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Synthesis and Structure of *trans*-Bis[2(3*H*)-benzimidazolethione]bis(thiourea)tellurium(II) Chloride, $[Te(CH_4N_2S)_2(C_7H_6N_2S)_2]Cl_2$

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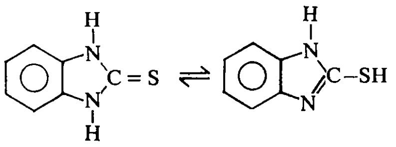
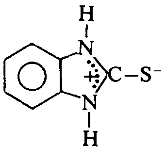
Abstract. $M_r = 651{\cdot}15$, monoclinic, $P2_1/c$, $a = 6{\cdot}623\,(1)$, $b = 11{\cdot}387\,(3)$, $c = 16{\cdot}085\,(3)$ Å, $\beta = 93{\cdot}90\,(2)°$, $V = 1210$ Å^3, $D_x = 1{\cdot}787$ Mg m^{-3}, $Z = 2$, $F(000) = 643{\cdot}99$, $\mu(\text{Mo}\,K\alpha) = 1{\cdot}808$ mm^{-1}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $T = 293$ K, final $R = 0{\cdot}029$ and $R_w = 0{\cdot}027$ for 2068 reflections. The Te atom, lying at the crystallographic centre of symmetry, is bonded to two thiourea S atoms and two 2(3*H*)-benzimidazolethione S atoms in a *trans*-square-planar arrangement. The TeS_4 group has the dimensions Te—S(1) = 2·694 (2), Te—S(2) = 2·685 (1) Å, and S(1)—Te—S(2) = 89·4 (1)°.

Introduction. Te^{II} is a typical soft acid and a large number of complexes of Te^{II} with S ligands have been reported (Foss, 1970). Of the S ligands, the most extensively studied unidentate types are thiourea and its derivatives. Particularly interesting are the square-planar complexes TeL_4X_2 [L: thiourea group; X: halides (Elder, Marcuso & Boolchand, 1977; Barnard, Donaldson, Grimsey, Dennes, Russo & Calogero, 1981; Anderson, 1971; Fosheim, Foss, Scheie & Solheimsnes, 1965; Ault & Husebye, 1978)] and $TeL_2L'_2$, the latter being a mixed-ligand complex of Te^{II} containing thiourea and thiosulphonate groups (Foss, Maroy & Husebye, 1965; Ase, Moe & Solheim, 1971; Ase, 1969; Foss, Lyssandtrae, Moe & Tysseland, 1973; Ase & Roti, 1974). The condensation product of *o*-phenylenediamine with carbon disulphide can have two extreme tautomeric forms, namely 2(3*H*)-benzimidazolethione (also known as phenylenethiourea) (ptu) (I) and (III), and 2-benzimidazolethiol (II). Generally, this compound is referred to as (II) in the literature, though photoelectron spectroscopy (Takahashi & Yabe, 1969), X-ray crystal structure (Form, Raper & Downie, 1976) and solution studies indicate that the compound is present mostly as (I). It was considered interesting to find the mode of ligation of the compound towards Te^{II}. In this paper the synthesis and structure of the title compound, an interesting mixed-ligand complex, are reported. The structure of a Te^{IV} complex with the 2(3*H*)-benzimidazolethione ligand has been reported (Deuten, Schnabel & Klar, 1979).



(I) (II)



(III)

Experimental. *Preparative method.* Single crystals grown as follows: 0·05 g (~0·1 m*M*) of tetrakis(thiourea)tellurium(II) chloride (Fosheim, Foss, Scheie & Solheimsnes, 1965) were dissolved in 10 ml of methanol containing 0·5 g (~6 m*M*) thiourea; 5 ml of concentrated HCl added followed by 0·10 g (~0·5 m*M*) of 2(3*H*)-benzimidazolethione dissolved in 5 ml methanol; mixture then diluted with another 10 ml methanol and kept aside for slow evaporation of the methanol; over 6 to 12 h transparent orange red crystals of the complex separated out; crystals first washed five times with 1*M* HCl and then twice with a 0·02*M* solution of 2(3*H*)-benzimidazolethione in acetone and vacuum dried.

D_m not determined. Single crystal *ca* 0·20 × 0·30 × 0·35 mm. Unit-cell parameters by least-squares refinement of setting angles of 22 centred high-angle reflections. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Intensities of all reflections (h: 0→8, k: 0→15, l: −21→21) with $2 < \theta < 28°$ measured at room temperature. ω–2θ scan mode, scan angle $\Delta\omega = (0{\cdot}80 + 0{\cdot}35\tan\theta)°$. Two standard reflections ($\bar{1}64$, $\bar{1}60$) monitored every hour:

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$); $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

	x	y	z	U_{eq}
Te	0	0	0	26 (1)
S(1)	631 (3)	−247 (1)	1663 (1)	45 (2)
C(1)	−1212 (9)	719 (5)	1959 (3)	35 (5)
N(1)	−690 (8)	1749 (5)	2297 (3)	49 (4)
N(2)	−3138 (8)	446 (5)	1871 (3)	46 (5)
S(2)	3552 (2)	1130 (1)	−28 (1)	34 (1)
C(2)	2948 (7)	2585 (4)	−41 (3)	25 (4)
N(3)	2775 (6)	3280 (4)	620 (2)	27 (4)
N(4)	2754 (6)	3270 (4)	−724 (2)	27 (4)
C(3)	2579 (7)	4446 (4)	362 (3)	25 (4)
C(4)	2553 (7)	4440 (5)	−500 (3)	27 (4)
C(5)	2429 (9)	5489 (5)	−953 (4)	38 (5)
C(6)	2304 (9)	6505 (5)	−503 (4)	41 (6)
C(7)	2301 (8)	6521 (5)	367 (4)	38 (5)
C(8)	2449 (9)	5483 (5)	805 (4)	37 (5)
Cl	4215 (2)	2620 (1)	2518 (1)	40 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Te—S(1)	2·694 (2)	Te—S(2)	2·685 (1)
S(2)—C(2)	1·704 (5)	S(1)—C(1)	1·734 (6)
C(1)—N(1)	1·329 (8)	C(1)—N(2)	1·311 (8)
C(2)—N(3)	1·337 (6)	C(2)—N(4)	1·346 (6)
N(3)—C(3)	1·395 (6)	N(4)—C(4)	1·389 (7)
C(3)—C(4)	1·386 (7)	C(4)—C(5)	1·399 (8)
C(5)—C(6)	1·370 (8)	C(6)—C(7)	1·400 (9)
C(7)—C(8)	1·376 (8)	C(8)—C(3)	1·385 (8)
S(1)—Te—S(2)	89·4 (1)		
Te—S(1)—C(1)	98·2 (2)	Te—S(2)—C(2)	105·1 (2)
S(1)—C(1)—N(1)	120·3 (4)	S(1)—C(1)—N(2)	121·2 (4)
N(1)—C(1)—N(2)	118·5 (4)	S(2)—C(2)—N(3)	126·8 (3)
S(2)—C(2)—N(4)	125·6 (3)	N(3)—C(2)—N(4)	107·3 (3)
C(2)—N(3)—C(3)	109·8 (3)	C(2)—N(4)—C(4)	110·5 (3)
N(3)—C(3)—C(4)	106·7 (3)	N(3)—C(3)—C(8)	131·8 (4)
C(3)—C(4)—N(4)	105·6 (3)	N(4)—C(4)—C(5)	133·4 (4)
C(3)—C(4)—C(5)	120·9 (4)	C(4)—C(5)—C(6)	116·7 (4)
C(5)—C(6)—C(7)	122·9 (5)	C(6)—C(7)—C(8)	119·7 (4)
C(7)—C(8)—C(3)	118·3 (4)	C(8)—C(3)—C(4)	121·5 (4)

no significant variation in intensity. Of 3389 reflections collected, 2068 reflections with $I > 3\sigma(I)$ considered as observed. No absorption correction. $R_{\rm int} = 0{\cdot}01$. Te atom positioned at the centre of symmetry (0,0,0). Fourier maps revealed the positions of the other nonhydrogen atoms. Isotropic refinement reduced R to 0·071 showing very little anisotropic motion of the atoms in the molecule. Refinement by full-matrix least squares on F with anisotropic thermal parameters for the nonhydrogen atoms. All H atoms (from $\Delta\rho$ map) refined isotropically. Refinement converged to final $R = 0{\cdot}029$ and $R_w = 0{\cdot}027$ for 2068 reflections; $w = 1/[\sigma^2(F_o) + 0{\cdot}003F_o^2]$ in the final stages. $(\Delta/\sigma)_{\rm max} = 0{\cdot}5$. 182 parameters refined. Final $\Delta\rho$ map shows max. and min. heights of 0·94 and −0·88 e $Å^{-3}$ and is featureless. All calculations carried out using *SHELX76* (Sheldrick, 1976). Atomic scattering factors for nonhydrogen atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion correction factors for nonhydrogen atoms from Cromer & Liberman (1970).

Discussion. Fractional coordinates, bond lengths and bond angles are given in Tables 1 and 2.[*]

Fig. 1 depicts the molecular configuration drawn by *ORTEP* (Johnson, 1965). The mixed-ligand complex consists of a $[Te(ptu)_2(tu)_2]^{2+}$ cation and Cl^- anions. The Te^{2+} has an S_4 ligand coordination which is very nearly square-planar. The two 2(3*H*)-benzimidazolethione ligands are *trans* to each other and similarly the two thioureas. The Te—S bond lengths are nearly symmetric with Te—S(tu) = 2·694 (2) and Te—S(ptu) = 2·685 (1) Å and an intraligand angle of 89·4 (1)°. Although the average Te—S bond length of 2·689 (9) Å is considerably longer than 2·36 Å (Alcock, 1972), the sum of the covalent single-bond radii of Te and S, it is typical for such bonds found in numerous Te^{II} complexes (Ault & Husebye, 1978) with monodentate S ligands. Following the notation given by Elder, Marcuso & Boolchand (1977) the cation has the ++−− conformation. The planar ligand molecules are arranged in such a manner that one pair, namely tu and ptu, lies above the other pair below the TeS_4 plane providing an inversion symmetry in the entire molecular fragment. This is the most common conformation found in similar compounds (Anderson, 1971; Fosheim, Foss, Scheie & Solheimsnes, 1965; Ault & Husebye, 1978; Foss, Maroy & Husebye, 1965; Ase, Moe & Solheim, 1971; Ase, 1969; Foss, Lyssandtrae, Moe & Tysseland, 1973; Ase & Roti, 1974), with the sole exception of $Te(etu)_4Cl_2$ (Elder, Marcuso & Boolchand, 1977).

In most Te^{II} complexes containing unidentate S ligands the TeS_4 chromophore shows inequivalence in bond lengths. These distortions could arise for two reasons: (*a*) the close proximity of counter ions with respect to the two lone pairs of electrons on Te^{II}, and (*b*) the close proximity of counter ions to the S ligands themselves. Data on (*b*) have been deposited.

In the ptu ligand in the present structure, the S(2)—C(2) bond length of 1·704 (5) Å corresponds to a

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[*] Lists of anisotropic thermal parameters, coordinates of the H atoms, hydrogen-bond parameters, least-squares planes, counter-ion positions and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39270 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

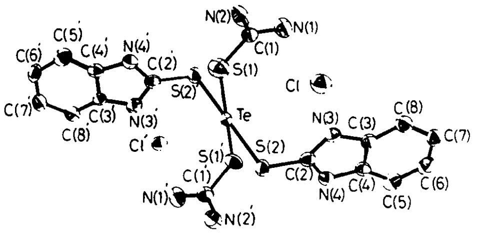

Fig. 1. *ORTEP* plot of the molecule, with 50% probability thermal ellipsoids.

partial double bond of 1·671 (8) Å observed in the free ligand (Form, Raper & Downie, 1976), but is much shorter than the 1·79 Å quoted in *cis*-bis[2(3*H*)-benzimidazolethione]tetrachlorotellurium(IV)–dioxane (Deuten, Schnabel & Klar, 1979). This S—C bond length also agrees with those obtained for similar compounds referred to in *Introduction*. The C(2)—N(3) and C(2)—N(4) bond lengths [1·337 (6) and 1·346 (6) Å] do not show significant variation in keeping with the thione structure and agree with the value [1·362 (6) Å] quoted in the free ptu crystal structure and with the 1·353 (14) and 1·317 (13) Å in the 2(3*H*)-benzimidazolethione–Te^{IV} complex (Deuten, Schnabel & Klar, 1979). Hence the bond parameters obtained for our compound clearly indicate the presence of thione form (III). C—C bond lengths are in the range 1·370 (8) to 1·400 (9) Å and C—C—C angles are in the range 116·7 (4) to 122·9 (5)°. The average N—H and C—H bond lengths in the ptu ligand are 0·84 (5) and 0·88 (6) Å respectively. The ptu group is planar within a maximum deviation of 0·041 (4) Å from the least-squares plane.

The thiourea SCN_2 moiety is planar with the maximum deviation from the least-squares plane through the atoms being 0·028 (5) Å. The S—C bond length [1·734 (6) Å] and C—N partial double bonds [1·329 (8) and 1·311 (8) Å] are normal for thiourea ligands. The average N—H bond is 0·87 (2) Å.

The Cl^- ions remain outside the coordination sphere of the Te atom, Te—Cl being 5·618 (2) Å. However, the Cl^- ion remains approximately in the least-squares plane of the SCN_2 thiourea and ptu groups, the deviation of the ion from these two planes being 0·014 (1) and 0·855 (1) Å respectively. Two N atoms of the thiourea group are involved in hydrogen bonding with the Cl^- ion, as revealed by the distances 3·292 (6) and 3·453 (6) Å. Furthermore, the same Cl^- ion participates in hydrogen bonding with the NH group of the ptu ligand also, with distances of 3·225 (4) and 3·214 (4) Å. There is a short intermolecular S···S van der Waals interaction [S(2)···S(2)($1-x$, $-y$, $-z$) = 3·207 (2) Å].

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Structure of Chloro(diethyldithiocarbamato)(triphenylphosphine)nickel(II), $[NiCl(C_5H_{10}NS_2)\{P(C_6H_5)_3\}]$

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Abstract. $M_r = 504·69$, triclinic, $P\bar{1}$, $a = 9·808$ (2), $b = 11·690$ (2), $c = 14·026$ (2) Å, $\alpha = 97·63$ (1), $\beta = 118·35$ (1), $\gamma = 108·81$ (1)°, $V = 1258·4$ Å^3, $Z = 2$, $D_x = 1·33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·049$ mm^{-1}, $T = 300$ K, $F(000) = 524$, final $R = 0·052$ for 1773 reflections. Ni^{II} displays planar fourfold coordination with the following parameters: Ni—S(*trans* to Cl) = 2·170 (4), Ni—S(*trans* to P)

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