

***trans*-Tetrachlorobis(*N,N'*-dimethylimidazolidine-2-thione)tellurium(IV), a thiourea complex of tellurium with asymmetric Te—S bonds**

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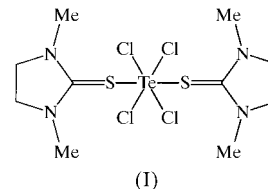
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The structure of the title compound,  $[\text{TeCl}_4(\text{C}_5\text{H}_{10}\text{N}_2\text{S})_2]$  or  $\text{C}_{10}\text{H}_{20}\text{Cl}_4\text{N}_4\text{S}_2\text{Te}$ , has been solved in order to study the stereochemical activity of the lone pair of electrons on  $\text{Te}^{\text{IV}}$ . The two crystallographically independent molecules in the asymmetric unit both show a distorted octahedral coordination of the Te atom. The two Te—S bonds are *trans* to each other in both molecules and are greatly asymmetric, with bond lengths of 2.5686 (7) versus 2.8557 (8) Å and 2.5859 (7) versus 2.8165 (9) Å. The Te—Cl bond lengths lie in the range 2.5236 (7)–2.5589 (8) Å. The asymmetric Te—S bonds and a large S—Te—Cl angle of *ca* 97° involving the long Te—S bonds indicate stereochemical activity of the lone pair of electrons on Te.

**Comment**

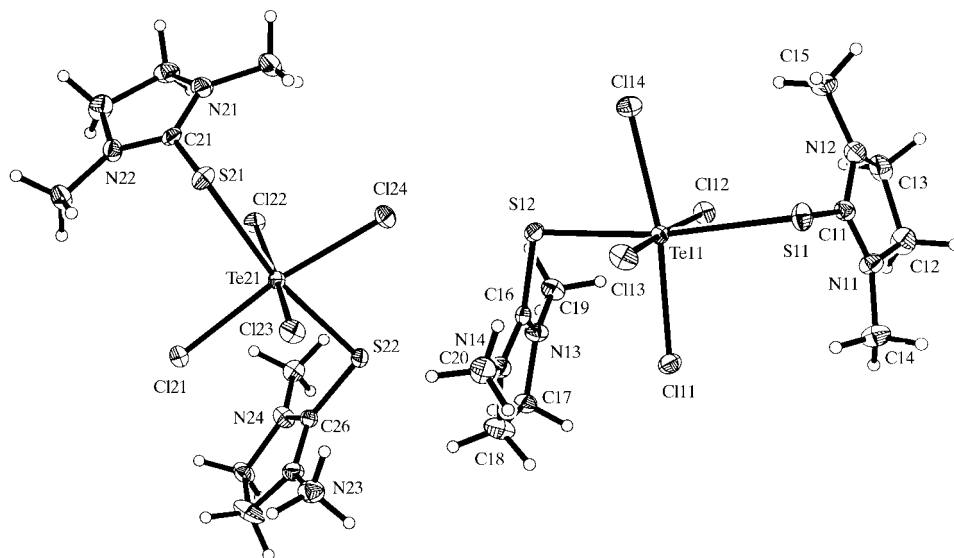
The reaction of  $\text{TeO}_2$  dissolved in HCl with thioureas typically results in  $\text{Te}^{\text{II}}$  complexes. This is caused by redox reactions where  $\text{Te}^{\text{IV}}$  is reduced to  $\text{Te}^{\text{II}}$ , whereas two thioureas are oxidized to the corresponding disulfide (Husebye, 1983). The only exceptions to this rule are represented by tetramethylthiourea (tmtu; Husebye & George, 1969; Esperås *et al.*, 1975) and benzimidazolethione (bit), a cyclic thiourea (Von Deuten *et al.*, 1979a). The ligand benzothiazolethione (btt), related to benzimidazolethione by replacing an NH group with S, also stabilizes the resulting  $\text{Te}^{\text{IV}}$  complex (Von Deuten *et al.*, 1979b). The  $\text{Te}^{\text{IV}}$  complexes above are octahedral with  $\text{TeX}_4\text{S}_2$  (*X* is a halogen) coordination spheres. The bit complex has a *cis* configuration and the others are *trans* complexes. Of these complexes, monoclinic *trans*- $[\text{TeCl}_4(\text{tmtu})_2]$  is the most interesting. It is greatly distorted from octahedral symmetry in a way which indicates the stereochemical activity of the lone pair of electrons on Te (Esperås *et al.*, 1975). The other complexes are either centrosymmetric {orthorhombic *trans*- $[\text{TeX}_4(\text{tmtu})_2]$ , *X* = Br or Cl, and *trans*- $[\text{TeCl}_4(\text{btt})_2]$ } or have a twofold rotation axis through the Te atom [*cis*- $[\text{TeCl}_4(\text{bit})_2]$ ]. The lone pair of electrons in these four compounds is stereochemically inert in the sense that it seems not to occupy

a site in the coordination sphere of Te. The average Te—S bond length in the three centrosymmetric thiourea compounds is 2.703 Å. To explore the lone pair activity in  $\text{Te}^{\text{IV}}$  complexes further, it was decided to synthesize another tetraalkylthiourea complex of  $\text{Te}^{\text{IV}}$ , the title complex, (I), and investigate its structure.



The structure of (I), *trans*- $[\text{TeCl}_4(\text{dit})_2]$  (dit is *N,N'*-dimethylimidazolidine-2-thione), is a racemic twin and has two crystallographically independent molecules in the asymmetric unit, as illustrated in Fig. 1. The two molecules are octahedral *trans* complexes and both show considerable distortion from ideal symmetry (Table 1). The equatorial  $\text{TeCl}_4$  groups are planar to within 0.175 Å for molecule 1 and 0.190 Å for molecule 2. In molecule 1, the interplanar angles between  $\text{TeCl}_4$  and the rings connected to S11 and S12 are 10.88 (15) and 17.71 (12)°, respectively. The corresponding angles in molecule 2 are 12.69 (14) and 18.77 (12)°, respectively. Superpositioning of molecules 1 and 2 reveals a difference in the orientation of the rings bonded to the S atoms. Whereas one pair of rings in molecules 1 and 2, bonded to S12 and S22, roughly coincide, the other two are related by an approximate mirror plane through S11, Te11, Cl11, Cl14 and S12. Thus, the structure of molecule 2 is related to that of molecule 1 by a rotation of approximately 170° around the Te11—S11 bond of molecule 1. The Cl14—Te11—S11—C11 and Cl24—Te21—S21—C21 torsion angles are −96.26 (10) and 97.48 (10)°, respectively. The torsion angles C11—S11—S12—C16 [78.35 (14)°] and C21—S21—S22—C26 [−79.57 (15)°] indicate that the rings in molecules 1 and 2 are synclinal with respect to one another.

There is a great asymmetry of the nearly linear S—Te—S sequences, where the long Te—S bonds are close to 2.84 Å and the short bonds are close to 2.58 Å. In addition, the Cl $n$ 1—Te $n$ 1—Sn1 angles (*n* = 1 or 2 for molecules 1 and 2, respectively) involving the longer Te—S bonds in both complexes are *ca* 97°, whereas 'trans' to these there are Cl—Te—S angles of about 78°. The three *fac*-positioned ligand donor atoms, Cl $n$ 1, Cl $n$ 3 and Sn1, form weaker bonds to the central Te atom than the other ligand atoms, although the differences in the Te—Cl bond lengths are small (average 0.025 Å). This may indicate some stereochemical activity of the lone pair of electrons on Te. Such activity was indicated in the related monoclinic tetramethylthiourea complex (Esperås *et al.*, 1975). In the latter, the asymmetry in the nearly linear S—Te—S sequence is less pronounced, with the long and short Te—S bonds being 2.726 (1) and 2.649 (1) Å, respectively. However, the greater asymmetry in the Te—Cl bonds and the bond angles around  $\text{Te}^{\text{IV}}$  in the latter complex indicate that the lone pair of electrons moves towards an equatorial position in a  $\Psi$ -pentagonal bipyramidal structure.



**Figure 1**

A view of the two molecules in (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The bonding in octahedral Te complexes may be described by three mutually perpendicular three-centre four-electron systems,  $L_1\text{--Te--}L_2$  (Husebye, 1983). These systems are based on the overlap of suitable ligand orbitals with the three  $5p$  orbitals of Te. The role of the lone pair of electrons can be seen in different ways. In the case of an 'inert' pair, it does not occupy a position in the coordination polyhedron but the Te–ligand bond lengths are greater than expected and the lone pair plays an antibonding role, occupying an  $a_{1g}^*$  antibonding orbital (Urch, 1964). Another possibility is, of course, for the lone pair to occupy a position in the coordination polyhedron fully. This is not quite the case here, but the three long *fac* bonds from Te<sub>1</sub> to Sn<sub>1</sub>, Cl<sub>1</sub> and Cl<sub>3</sub> may indicate a lone pair beginning to make its presence felt in a monocapped octahedral position between the three latter atoms; the asymmetry in the Te–Cl bonds is, however, small. For an octahedral molecule with seven electron pairs in the valency shell of the central atom, there is a triply degenerate stretching vibration of  $t_{1u}$  symmetry that could lead to a short bond with a long bond *trans* to it (Burdett, 1980); in the local  $D_{4h}$  symmetry here, an  $a_{2u}$  stretching vibration can, by a similar mechanism, lead to just one *trans* long/short pair, leaving the four remaining bonds unperturbed. This is likely to be the case here, with the stronger Te<sub>1</sub>–Sn<sub>2</sub> bonds on average being 0.26 Å shorter than Te<sub>1</sub>–Sn<sub>1</sub>.

The asymmetry in Te–S bonding in molecules 1 and 2 is reflected in the S=C bonds of the ligand, which in turn influences the C=N bond lengths. For the long Te–S bonds, the average S=C and C=N bond lengths are 1.724 and 1.337 Å, respectively. For the short Te–S bonds, the corresponding lengths are 1.749 and 1.328 Å, respectively. Although they are statistically less significant for the C=N bonds, these values agree well with those found for the [TeCl<sub>4</sub>(tmtu)<sub>2</sub>] complex (Esperås *et al.*, 1975; Husebye &

George, 1969). In free thioureas, C=S = 1.681 (20) Å and C=N = 1.35 (2) Å (Allen *et al.*, 1987). In the uncomplexed dit ligand, these bond lengths are 1.673 (4) and 1.338 Å (averaged), respectively (Chieh & Cheung, 1983). The lengthening of the C=S bonds and the shortening of the N=C bonds upon complex formation illustrates the partial  $\pi$ -bonding and the delocalization of charge from the N towards the S atoms upon formation of the Te–S bonds.

The angles and planarity of the ligands illustrate the  $sp^2$  character of the C(S) and N atoms. The ligand rings connected to S11 and S21 are planar to within 0.095 Å, and those connected to S12 and S22 are planar to within 0.015 Å. This also reflects a stronger mesomeric shift of electron density

from the N atoms towards S in the more planar rings, corresponding to stronger Te–S bonds from S12 and S22 compared with S11 and S21. The interplanar ring angles are 26.06 (16)° for molecule 1 and 28.71 (16)° for molecule 2.

## Experimental

Tellurium dioxide (0.798 g, 5 mmol) was dissolved in hot concentrated HCl (7 ml). To this solution was added MeOH (10 ml). The ligand *N,N'*-dimethylimidazole-2-thione was prepared according to the literature procedures of Maier (1970) and Chieh & Cheung (1983). This ligand (2.604 g, 20 mmol) was dissolved in hot concentrated HCl (10 ml) and MeOH (10 ml) was added. The two solutions were mixed while warm and a red-brown solid was formed. The product was separated by filtration and washed with MeOH and ether [yield 2.45 g, 92%; m.p. 477–479 K (decomposition)]. Recrystallization from dimethylformamide gave crystals suitable for X-ray analysis.

### Crystal data

C<sub>10</sub>H<sub>20</sub>Cl<sub>4</sub>N<sub>4</sub>S<sub>2</sub>Te  
 $M_r = 529.82$   
 Orthorhombic, *Pna*2<sub>1</sub>  
 $a = 14.2386$  (9) Å  
 $b = 9.4823$  (7) Å  
 $c = 28.063$  (2) Å  
 $V = 3788.8$  (5) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.858$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 8192 reflections  
 $\theta = 2.27\text{--}32.41^\circ$   
 $\mu = 2.353$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Plate, red-brown  
 0.35 × 0.17 × 0.08 mm

### Data collection

Bruker SMART 2K CCD diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (*SHELXTL*; Sheldrick 1997)  
 $T_{\min} = 0.493$ ,  $T_{\max} = 0.843$   
 62 390 measured reflections

6655 independent reflections (plus 6090 Friedel-related reflections)  
 12 135 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\max} = 32.41^\circ$   
 $h = -20 \rightarrow 20$   
 $k = -14 \rightarrow 14$   
 $l = -40 \rightarrow 40$

## Refinement

Refinement on  $F^2$

$R(F) = 0.026$

$wR(F^2) = 0.052$

$S = 1.182$

12 745 reflections

388 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0114P)^2 + 3.9629P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 1.24 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.70 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983)

Flack parameter = 0.296 (10)

Methyl H atoms were calculated by refinement of the torsion angles involving N—Me after localizing the pertinent H-atom positions by difference electron-density analysis (C—H = 0.93 Å and O—H = 0.90 Å).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

**Table 1**

Selected geometric parameters (Å, °).

Te11—Cl11	2.5392 (7)	Te21—Cl21	2.5453 (7)
Te11—Cl12	2.5270 (7)	Te21—Cl22	2.5256 (7)
Te11—Cl13	2.5589 (7)	Te21—Cl23	2.5589 (7)
Te11—Cl14	2.5276 (7)	Te21—Cl24	2.5236 (7)
Te11—S11	2.8557 (8)	Te21—S21	2.8165 (8)
Te11—S12	2.5686 (7)	Te21—S22	2.5859 (7)
S11—C11	1.718 (3)	S21—C21	1.730 (3)
S12—C16	1.747 (3)	S22—C26	1.750 (3)
C11—N11	1.337 (4)	C21—N21	1.335 (4)
C11—N12	1.341 (4)	C21—N22	1.337 (4)
N13—C16	1.331 (4)	N23—C26	1.325 (4)
N14—C16	1.328 (4)	N24—C26	1.328 (4)
Cl11—Te11—Cl13	91.66 (2)	Cl21—Te21—Cl23	91.41 (2)
Cl12—Te11—Cl11	89.06 (2)	Cl22—Te21—Cl21	89.33 (2)
Cl12—Te11—Cl13	174.40 (2)	Cl22—Te21—Cl23	173.05 (2)
Cl12—Te11—Cl14	89.45 (2)	Cl24—Te21—Cl22	89.31 (2)
Cl14—Te11—Cl11	169.94 (2)	Cl24—Te21—Cl21	170.01 (2)
Cl14—Te11—Cl13	90.80 (2)	Cl24—Te21—Cl23	91.13 (2)
Cl11—Te11—S11	96.12 (2)	Cl21—Te21—S21	97.84 (2)
Cl12—Te11—S11	89.91 (2)	Cl22—Te21—S21	90.16 (2)
Cl13—Te11—S11	84.49 (2)	Cl23—Te21—S21	82.89 (2)
Cl14—Te11—S11	93.83 (2)	Cl24—Te21—S21	92.06 (2)
Cl11—Te11—S12	92.15 (2)	Cl21—Te21—S22	92.57 (2)
Cl12—Te11—S12	91.95 (2)	Cl22—Te21—S22	92.10 (2)
Cl13—Te11—S12	93.57 (2)	Cl23—Te21—S22	94.77 (2)
Cl14—Te11—S12	77.96 (2)	Cl24—Te21—S22	77.59 (2)
S12—Te11—S11	171.55 (2)	S22—Te21—S21	169.38 (2)
C11—S11—Te11	99.41 (10)	C21—S21—Te21	99.59 (9)
C16—S12—Te11	102.41 (9)	C26—S22—Te21	102.25 (9)
N11—C11—S11	124.5 (2)	N21—C21—S21	125.7 (2)
N11—C11—N12	110.0 (3)	N21—C21—N22	110.6 (2)
N12—C11—S11	125.5 (2)	N22—C21—S21	123.7 (2)
N13—C16—S12	123.6 (2)	N23—C26—S22	123.8 (2)
N14—C16—S12	124.2 (2)	N24—C26—S22	123.6 (2)
N14—C16—N13	112.2 (2)	N23—C26—N24	112.6 (3)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1048). Services for accessing these data are described at the back of the journal.

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