

Chlorotrakis(*N,N'*-dicyclohexylthiourea-*S*)tellurium(II) chloride, a tellurium complex with a TeClS_3 coordination sphere

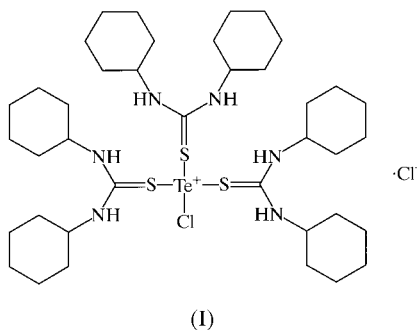
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During the synthesis of a series of square-planar $[\text{TeCl}_2(\text{stu})_2]$ complexes, where stu represents bulky di- or tetrasubstituted thioureas, the title compound, $[\text{TeCl}\{(\text{C}_6\text{H}_{11}\text{NH})_2\text{CS}\}_3]\text{Cl}$ or $\text{C}_{39}\text{H}_{72}\text{ClN}_6\text{S}_3\text{Te}^+\text{Cl}^-$, was the unexpected result when stu was *N,N'*-dicyclohexylthiourea. The complex is square planar, with Te—S distances of 2.5803 (4), 2.6211 (4) and 2.8214 (4) Å, and a Te—Cl distance of 2.6485 (4) Å, indicating a small *trans* influence of the thiourea ligand.

Comment

The expected reaction between thiourea and TeO_2 dissolved in HCl is $\text{Te}^{4+} + 4\text{stu} + 4\text{Cl}^- = [\text{TeCl}_2(\text{stu})_2] + (\text{stu})_2\text{Cl}_2$ (Foss & Hauge, 1959; Husebye, 1983). In the present case, a third stu ligand has displaced one of the two chloride ligands to give the title $[\text{TeCl}(\text{stu})_3]\text{Cl}$ product, (I), where stu is $(\text{C}_6\text{H}_{11}\text{NH})_2\text{CS}$.



The structure of the cation in (I) is square planar, with a TeClS_3 coordination sphere. This is the first time such coordination has been observed for tellurium. The two thiourea ligands *trans* to each other point up from the coordination plane, whereas the third points down. This conformation has minimized steric interactions between the ligands (Fig. 1).

The SCN_2 units of the thiourea ligands are approximately planar and the SCN_2 units *trans* to each other (S1 and S3) form angles with the coordination plane of 67.80 (3) and 74.75 (3)°, respectively. The remaining thiourea assumes a corresponding

angle of 74.31 (3)°. Angles around 70° seem to be common for *trans*- $[\text{TeCl}_2(\text{stu})_2]$ complexes (Husebye *et al.*, 2001).

The interplanar $\text{SCN}_2/\text{SCN}_2$ angle is 54.69 (6)° for the two *trans*-related thioureas. This is a rather large angle compared with the values in the *trans* complexes mentioned above, which are around 13° (Husebye *et al.*, 2001). An analogous bromide, $[\text{TeBr}(\text{stu})_3]\text{Br}$, has been synthesized and its structure reported by Kumar *et al.* (1990). Here, stu is 1-methylimidazole-2(3*H*)-thione, an *N,N'*-dimethyl-substituted ethylthiourea ligand. In this complex, two adjacent thiourea ligands point to the same side of the coordination plane, whereas the third points to the opposite side. This is a geometry that brings the thiourea ligands into closer contact compared with the geometry of the present chloride analogue, but then the bulk of the thiourea ligand is smaller in the bromide.

The Te—S bond lengths in (I) vary considerably. Bonding in square-planar Te^{II} complexes is of the three-centre four-electron (3c-4e) type, with a bond order of 0.5. In the near linear S1—Te—S3 sequence, Te—S1 is 2.5803 (4) Å and Te—S3 2.8214 (4) Å. Asymmetry in two such weak and chemically equivalent bonds is not uncommon in Te^{II} compounds. The average bond length of 2.7009 Å is slightly longer than 2.68 Å, the average found for such 3c-4e systems (Husebye, 1983; Haiduc *et al.*, 1994). However, great asymmetry in the two Te—S bond lengths often results in an increase in the average bond lengths in linear S—Te—S systems (Husebye, 1983). It is

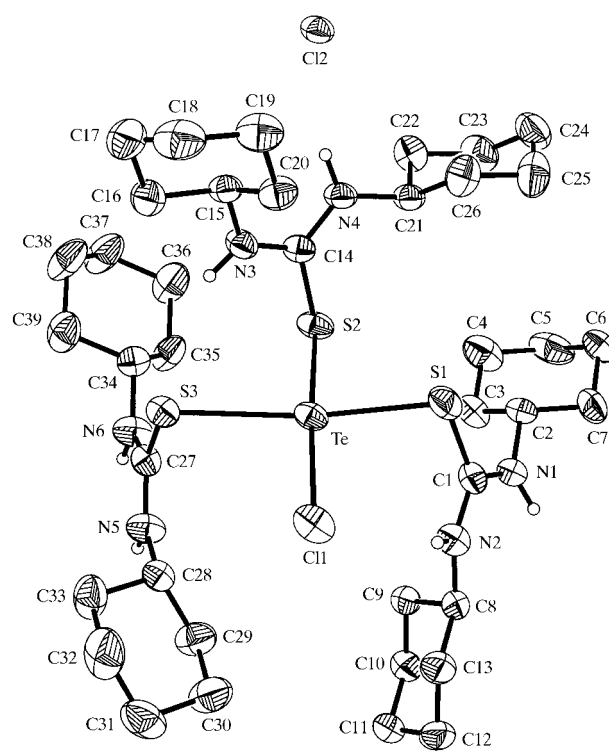


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and cyclohexyl H atoms have been omitted for clarity. H atoms on N are shown as small spheres of arbitrary radii.

interesting to note that the corresponding average Te—S bond length in the bromide complex with a nearly symmetric S—Te—S sequence is 2.701 Å (Kumar *et al.*, 1990), the same value as that found in the present chloride. The Te—S2 bond length in (I) is 2.6211 (4) Å and it is positioned *trans* to Te—Cl1, which has a bond length of 2.6485 (4) Å, indicating a weak *trans* influence of the *N,N'*-dicyclohexylthiourea ligand. However, this influence is still greater than that of the Cl[−] ligand, indicated by the shortening of the Te—S bond at the

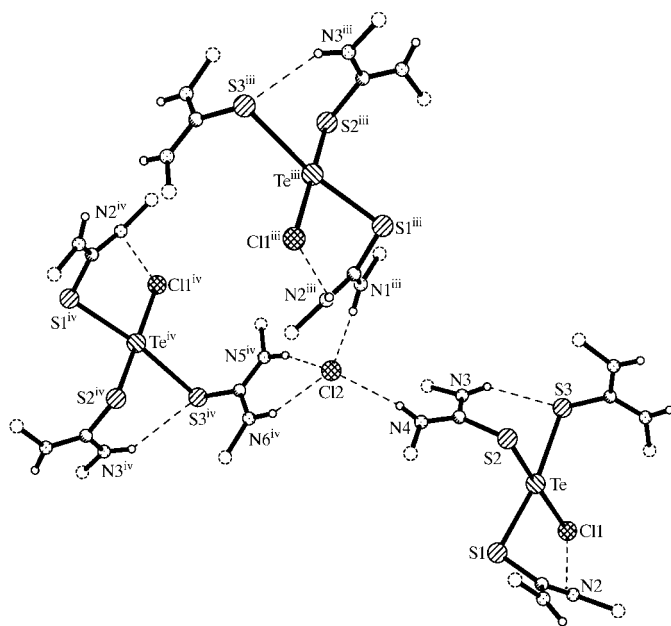


Figure 2

The molecular packing in (I), with hydrogen bonds indicated by dotted lines. For clarity, only the C atoms (dotted circles) joined to the main structural unit in the cyclohexyl groups are shown [symmetry codes: (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$].

expense of the Te—Cl bond, which lengthens relative to the average found in Cl—Te—Cl 3c-4e systems (Husebye *et al.*, 2001).

In the ligands, the C=S bond lengths are C1=S1 1.7576 (17), C14=S2 1.7504 (14) and C27=S3 1.7336 (14) Å. These values may be compared with the corresponding length of 1.681 (20) Å found in free thioureas (Allen *et al.*, 1987) and reflect a normal lengthening upon coordination, a long Te—S bond corresponding to a short C=S bond and *vice versa*. The C—N bond length within the SCN₂ group of the three thioureas has an average value of 1.328 Å. This indicates partial double-bond character through transfer of charge from N to S.

The Cl[−] anion is connected to the S2 thiourea by an N4—H4...Cl2 hydrogen bond. The Cl[−] ligand forms an intramolecular N2—H2...Cl1 bond with the S1 thiourea; this is reflected in a small S1—C1—N2 angle of only 117.57 (13)°. There is also a possible weak intramolecular N3—H3...S3 hydrogen bond. Intermolecular N—H...Cl hydrogen bonds connect the ions into a three-dimensional network, as shown in Fig. 2; data for the hydrogen bonds are given in Table 2.

Experimental

N,N'-Dicyclohexylthiourea was obtained from Lancaster Synthesis. The synthesis of the tellurium complex followed a modification of the literature method of Foss & Hauge (1959, 1961). TeO₂ (1.603 g, 10 mmol) was dissolved in hot concentrated HCl (20 ml). This solution was added rapidly with stirring to *N,N'*-dicyclohexylthiourea (9.62 g, 40 mmol) dissolved in hot 95% ethanol (110 ml). Upon cooling the resulting red-brown solution to room temperature, small yellow crystals of (I) and some red lumps formed. The latter were discarded and the remainder was filtered and washed with cold ethanol to which a few drops of concentrated HCl had been added [yield 6.1 g, 66.7%; m.p. 415–417 K (decomposition)]. Analysis, found: Cl 7.75, S 10.45%; calculated for C₃₉H₇₂Cl₂N₆S₃Te: Cl 7.73, S 10.49%.

Crystal data

C₃₉H₇₂ClN₆S₃Te⁺·Cl[−]
M_r = 919.71
 Orthorhombic, *Pbca*
a = 20.1931 (5) Å
b = 20.2156 (4) Å
c = 23.1990 (4) Å
V = 9470.2 (3) Å³
Z = 8
D_x = 1.290 Mg m^{−3}

Mo *Kα* radiation
 Cell parameters from 8192 reflections
 $\theta = 1.7\text{--}32.9^\circ$
 $\mu = 0.91\text{ mm}^{-1}$
T = 173 (2) K
 Octahedron, yellow
 0.37 × 0.25 × 0.22 mm

Data collection

Bruker SMART 2K CCD diffractometer
 10 136 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 32.9^\circ$
 $h = -30 \rightarrow 30$
 $k = -30 \rightarrow 29$
 $l = -34 \rightarrow 33$

17 005 independent reflections
 10 136 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 32.9^\circ$
 $h = -30 \rightarrow 30$
 $k = -30 \rightarrow 29$
 $l = -34 \rightarrow 33$

Refinement

Refinement on F^2
 $R(F) = 0.030$
 $wR(F^2) = 0.066$
 $S = 0.92$
 17 005 reflections
 460 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.47\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Te—S1	2.5803 (4)	N3—C14	1.3290 (18)
Te—S2	2.6211 (4)	N3—C15	1.4774 (17)
Te—S3	2.8214 (4)	S3—C27	1.7336 (14)
Te—Cl1	2.6485 (4)	N4—C14	1.3232 (17)
S1—C1	1.7576 (17)	N4—C21	1.4743 (19)
N1—C1	1.324 (2)	N5—C27	1.3337 (18)
N1—C2	1.4766 (19)	N5—C28	1.4660 (19)
N2—C1	1.326 (2)	N6—C27	1.3341 (19)
N2—C8	1.478 (2)	N6—C34	1.4568 (19)
S2—C14	1.7504 (14)		
S1—Te—S2	88.971 (15)	S1—C1—N1	120.81 (12)
S1—Te—S3	169.951 (12)	S1—C1—N2	117.57 (13)
S1—Te—Cl1	88.782 (15)	N1—C1—N2	121.58 (15)
S2—Te—S3	90.956 (13)	N3—C14—N4	120.85 (13)
S2—Te—Cl1	174.031 (13)	S2—C14—N3	118.07 (11)
S3—Te—Cl1	92.220 (13)	S2—C14—N4	121.08 (11)
Te—S1—C1	100.63 (5)	S3—C27—N5	121.23 (12)
Te—S2—C14	100.85 (5)	S3—C27—N6	121.90 (12)
Te—S3—C27	102.70 (5)	N5—C27—N6	116.87 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2A...C11	0.88	2.56	3.2431 (15)	135
N3—H3A...S3	0.88	2.79	3.5618 (12)	147
N1—H1A...Cl2 ⁱ	0.88	2.46	3.3007 (14)	160
N4—H4A...Cl2	0.88	2.39	3.2294 (12)	160
N5—H5A...Cl2 ⁱⁱ	0.88	2.39	3.2290 (13)	160
N6—H6A...Cl2 ⁱⁱ	0.88	2.42	3.2445 (13)	157

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

All H atoms were treated as riding, with N—H = 0.88, C—H (CH) = 1.00 and C—H (CH₂) = 0.99 Å. The isotropic displacement parameters of the H atoms were fixed at $1.2U_{eq}$ of their parent atoms. The maximum residual peak was located 0.82 Å from Te.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1475). Services for accessing these data are described at the back of the journal.

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