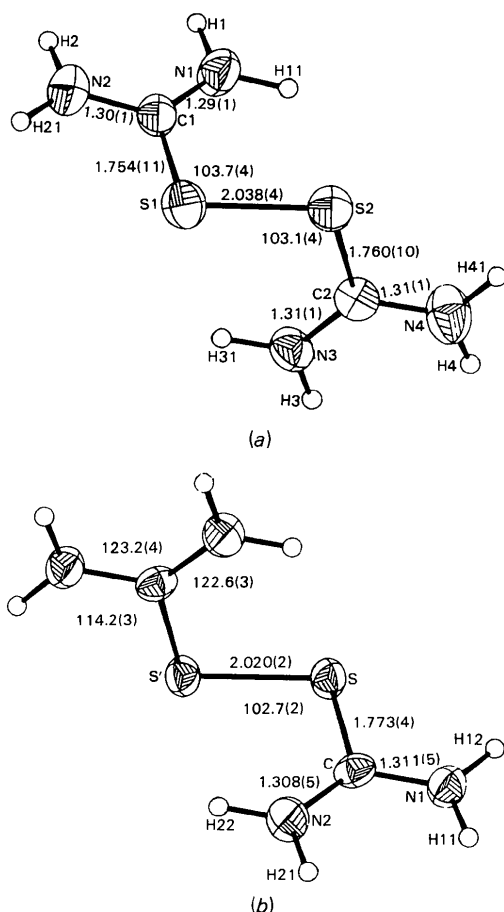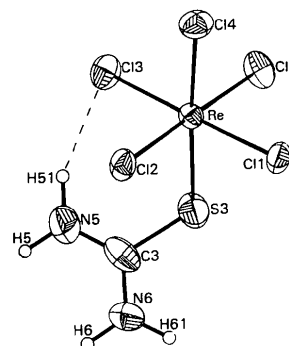

Fig. 1. Molecular diagrams of the dithiobisformamidinium dications. (*a*) Dication of (I) showing the numbering scheme, (*b*) view of dication of (II) along the twofold axis; with bond distances (Å) and angles (°).

Fig. 2. An *ORTEP* (Johnson, 1976) view of the [ReCl₅(thiourea)]⁻ ion. The dotted line denotes the intramolecular hydrogen bond.
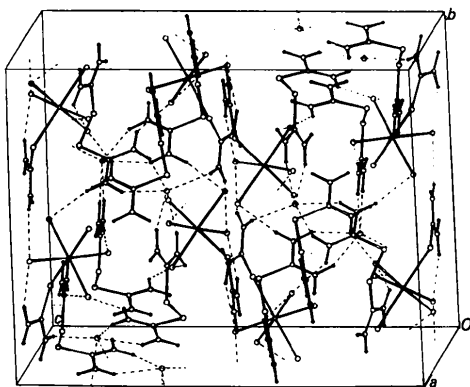
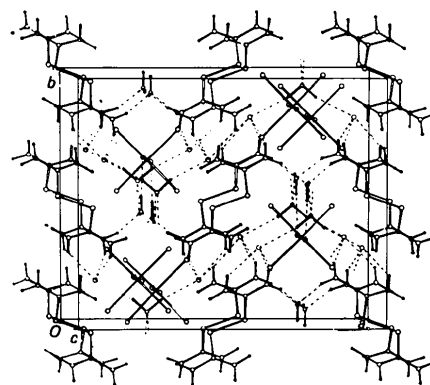Fig. 3. Crystal packing of structure (I).

Fig. 4. Unit-cell diagram, illustrating intermolecular hydrogen bonds (dotted lines) for structure (II). (Oc out of the page.)

The hexachlororhenate(IV) dianion, being placed in the *mm* (C_{2v}) special position, retains in general its internal O_h symmetry. One mirror plane is through four Cl atoms whereas the other one is placed across the Cl—Re—Cl dihedral angles. The Re—Cl distances are equal within the experimental precision and the average Re—Cl distance of 2·361 (2) Å agrees with that of 2·361 (3) Å found in (NH₄)₂ReCl₆ (Lisher, Cowlam & Gillott, 1979) and that of 2·353 (4) Å found in K₂ReCl₆ (Grundy & Brown, 1970). However, the angles are slightly displaced from 90°, the most severe deviation being 1·7 (1)° for Cl(2)—Re—Cl(2′).

The crystal packing is shown in Figs. 3 and 4 for (I) and (II), respectively. The structure in both crystals is held together by a three-dimensional hydrogen-bond network and electrostatic interactions. (The hydrogen bonds for both crystals are listed in Table 4.) The packing of the Cl⁻ ions is similar in both crystals. Each chloride ion participates in five hydrogen bonds

spanning irregular polyhedra. All H atoms from water molecules of (II) are used in the hydrogen bonds.

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Structure d'un Complexe Binucléaire du Nitrate d'Uranyle et du N,N-Diméthyl-formamide: μ-Peroxo-bis[bis(N,N-diméthyl-formamide)nitratodioxouranium(VI)], [(UO₂)₂(NO₃)₂O₂(C₃H₇NO)₄]

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Abstract. $M_r = 988·45$, triclinic, $P\bar{1}$, $a = 8·564$ (2), $b = 8·990$ (4), $c = 20·063$ (4) Å, $\alpha = 75·50$ (2), $\beta = 79·13$ (2), $\gamma = 65·58$ (3)°, $V = 1355·4$ Å³, $Z = 2$, $D_x = 2·423$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu(\text{Mo } K\alpha) = 113·63$ cm⁻¹, $F(000) = 454$, $T = 295$ K, $R_F = 0·033$ for 2029 independent reflexions [$I > 3\sigma(I)$]. The eight-coordinated uranium lies at the centre of a distorted hexagonal bipyramid. One oxo group links two polyhedra into a dimer. The remaining four equatorial O atoms in both bipyramids are from one nitrate group and two dmf molecules. The formation of the peroxo complex is discussed.