to the sulfur atom of the tetrahydrothiophene ligand in a distorted tetrahedral array shown in Fig. 1. The shortest interligand C—C distance is 3·26 Å.

The structures of $(CH_3C_5H_4)_3U(SC_4H_8)$ and $(C_5H_5)_3U(OC_4H_8)$ (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983) are similar. The lack of planarity of the three atoms bonded to the sulfur atom in the tetrahydrothiophene complex and to the oxygen atom in the tetrahydrofuran complex suggests but one lone pair of electrons in the U—S and U—O bonds. The U—S and U—O distances are 2·986 (5) and 2·55 (1) Å respectively.

A comparison of the structures of $(CH_3C_5H_4)_3$-$U(SC_4H_8)$ and $(CH_3C_5H_4)_3U\{P(CH_3)_3\}$ (Brennan & Zalkin, 1985) shows some geometrical differences. The Cp—U—Cp angles in the tetrahydrothiophene complex are all within 0·4° from 118°, a small distortion from what would be expected for the base-free complex, whereas the comparable angles in the trimethylphosphine complex (106·0, 119·8 and 119·4°) indicate considerable distortion. The tetrahydrothiophene ligand, with its polarizable lone pair of electrons instead of a methyl group, could be sterically less restricting than the trimethylphosphine ligand, thus decreasing ligand–cyclopentadienyl repulsive interactions. The average U—Cp distances in the tetrahydrothiophene and the trimethylphosphine complexes are 2·54 (1) and 2·52 (2) Å respectively. The U—S and U—P distances in the two structures are 2·986 (5) and 2·972 (6) Å respectively.

The U^{III}—S distance reported here [2·986 (5) Å] is similar to the U^{VI}—S distance [2·94 (1) Å] found in the uranium thioether coordination complex, *cis*-dichloro-[*meso*-bis(*trans*-2-hydroxycyclohexyl) sulfide-*O,O,S*]-dioxouranium(VI) (Baracco *et al.*, 1975), and the difference in the above distances is much smaller than expected. For a coordination number of six, the estimated ionic radius of U^{III} is 0·295 Å larger than that for U^{VI} (Shannon, 1976); and the difference is even larger when the effect of a larger coordination number of the U^{III} complex (ten *vs* seven) is considered.

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References

BARACCO, L., BOMBIERI, G., DEGETTO, S., FORSELLINI, E., MARANGONI, G., PAOLUCCI, G. & GRAZIANI, R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2161–2164.
BRENNAN, J. G. & ANDERSEN, R. A. (1985). *J. Am. Chem. Soc.* **107**, 514–516.
BRENNAN, J. G. & ZALKIN, A. (1985). *Acta Cryst.* C**41**, 1038–1040.
International Tables for X-ray Crystallography (1974). Vol. IV. Table 2.2, pp. 71–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
PERRY, D. L., ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1982). *Inorg. Chem.* **21**, 237–240.
SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–757.
WASSERMAN, H. J., ZOZULIN, A. J., MOODY, D. C., RYAN, R. R. & SALAZAR, K. V. (1983). *J. Organomet. Chem.* **254**, 305–311.

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Refinement of Trimethylammonium Trichlorocuprate(II) Dihydrate, $[NH(CH_3)_3][CuCl_3].2H_2O$

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Abstract. $M_r = 266·05$, monoclinic, $P2_1/c$, $a = 7·5066$ (8), $b = 7·8873$ (5), $c = 16·758$ (1) Å, $\beta = 91·914$ (9)°, $V = 991·6$ (3) Å^3, $Z = 4$, $D_x = 1·781$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 29·76$ cm^{-1}, $F(000) = 540$, $T = 297$ K, $R = 0·028$ for 2655 observed independent reflections. The previous determination [Losee, McElearney, Siegel, Carlin, Kahn, Roux & James (1972). *Phys. Rev.* B, **6**, 4342–4348] is confirmed and improved. All H atoms are located. The two independent square-planar $CuCl_2$.-$2H_2O$ subunits have significantly different bond lengths due to distortions by long Cu—Cl contacts. The Cl^- anion is involved in four hydrogen bonds of intermediate strength with the hydrate groups. The cation is connected by a very weak bifurcated hydrogen bond to the $CuCl_2.2H_2O$ chains.

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Introduction. The magnetic properties of the title compound have been the subject of several studies (Losee, McElearney, Siegel, Carlin, Khan, Roux & James, 1972; Algra, de Jongh, Huiskamp & Carlin, 1977; Ritter, Drumheller, Kite, Snively & Emerson, 1983). It corresponds to a linear chain compound and behaves as a very weak one-dimensional spin $= \frac{1}{2}$ Heisenberg ferromagnet. Magnetic ordering occurs below 1 K. The crystal structure was reported by Losee *et al.* (1972), but was of low accuracy ($R = 0{\cdot}088$). Therefore a redetermination of the structure was undertaken.

Experimental. Green transparent crystals by slow evaporation of an aqueous solution of $[NH(CH_3)_3]Cl$ and $CuCl_2.2H_2O$, crystal used: $0{\cdot}125 \times 0{\cdot}30 \times 0{\cdot}34$ mm, Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $\omega/1\theta$ scan, cell parameters from setting angles of 25 reflections with $18 < \theta < 24°$, hemisphere up to $2\theta = 60°$, range of hkl: $0\rightarrow10$, ±11, ±23, 5525 reflections measured, max. $(\sin\theta/\lambda) = 0{\cdot}70$ Å^{-1}, 2877 unique, three standard reflections every 5500 s; strongest standard increased 20% because of decreasing amount of extinction, weak standards remained stable; empirical absorption correction based on ψ scans of six reflections (North, Phillips & Mathews, 1968), relative transmission range: 0·68–1·00, equivalent reflections averaged: $R_{int} = 0{\cdot}025$, 2655 reflections with $I > 0{\cdot}5\sigma(I)$ used, weighting according to $w(F^2) = [\sigma^2(F^2) + (0{\cdot}03F^2)^2]^{-1}$, structure redetermined from Patterson and Fourier syntheses, all H atoms from $\Delta\rho$ map, refinement on $|F|$ with anisotropic thermal parameters (H atoms isotropic), isotropic extinction coefficient $g = 1{\cdot}88\ (2) \times 10^{-6}$, final $R = 0{\cdot}028$, $wR = 0{\cdot}028$, $S = 1{\cdot}13$, $(\Delta/\sigma)_{max} = 0{\cdot}07$, final $\Delta\rho$ less than $0{\cdot}35$ e Å^{-3}, scattering and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974), calculations with *SDP* program system (Enraf–Nonius, 1982).

Discussion. The positional parameters are reported in Table 1,* the relevant bond distances and angles in Table 2. The present study confirms the result of Losee *et al.* (1972) but is an order of magnitude more accurate. Comparison of both determinations by a half-normal-probability plot of the fractional coordinates gave no significant differences. The structure contains square-planar $CuCl_2.2H_2O$ subunits stacked along **a** (Fig. 1).

Distorted octahedral coordination at Cu is completed by two rather long Cu—Cl bonds with the next layers. The octahedra form one-dimensional chains by edge-sharing. Similar chains are observed in the crystal structure of $CuCl_2.2H_2O$ (Engberg, 1970). There is a clear correlation between the long and short Cu—Cl

Table 1. *Positional parameters and isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B(Å^2)
Cu(1)	0·0	0·0	0·0	1·792 (4)
Cu(2)	0·5	0·0	0·0	1·702 (4)
Cl(1)	0·29831 (5)	0·07787 (5)	−0·10017 (2)	2·078 (6)
Cl(2)	0·21490 (4)	−0·00432 (5)	0·09914 (2)	1·946 (6)
Cl(3)	0·25381 (5)	0·49776 (5)	0·08284 (2)	2·334 (6)
O(1)	0·0363 (1)	−0·2432 (1)	−0·02119 (7)	2·16 (2)
O(2)	0·4578 (1)	−0·2448 (1)	−0·02674 (6)	1·91 (2)
N	0·2562 (2)	−0·2997 (2)	−0·18372 (7)	2·13 (2)
C(1)	0·2484 (3)	−0·4828 (2)	−0·1661 (1)	3·06 (4)
C(2)	0·4171 (2)	−0·2565 (2)	−0·2293 (1)	3·02 (4)
C(3)	0·0914 (2)	−0·2387 (3)	−0·2260 (1)	3·17 (4)
H(1)	0·082 (2)	−0·295 (3)	0·011 (1)	3·8 (5)
H(2)	−0·048 (2)	−0·301 (2)	−0·036 (1)	3·2 (4)
H(3)	0·414 (2)	−0·301 (3)	0·010 (1)	3·6 (4)
H(4)	0·541 (2)	−0·287 (2)	−0·038 (1)	3·4 (4)
H(5)	0·262 (2)	−0·254 (2)	−0·142 (1)	1·8 (3)
H(6)	0·350 (3)	−0·512 (2)	−0·133 (1)	3·5 (5)
H(7)	0·167 (3)	−0·500 (2)	−0·130 (1)	4·9 (6)
H(8)	0·249 (2)	−0·549 (2)	−0·212 (1)	3·1 (4)
H(9)	0·400 (2)	−0·312 (2)	−0·276 (1)	3·1 (4)
H(10)	0·516 (3)	−0·287 (3)	−0·201 (1)	4·1 (5)
H(11)	0·408 (3)	−0·138 (3)	−0·231 (1)	5·0 (5)
H(12)	0·089 (2)	−0·292 (2)	−0·274 (1)	3·3 (4)
H(13)	0·002 (3)	−0·273 (3)	−0·193 (1)	4·4 (5)
H(14)	0·108 (2)	−0·123 (3)	−0·232 (1)	4·0 (5)

Table 2. *Bond distances* (Å) *and angles* (°)

2× Cu(1)—Cl(1)	2·9087 (5)	N—C(1)	1·475 (2)
2× Cu(1)—Cl(2)	2·2770 (5)	N—C(2)	1·490 (2)
2× Cu(1)—O(1)	1·971 (1)	N—C(3)	1·486 (2)
2× Cu(2)—Cl(1)	2·3060 (5)		
2× Cu(2)—Cl(2)	2·7530 (5)		
2× Cu(2)—O(2)	2·005 (1)		

2× Cl(1)—Cu(1)—Cl(2)	83·34(1),96·66(1)	Cu(1)—Cl(1)—Cu(2)	91·32 (1)
2× Cl(1)—Cu(1)—O(1)	89·31(4),90·69(4)	Cu(1)—Cl(2)—Cu(2)	96·06 (1)
2× Cl(2)—Cu(1)—O(1)	88·96(4),91·04(4)	C(1)—N—C(2)	111·4 (2)
2× Cl(1)—Cu(2)—Cl(2)	86·44(1),93·56(1)	C(1)—N—C(3)	112·0 (2)
2× Cl(1)—Cu(2)—O(2)	89·93(3),90·07(3)	C(2)—N—C(3)	111·0 (2)
2× Cl(2)—Cu(2)—O(2)	89·85(3),90·15(3)		

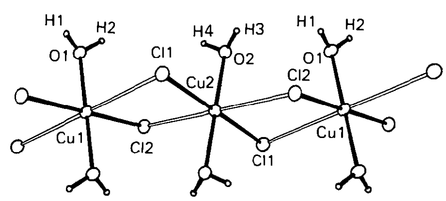

Fig. 1. View of the $CuCl_2.2H_2O$ subunits stacked along **a**. The thermal ellipsoids correspond to the 30% probability surfaces; H atoms on arbitrary scale.

* Lists of structure factors, anisotropic temperature factors and hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42228 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

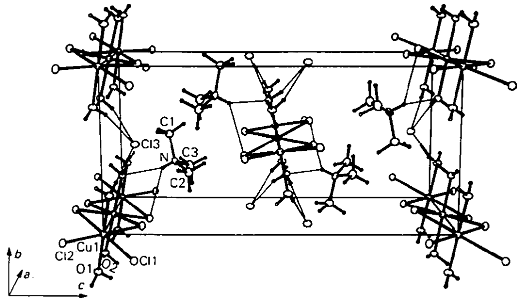

Fig. 2. View of the crystal structure of $[NH(CH_3)_3][CuCl_3].2H_2O$ along **a**. The thermal ellipsoids correspond to the 20% probability surfaces.

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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References

ALGRA, H. A., DE JONGH, L. J., HUISKAMP, W. J. & CARLIN, R. L. (1977). *Physica* (*Utrecht*), **92**B, 187–200.
ENGBERG, A. (1970). *Acta Chem. Scand.* **24**, 3510–3526.
Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
LOSEE, D. B., MCELEARNEY, J. N., SIEGEL, A., CARLIN, R. L., KAHN, A. A., ROUX, J. P. & JAMES, W. J. (1972). *Phys. Rev. B*, **6**, 4342–4348.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
RITTER, M. B., DRUMHELLER, J. E., KITE, T. M., SNIVELY, L. O. & EMERSON, K. (1983). *Phys. Rev. B*,**28**, 4949–4954.

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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) $[(NH_2)_2CSSC(NH_2)_2]Cl[ReCl_5\{SC(NH_2)_2\}]$, $M_r = 627·3$, orthorhombic, *Pbca*, $a = 11·082$ (7), $b = 15·850$ (13), $c = 19·864$ (14) Å, $V = 3489$ Å^3, $Z = 8$, $D_m = 2·38$, $D_x = 2·39$ Mg m^{-3}, $F(000) = 2376$, μ(Mo $K\alpha$, $\lambda = 0·71069$ Å) $= 8·61$ mm^{-1}, room temperature, final $R = 0·035$ and $wR = 0·033$ for 2257 non-zero reflexions. (II) $[(NH_2)_2CSSC(NH_2)_2]_2Cl_2[ReCl_6].3H_2O$, $M_r = 828·4$, orthorhombic, *Amam* (D_{2h}^{17}), $a = 16·768$ (6), $b = 13·672$ (8), $c = 11·348$ (5) Å, $V = 2601·6$ Å^3, $Z = 4$, $D_m = 2·10$, $D_x = 2·11$ Mg m^{-3}, $F(000) = 1604$, μ(Mo $K\alpha$) $= 6·09$ 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 $[ReCl_6]^{2-}$ 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 $[ReCl_5\{SC(NH_2)_2\}]^-$ 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 ReO_4^- and $ReCl_6^{2-}$ 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 K_2ReCl_6 in dilute HCl is exposed to air. After some days at the top of the solution yellow crystals are

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