

Structure of Bis(dithiobisformamidinium) Aquapentachlororhenate(IV) Trichloride Dihydrate

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Abstract. $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{ReCl}_5(\text{H}_2\text{O})]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, $2\text{C}_2\text{H}_8\text{N}_4\text{S}_2^{2+} \cdot \text{Cl}_5\text{H}_2\text{ORe}^- \cdot 3\text{Cl}^- \cdot 2\text{H}_2\text{O}$, orthorhombic, *Pnam*, $a = 17.576$ (9), $b = 8.948$ (4), $c = 16.776$ (7) Å, $M_r = 828.4$, $V = 2638.4$ Å³, $Z = 4$, $D_m = 2.074$, $D_x = 2.085$ Mg m⁻³, $\mu(\text{Mo K}\alpha, \lambda = 0.71069 \text{ Å}) = 6.00$ mm⁻¹; final $R = 0.046$ and $R_w = 0.032$ for 1905 non-zero reflexions. The crystals are composed of dithiobisformamidinium cations, aquapentachlororhenate(IV) anions, Cl⁻ anions and water molecules. The bond lengths in the complex anion are Re–H₂O 2.076 (10), Re–Cl_{trans} 2.303 (4) and Re–Cl_{cis} 2.345 (2)–2.351 (2) Å; the H₂O–Re–Cl_{trans} bond angle is 179.8 (3)°. The disulphide group has the normal configuration and dimensions, with an S–S distance of 2.026 (3) Å and a CSS/SSC torsion angle of 100.2 (5)°. The thiourea groups are planar.

Introduction. In the course of investigations on crystal structures of complexes isolated in the reaction system $\text{ReO}_4^- + (\text{NH}_2)_2\text{CS} + \text{HCl}$ (Lis, 1976, 1977, 1979), the crystal structure of the title compound has been determined. The compound was obtained as follows: to 0.1 g NH_4ReO_4 and 0.1 g $(\text{NH}_2)_2\text{CS}$, 10–20 ml of concentrated HCl was added. The solution was left in a desiccator over P_2O_5 . Usually, after 2–4 weeks green and yellow crystalline compounds precipitated. The green platy crystals were investigated in this work; they are rather unstable in air but quite stable in paraffin oil.

Examination of Weissenberg photographs showed that the crystals are orthorhombic; the systematic absences were: $h0l$ for $h = 2n + 1$, $0kl$ for $k + l = 2n + 1$; space group *Pnam* (D_{2h}^{16}) or *Pna2*₁ (C_{2v}^9). A crystal of approximate dimensions 0.12 × 0.11 × 0.10 mm was chosen and coated with paraffin oil to prevent crystal decomposition. A Syntex *P2*₁ diffractometer and Mo *K*α radiation with a graphite monochromator were used for lattice-parameter and intensity measurements by the 2θ – ω scan technique. The intensity of one periodically monitored reflexion displayed no observable trends. The data were corrected for Lorentz and polarization effects. Of 4247 accessible reflexions, 1905 with $I > 3\sigma(I)$ were used for the structure

determination. All calculations were performed on a Nova minicomputer with programs supplied by Syntex. Neutral-atom scattering factors used were those listed in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for Re, Cl and S atoms.

Of the two possible space groups, *Pnam* and *Pna2*₁, the centrosymmetric, *Pnam*, was the first choice. A three-dimensional Patterson map revealed the Re atoms in a crystallographic mirror plane at $z = \frac{1}{2}$. All further non-H atoms were found from subsequent difference maps; R then dropped to 0.10. The compound was identified as $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{ReCl}_5(\text{H}_2\text{O})]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. This structure was then refined by least-squares techniques, first with isotropic, then with anisotropic thermal parameters. Eight H atoms (bonded to N atoms) were placed in geometrically calculated positions at a distance of 1.0 Å from the bonded atoms. The remaining H atoms were found from a difference synthesis. Further refinement with fixed positional parameters for N-bonded H atoms reduced R to 0.046 and R_w to 0.032.* The final difference synthesis was featureless; the highest four peaks appeared about Re, corresponding in height to the H atoms of the earlier difference synthesis.

Discussion. The final atomic coordinates and their estimated standard deviations are listed in Table 1. Crystals of $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{ReCl}_5(\text{H}_2\text{O})]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ are composed of aquapentachlororhenate(IV) anions, Cl⁻ anions, dithiobisformamidinium cations and water of crystallization. The arrangement of the molecules in projection on the (001) plane is shown in Fig. 1. The more important interatomic distances and bond angles are listed in Table 2.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35426 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. The final positional parameters with e.s.d.'s in parentheses

	x	y	z	B _{eq} (Å ²)
Re	0.0638 (1)	0.1549 (1)	0.25	2.23
Cl(1)	0.1322 (2)	0.2846 (3)	0.1514 (2)	3.44
Cl(2)	0.0031 (2)	0.0144 (3)	0.1506 (2)	3.11
Cl(3)	-0.0305 (2)	0.3337 (5)	0.25	4.46
Cl(4)	0.3457 (2)	0.8913 (3)	0.0810 (2)	3.77
Cl(5)	0.1571 (2)	0.6657 (4)	0.25	3.41
S(1)	0.1512 (2)	0.7252 (3)	0.0548 (2)	3.31
S(2)	0.1720 (2)	0.7815 (3)	-0.0601 (2)	3.12
C(1)	0.0519 (5)	0.6799 (9)	0.0528 (5)	2.96
C(2)	0.1711 (5)	0.9802 (10)	-0.0574 (6)	2.79
N(1)	0.0277 (4)	0.6209 (8)	0.1196 (5)	3.31
N(2)	0.0092 (4)	0.7001 (8)	-0.0090 (5)	3.64
N(3)	0.1904 (5)	1.0458 (8)	-0.1233 (5)	3.82
N(4)	0.1541 (5)	1.0537 (9)	0.0073 (5)	4.10
O(1)	0.1490 (6)	-0.0058 (12)	0.25	4.72
O(2)	0.2928 (6)	0.0303 (13)	0.25	3.66
O(3)	0.2956 (10)	0.3474 (16)	0.25	5.42
H(11)	-0.027	0.591	0.125	7.7
H(12)	0.064	0.606	0.165	4.3
H(21)	-0.046	0.672	-0.007	5.5
H(22)	0.031	0.742	-0.059	5.0
H(31)	0.191	1.158	-0.127	4.5
H(32)	0.204	0.984	-0.170	2.9
H(41)	0.154	1.166	0.007	4.1
H(42)	0.142	0.999	0.057	5.7
H(1)	0.126 (10)	-0.107 (21)	0.25	7.2
H(10)	0.199 (9)	0.027 (15)	0.25	5.8
H(2)	0.305 (5)	-0.024 (9)	0.216 (5)	2.4
H(3)	0.243 (14)	0.341 (27)	0.25	16.6
H(30)	0.325 (14)	0.252 (30)	0.25	15.9

Table 2. Selected intramolecular distances (Å) and angles (°) in the title compound

Atoms marked with a prime are related to those at x,y,z by a mirror plane at x,y,½.

Re—Cl(1)	2.351 (2)	Re—Cl(2)	2.345 (2)
Re—Cl(3)	2.303 (4)	Re—O(1)	2.076 (10)
S(1)—C(1)	1.792 (9)	S(2)—C(2)	1.778 (9)
C(1)—N(1)	1.309 (11)	C(2)—N(3)	1.296 (12)
C(1)—N(2)	1.292 (11)	C(2)—N(4)	1.305 (12)
S(1)—S(2)	2.026 (3)	O(1)—Re—Cl(3)	179.8 (3)
O(1)—Re—Cl(1)	88.5 (3)	O(1)—Re—Cl(2)	87.5 (3)
Cl(3)—Re—Cl(1)	91.4 (1)	Cl(3)—Re—Cl(2)	92.6 (1)
Cl(1)—Re—Cl(1')	89.4 (1)	Cl(2)—Re—Cl(2')	90.6 (1)
Cl(1)—Re—Cl(2)	89.8 (1)	Cl(1)—Re—Cl(2')	175.9 (1)
S(2)—S(1)—C(1)	102.4 (3)	S(1)—S(2)—C(2)	102.9 (3)
S(1)—C(1)—N(1)	113.0 (6)	S(2)—C(2)—N(3)	115.4 (7)
S(1)—C(1)—N(2)	123.3 (7)	S(2)—C(2)—N(4)	121.9 (7)
N(1)—C(1)—N(2)	123.7 (8)	N(3)—C(2)—N(4)	122.7 (9)

Compounds of the type [MCl₅(H₂O)]ⁿ⁻ occur rather infrequently; in the case of Re it is, to the author's knowledge, the first example of the isolation of the [ReCl₅(H₂O)]⁻ anion. In the aquapentachlororhenate(IV) anions the water molecule, the Re atom and one Cl atom lie on the mirror plane. Thus, the complex anion has *m* (C_s) crystallographic symmetry.

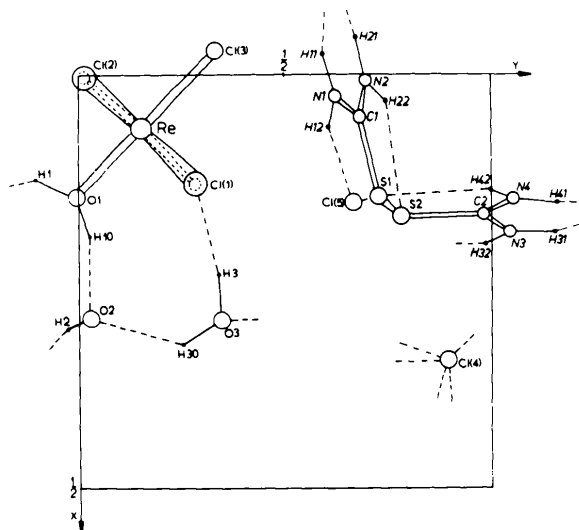


Fig. 1. The crystal structure of [(NH₂)₂CSSC(NH₂)₂]₂[ReCl₅(H₂O)]Cl₃·2H₂O: projection on the (001) plane.

The Re atom lies out of the plane of the four Cl_{cis} atoms at a distance of 0.082 (1) Å towards the Cl_{trans} atom, and the resulting Cl_{cis}—Re—Cl_{trans} angles exceed 90° [91.4 (1) and 92.6 (1)°]. The Re—Cl_{cis} distances of 2.351 (2) and 2.345 (2) Å are practically the same and comparable to those found in ReCl₆²⁻ anions: cf. 2.35 (1) (average) in (*p*-toluidinium)₂[ReCl₆] (Adman & Margulis, 1967), 2.353 (4) in K₂[ReCl₆] (Grundy & Brown, 1970) and 2.361 (3) Å in (NH₄)₂[ReCl₆] (Lisher, Cowlam & Gillott, 1979). The Re—Cl_{trans} distances of 2.303 (4) Å are only slightly, but significantly, shorter than the remaining Re—Cl bonds. The Re—aqua bond lengths of 2.076 (10) Å are shorter than distances in compounds of Re^{VII} (Beyer, Glemser & Krebs, 1968), Re^{VI} (Fraiss & Lock, 1972), Re^V (Lis, 1979) and Re^{III} (Koz'min, Novitskaia & Kuznetsov, 1973; Cotton, Frenz & Shive, 1975).

The dimensions of the dithiobisformamidinium cation are listed in Table 2. The bond lengths S—S of 2.026 (3), S—C of 1.792 (9) and 1.778 (9) and C—N

Table 3. Probable hydrogen bonds

Distances are in Å, angles in deg.			
X—H...Y	X...Y	X—H	H...Y / X—H...Y
N(1)—H(11)...Cl(4)	3.266 (7)	1.00	2.37 149
N(1)—H(12)...Cl(5)	3.180 (7)	1.00	2.23 157
N(2)—H(21)...Cl(4)	3.347 (7)	1.00	2.47 146
N(2)—H(22)...S(2)	3.075 (7)	1.00	2.50 117
N(3)—H(31)...Cl(4)	3.234 (7)	1.00	2.32 152
N(3)—H(32)...O(3)	2.781 (12)	1.00	1.81 164
N(4)—H(41)...Cl(4)	3.364 (8)	1.00	2.50 144
N(4)—H(42)...S(1)	3.046 (8)	1.00	2.45 118
O(1)—H(1)...Cl(5)	2.943 (11)	0.99 (19)	2.11 (19) 141 (11)
O(1)—H(10)...O(2)	2.547 (14)	0.93 (16)	1.65 (16) 163 (11)
O(2)—H(2)...Cl(4)	3.233 (6)	0.78 (8)	2.50 (8) 159 (8)
O(3)—H(3)...Cl(1)	3.363 (15)	0.93 (26)	2.61 (20) 139 (16)
O(3)—H(30)...O(2)	2.838 (17)	1.00 (27)	2.06 (28) 133 (16)

of 1.292 (11)–1.309 (11) Å are in agreement with those found in other dithiobisformamidinium salts (Villa, Manfredotti, Nardelli & Tani, 1972; Lis, 1979). Also, the S valency angles [102.9 (4) and 102.4 (3)°] and the torsion angle of the disulphide group [100.2 (5)°] lie in the normal range. The two thiourea parts of the cation are both planar.

The structure is held together by hydrogen bonds utilizing all H atoms. The data on these hydrogen bonds are given in Table 3. Two [O(1)–H(1)···Cl(5) and O(1)–H(10)···O(2)] may be classified as relatively strong.

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Bis(tetraethylammonium) Di- μ -sulphido-bis[oxo(disulphido)molybdenum]

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Abstract. [N(C₂H₅)₄]₂[Mo₂O₂S₂(S₂)₂], 2C₈H₂₀N⁺·Mo₂O₂S₆²⁻, *M*_r = 676.6, monoclinic, *P*2₁/c, *a* = 13.485 (3), *b* = 14.354 (3), *c* = 14.749 (3) Å, β = 97.50 (2)°, *U* = 2830.2 Å³, *Z* = 4, *D*_x = 1.588 Mg m⁻³; final *R* = 0.0358 for 4025 reflexions. The anion contains two Mo^v atoms, each with a terminal O²⁻ and an edge-on (S₂)²⁻ ligand, bridged by two S²⁻ ligands, and has approximate *C*_{2v} (*mm*) symmetry.

Introduction. The compound was obtained from a reaction between MoCl₃ and NaSph (1:5 molar ratio) in methanol, followed by treatment with NEt₄Cl, and was recrystallized from a methyl cyanide–diethyl ether mixture. Intensities were collected from a crystal of average dimension 0.28 mm by a profile-fitting procedure (Clegg, 1981) with graphite-monochromated Mo *K* α radiation (λ = 0.71069 Å) and a Stoe–Siemens AED four-circle diffractometer. 4025 unique reflexions with $7 \leq 2\theta \leq 60^\circ$ and $I \geq 2\sigma(I)$ were measured and corrected for absorption by an empirical method based on measurements of sets of

reflexions at different azimuthal angles (μ = 1.31 mm⁻¹; transmission factors range from 0.588 to 0.654). Cell dimensions were obtained from the diffractometer angles for 50 centred reflexions with $20 \leq 2\theta \leq 25^\circ$.

The structure was solved by Patterson and Fourier methods, and refined to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o)$]. Anisotropic thermal parameters were refined for all non-H atoms. H atoms were assigned isotropic thermal parameters fixed at 1.3 times the equivalent isotropic value for the corresponding C atom. C–H lengths and H–C–H angles were constrained to 0.96 Å and 109.5°.

The final *R* is 0.0358, with $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.0291$. Coordinates and derived bond lengths and angles are given in Tables 1 and 2.*

* Lists of structure factors, H atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35466 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.