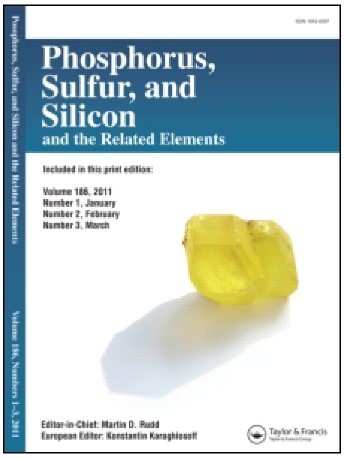

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Cis-Trans Isomerism in Square Planar [TeX 2 (stu) 2] Complexes (X = Br - , I -) with Bulky Substituted Thiourea (stu) Ligands. Syntheses and Structures of Four New Tellurium(II) Complexes

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CIS-TRANS ISOMERISM IN SQUARE PLANAR $[TeX_2(stu)_2]$ COMPLEXES ($X = Br^-, I^-$) WITH BULKY SUBSTITUTED THIOUREA (stu) LIGANDS. SYNTHESES AND STRUCTURES OF FOUR NEW TELLURIUM(II) COMPLEXES

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The complexes were synthesised by adding a hot solution of the appropriate substituted thiourea in MeOH (Br^- complexes) or DMF (I^- complexes) to a solution of TeO_2 dissolved in hot conc. HCl. The structures of the resulting four-coordinate square planar complexes, cis-$[TeBr_2\{(^iPrNH)_2CS\}_2]$ (**1**), cis-$[TeBr_2\{(^iBuNH)_2CS\}_2]$ (**2**), trans-$[TeI_2\{(^iPrNH)_2CS\}_2]$ (**3**), *and* trans-$[TeI_2\{(^iBuNH)_2CS\}_2]$ (**4**), *were studied by means of X-ray crystallographic methods. The average Te-S bond length in* **1** *and* **2** *is 2.5364 Å. The corresponding average Te-Br bond length is 2.9639 Å, reflecting the stronger* trans *influences of the two thioureas as compared to that of bromide. In* **3** *and* **4** *where there is no* trans *influence affecting the Te-ligand bonds, the average Te-S and Te-I bond lengths are 2.6926 and 2.9761 Å respectively. Tetraalkyl- or aryl-substituted thioureas alone as well as bulky disubstituted thioureas together with I^- ligands seem to favor formation of* trans *complexes.*

Keywords: Cis-trans isomerism; large thiourea ligands; synthesis; Te(II) complexes; X-ray structure

The present work represents a continuation of our study of tellurium(II) complexes with thiourea and halide ligands. In a recent article,[1] we discussed the structure and bonding of four complexes of the type $[TeCl_2(stu)_2]$ with stu being the substituted thioureas $(^iPrNH)_2CS$, $(^iBuNH)_2CS$, $(PhNMe)_2CS$, and $(Et_2N)_2CS$. In order to study the influence of the larger halides on the complex geometry and bonding in such complexes with bulky thiourea ligands, we synthesized the complexes of the first two thioureas above with bromide and iodide as halide

Dedicated to the memory of Professor William E. McErwen.

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ligands and studied their structures by means of x-ray crystallographic methods.

RESULTS AND DISCUSSION

The four complexes, $[TeBr_2\{(^iPrNH)_2CS\}_2]$ (**1**), $[TeBr_2\{(^iBuNH)_2CS\}_2]$ (**2**), $[TeI_2\{(^iPrNH)_2CS\}_2]$ (**3**), and $[TeI_2\{(^iBuNH)_2CS\}_2]$ (**4**), were prepared in a manner similar to that of the chloride analogs[1] according to the equation $TeO_2 + 4HX + 4stu = [TeX_2(stu)_2] + (stu)_2X_2 + 2H_2O$. Complex **3** crystallized with two DMF molecules per complex molecule. For $X = I^-$, the complexes could be prepared by adding a saturated solution of sodium iodide in methanol to a methanolic solution of the corresponding chloride complex but for **3** the resulting crystals were not suitable for structural analysis. The molecular structures of **1** and **2** are shown in Figure 1, while those of **3** and **4** are shown in Figure 2. Hydrogen bonding is shown in Figures 3–6. Bond lengths and angles are listed in Tables I–III.

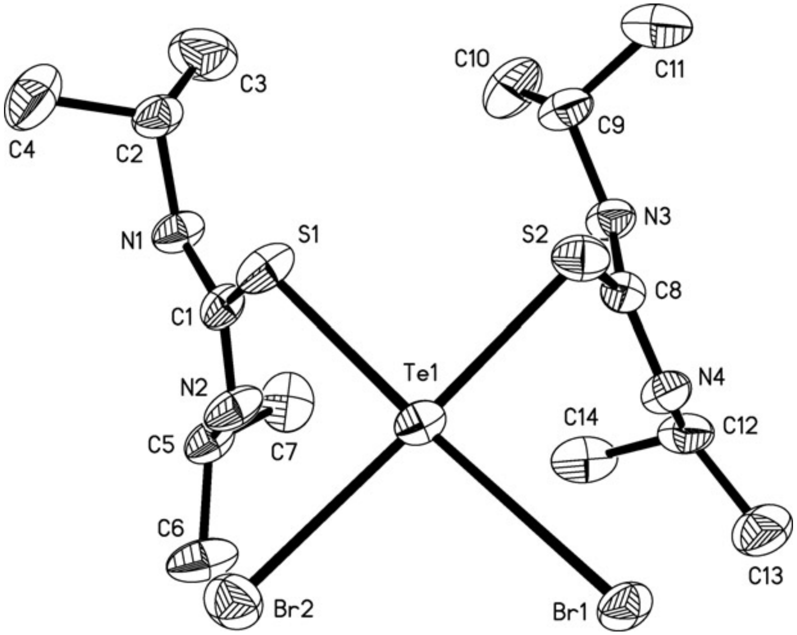

FIGURE 1 The structures of the *cis*-complexes, $[TeBr_2\{(^iPrNH)_2CS\}_2]$, **1** (one of the two similar but crystallographically nonequivalent molecules, left), and $[TeBr_2\{(^iBuNH)_2CS\}_2]$, **2** (right).

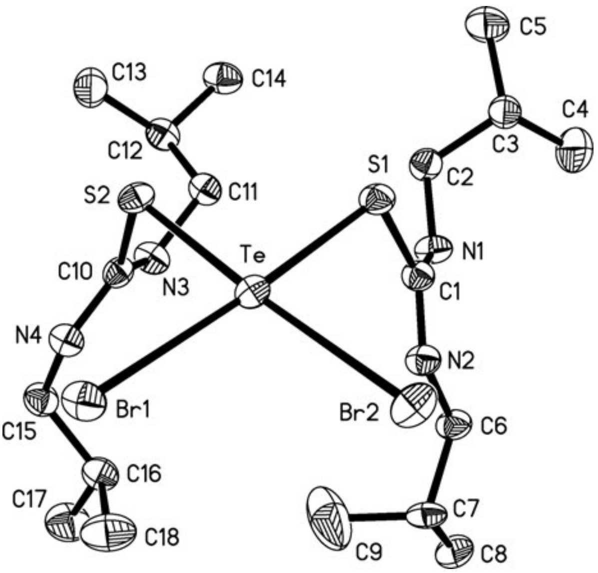

FIGURE 2 The structure of the *trans* complexes, $[TeI_2\{(^{i}PrNH)_2CS\}_2]$, **3** (The DMF disolvate left), and $[TeI_2\{(^{i}BuNH)_2CS\}_2]$ **4** (right).

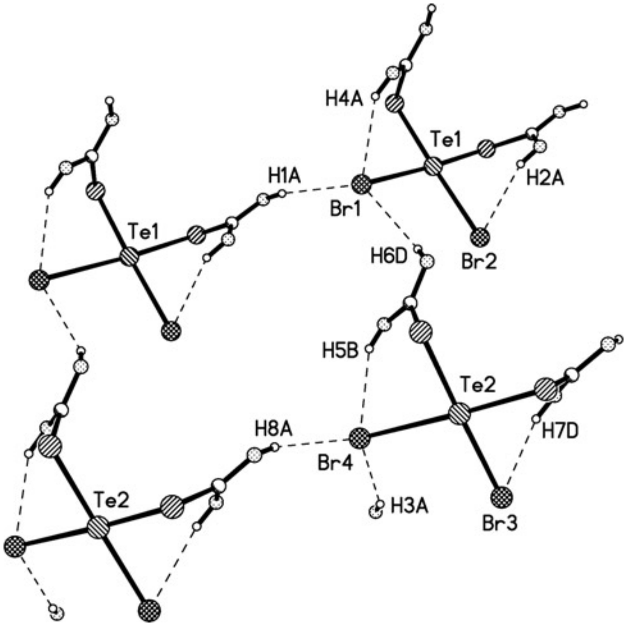

FIGURE 3 Hydrogen bonding in **1**. Isopropyl groups omitted.

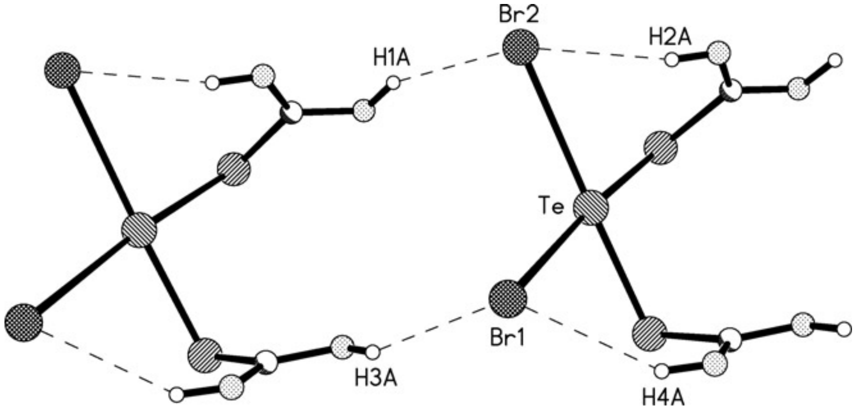

FIGURE 4 Hydrogen bonding in **2**. Isobutyl groups omitted.

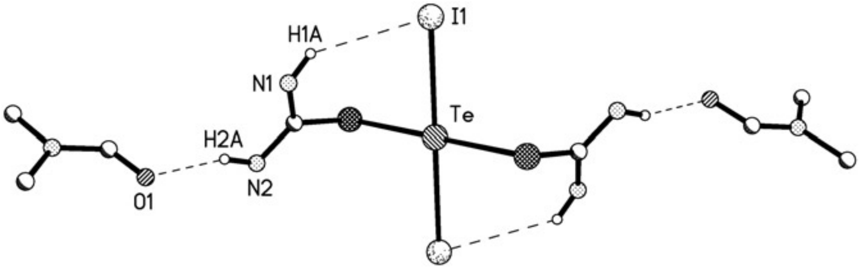

FIGURE 5 Hydrogen bonding in **3**. Isopropyl groups omitted.

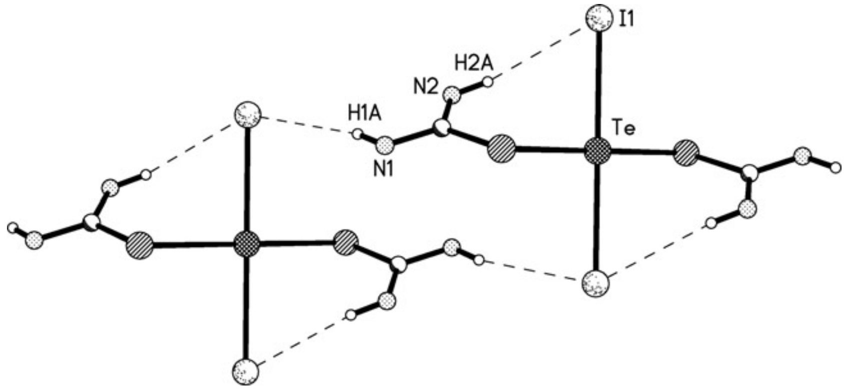

FIGURE 6 Hydrogen bonding in **4**. Isobutyl groups omitted.

TABLE I Selected Bond Lengths (Å) and Angles (°) for the *cis*-Complexes **1** and **2**

Complex **1**	Bond		Bond Angle
Te1-S1	2.5176(7)	S1-Te1-S2	89.10(3)
Te1-S2	2.5671(8)	S1-Te1-Br1	176.95(2)
Te1-Br1	3.0058(3)	S2-Te1-Br2	177.96(2)
Te1-Br2	2.8435(4)	S1-Te1-Br2	88.93(2)
C1-S1	1.756(3)	S2-Te1-Br1	88.00(2)
C1-N1	1.324(3)	Br1-Te1-Br2	93.95(1)
C1-N2	1.321(4)	Te1-S1-C1	106.4(1)
C8-S2	1.759(3)	Te1-S2-C8	100.2(1)
C8-N3	1.320(4)	S1-C1-N1	118.7(2)
C8-N4	1.325(4)	S1-C1-N2	120.1(2)
Te2-S3	2.6087(7)	N1-C1-N2	121.1(2)
Te2-S4	2.4792(7)	S2-C8-N3	120.1(2)
Te2-Br3	2.8003(4)	S2-C8-N4	118.0(2)
Te2-Br4	3.1519(4)	N3-C8-N4	121.9(3)
C15-S3	1.752(3)	S3-Te2-S4	91.04(2)
C15-N5	1.329(3)	S3-Te2-Br3	178.17(2)
C15-N6	1.322(3)	S4-Te2-Br4	176.92(2)
C22-S4	1.761(3)	S4-Te2-Br3	87.29(2)
C22-N7	1.322(4)	S3-Te2-Br4	88.26(2)
C22-N8	1.321(3)	Br3-Te2-Br4	93.44(1)
		Te2-S3-C15	103.1(1)
		S3-C15-N5	118.3(2)
		S3-C15-N6	120.0(2)
		N5-C15-N6	121.6(3)
		Te2-S4-C22	104.6(1)
		S4-C22-N7	120.0(2)
		S4-C22-N8	118.8(2)
		N7-C22-N8	121.1(3)
Complex **2**			
Te-S1	2.5466(5)	S1-Te-S2	89.91(2)
Te-S2	2.4994(5)	S1-Te-Br1	175.24(1)
Te-Br1	2.9651(2)	S2-Te-Br2	176.51(2)
Te-Br2	3.0166(3)	S1-Te-Br2	86.74(1)
C1-S1	1.761(2)	S2-Te-Br1	85.48(1)
C1-N1	1.324(2)	Br1-Te-Br2	97.89(1)
C1-N2	1.320(6)	Te-S1-C1	103.1(1)
C10-S2	1.767(2)	S1-C1-N1	119.5(1)
C10-N3	1.318(2)	S1-C1-N2	119.7(6)
C10-N4	1.324(2)	N1-C1-N2	120.4(6)
		Te-S2-C10	98.61(6)
		S2-C10-N3	121.3(1)
		S2-C10-N4	117.0(1)
		N3-C10-N4	121.6(2)

TABLE II Selected Bond Lengths (Å) and Angles (°) for the *trans*-Complexes **3** and **4**

Bond/Angle	**3**	**4**
Te-S1	2.6836(4)	2.7016(5)
Te-I1	2.98195(14)	2.9701(2)
C1-S1	1.744(2)	1.731(2)
C1-N1	1.326(2)	1.338(2)
C1-N2	1.324(2)	1.327(2)
S1-Te-I1	89.14(1)	90.47(1)
S1-Te-I1A[a]	90.86(1)	89.53(1)
Te-S1-C1	99.74(5)	105.00(6)
S1-C1-N1	118.0(1)	120.2(2)
S1-C1-N2	121.7(1)	121.0(1)
N1-C1-N2	120.3(2)	118.8(2)

[a] A indicates an atom related to the unique one by a molecular center of symmetry.

Complex Structures

The four [$TeX_2(stu)_2$] ($X = Br^-, I^-$) complexes are all four-coordinate and square planar. Complexes **1** and **2** with $X = Br^-$ have a *cis* configuration while **3** and **4** with $X = I^-$ have a *trans* configuration. In **1** there are two crystallographically independent, but quite similar molecules in the unit cell. The maximum deviation of any atom in the coordination

TABLE III Hydrogen Bonding (Å, °) in Complexes **1–4**

Ident.	D-H···A	D-H	H···A	D···A	D-H···A	Pos. of A
1	N1-H1A···Br1	0.88	2.66	3.489(2)	156.4	x, y − 1, z
	N2-H2A···Br2	0.88	2.63	3.420(3)	150.6	
	N3-H3A···Br4	0.88	2.70	3.444(2)	143.8	x, y − 1, z + 1
	N4-H4A···Br1	0.88	2.71	3.511(3)	151.6	
	N5-H5B···Br4	0.88	2.64	3.443(2)	153.0	
	N6-H6D···Br1	0.88	2.96	3.726(2)	146.3	
	N7-H7D···Br3	0.88	2.59	3.428(3)	158.9	
	N8-H8A···Br4	0.88	2.64	3.419(2)	148.8	x, y − 1, z
2	N1-H1A···Br2	0.88	2.60	3.424(2)	156.3	x − 1, y, z
	N2-H2A···Br2	0.88	2.57	3.40(1)	157.1	
	N3-H3A···Br1	0.88	2.57	3.320(2)	143.2	x − 1, y, z
	N4-H4A···Br1	0.88	2.72	3.494(2)	146.9	
3	N1-H1A···I1	0.88	3.02	3.723(1)	137.8	− x + 2, − y, − z + 1
	N2-H2A···O1	0.88	2.03	2.880(2)	161.0	
4	N1-H1A···I1	0.88	2.91	3.755(2)	161.9	− x + 1, − y, − z
	N2-H2A···I1	0.88	2.92	3.751(2)	157.2	− x, − y, − z

spheres of **1** and **2** from their least squares plane is 0.028 Å. Complexes **3** and **4** are centrosymmetric and therefore have exactly planar coordination spheres. The maximum deviation from the least-squares planes through the central SCN_2 part of the thiourea groups is 0.016 Å (except for the partly disordered thiourea group in **2**, (N2-alkyl), where it is 0.038 Å). All thioureas are slightly pyramidal with the central C atom apical. In the *cis*-complexes **1** and **2** the two thiourea groups point to the same side of the coordination plane. This is rather unusual for a dihalodithioureatellurium(II) complex,[2,3] but has recently been observed in the dichloro complex analogous to **2**.[1] Locating the bulky thioureas on different sides of the coordination plane is expected to reduce steric interaction between them. With only two alkyl substituents on each thiourea they may coordinate so that the bulky RNH groups in different thioureas are placed roughly "parallel" to each other to minimize steric interaction as seen in Figure 1. The SCN_2/TeS_2Br_2 interplanar angles have a range of 63.20(8)–78.53(5)° in **1** and **2**. The corresponding angles in **3** and **4** are in, or close to, this range. For the corresponding chloride complexes the *cis* complexes also are within this range while the *trans* complexes have larger angles (78.5–89.0°). The angles $S(1)CN_2/S(2)CN_2$ are between 41.38(6) and 43.18(9)° for **1** and **2** as compared to 0° as required by symmetry for **3** and **4**. The comparatively large angles found in **1** and **2** are probably a result of steric repulsion as proposed for the large angle of 54.7° found for *cis*-$[TeCl_2\{(^iBuNH)_2CS\}_2]$ where the two thioureas also point to the same side of the coordination plane.[1]

Cis-Trans Isomerism

A survey of *cis-trans* isomerism in square-planar Te(II) complexes of the type $[TeX_2(stu)_2]$ where $X = Cl^-$, Br^-, I^-, SCN^-, and $SeCN^-$, and stu is thiourea or substituted thioureas, was reported in a recent article.[1] Of the 24 complexes included, 12 were *cis* and 12 *trans*. Of the 8 complexes where the stu's are tetraalkyl- or diaryldialkylthioureas, 7 are *trans*, regardless of X. This is clearly a steric effect as this configuration gives the largest separation of the two bulky tetrasubstituted stu ligands. Unexpectedly, in the eighth complex where $X = Cl^-$ and stu is 1,3-dimethyl-2(3H)-imidazolethione (a cyclic thiourea), a *cis*-configuration is found.[4] However, the five-membered ring makes the ligand less bulky than its non-cyclic analogues.

Of the 12 dialkylsubstituted stu complexes, 5 are *trans* and seven are *cis*. The stabilities of the two configurations are probably similar as illustrated by the complexes $[Te(SCN)_2(etu)_2]$ and $[Te(SeCN)_2(trtu)_2)]$

which are found in both configurations.[5–7] Here etu is ethylenethiourea and trtu is trimethylenethiourea, two cyclic thioureas. A factor that seems to promote formation of *cis* complexes of dialkylsubstituted thioureas, is a high *trans* influence of the substituted thiourea ligand.[8] Also unsubstituted thiourea itself has a large *trans* influence and yields *cis* complexes only, regardless of X[1] (In Husebye et al.[1] the iodine complex is erroneously reported as *trans*).

In the present investigation where all complexes contain disubstituted thioureas, *cis* conformations are found for the two complexes with $X = Br^-$, similar to the chloro analogs.[1] The two complexes with $X = I^-$ have *trans* conformations. Here the large iodo ligand may induce a *trans* configuration for steric reasons. Both stu ligands used here, N,N′- diisopropyl- and N,N′- diisobutylthiourea, show intermediate *trans* influences.[1]

Tellurium-Ligand Bonding

The *cis* complexes **1** and **2** have relatively short Te-S bond lengths varying from 2.4792(7) to 2.6087(7) Å with an average value of 2.5364 Å. These Te-S bonds are all located *trans* to Te-Br bonds forming almost linear S-Te-Br three-center four-electron (3c–4e) systems. Since the *trans* influence is larger for a thiourea than for a halide ion, the Te-S bonds are shortened while the Te-Br bonds are lengthened as compared to corresponding bond lengths found in symmetric S-Te-S (Te-S = 2.68 Å) and Br-Te-Br (Te-Br = 2.78 Å) 3c–4e systems where the bond lengths are ca. 0.27 Å longer than the sum of the respective covalent radii.[3,9] The elongation is due to the fact that in 3c–4e bonding, there is only one bonding electron per bond, the other two electrons being essentially nonbonding. The Te-Br bond lengths vary from 2.8003(4) to 3.1519(4) Å with an average of 2.9639 Å. Large variations in equivalent Te-S and Te-halogen bond lengths are quite often found in compounds with relatively weak tellurium to ligand bonds and may be due to secondary bonding, hydrogen bonding, and packing effects.[1] This is illustrated by the Te-Br bond lengths. In **1**, Br1 participates in three hydrogen bonds, Br2 and Br3 in one, and Br4 in three. The corresponding Te-Br bond lengths are 3.0058(3), 2.8435(4), 2.8003, and 3.1519(4) Å, those with most hydrogen bonds being the longest. In **2**, both bromide ligands participate in two hydrogen bonds, and the resulting bond lengths are Te-Br1 = 2.9651(2) and Te-Br2 = 3.0166(3) Å. Usually a longer Te-ligand bond in a 3c–4e system results in a shorter Te-ligand bond *trans* to itself and vice versa. Comparison with the *cis* dichloro complexes corresponding to **1** and **2** shows that the average Te-S bond length there is 2.5103 Å, a bit shorter than that found in **1** and **2**. This is probably due to the slightly lower *trans* influence of Cl^- as compared to Br^-.

In the centrosymmetric *trans* diiodo complexes **3** and **4**, there are mutually perpendicular and symmetric S-Te-S and I-Te-I 3c-4e systems. There is no difference in *trans* influence of the ligands in each of these symmetric systems, and the Te-S bond lengths are 2.6836(4) and 2.7016(5) Å for **3** and **4** respectively. They agree well with the normal value of 2.68 Å for such 3c-4e systems as cited above. That the Te-S bonds are longer in the *trans* complexes as compared to the *cis* complexes is reflected in a lowering of the Te-S stretching frequency from around 290 to around 240 cm^{-1} going from *cis* to *trans*. The corresponding Te-I bond lengths in **3** and **4** are 2.9820(2) and 2.9701(2) Å, very close to the predicted value of 2.97 Å based on the sum of the covalent radii of Te and I plus the elongation factor of 0.27 Å. These Te-I bond lengths also may be compared to those found in the *trans* complexes $[TeI_2(etu)_2]$ and $[TeI_2(tmtu)_2]$, 2.955(1) and 2.956 Å, the latter being an average value.[10,11]

Bonding in the Thiourea Ligands

This bonding is characterized by resonance resulting in partial double bonding from the central sp^2 hybridized carbon atom of each ligand to the neighbouring S and N atoms.[1] The Te-S bonding influences the ligand bonding. Relatively short, strong bonds, such as found in the *cis* complexes, give long C-S bonds which consequently results in shorter C-N bonds (small effect). In the *trans* complexes with longer Te-S bonds, the opposite effect is observed. Thus in **1** and **2** the average Te-S, C-S, and C-N bond lengths are 2.5364, 1.759, and 1.323 Å, respectively (the latter two show partial double bonding), as compared to 2.6926, 1.738, and 1.329 Å for the corresponding average bond lengths in **3** and **4**. These bond lengths may also be compared to the average C=S and C-N bond lengths of free thioureas, 1.681(20) and 1.346(23) Å respectively.[12] The elongation of the C=S bond upon complexation is also reflected in the lowering of the stretching frequency of this bond (ca. 60 cm^{-1}) in all four complexes. The average C_{alkyl}—N bond length for **1–4** is normal at 1.471 Å. The Te-S-C angles vary between 98.61(6) and 106.4 (1). These are normal sulfur valency angles.

Hydrogen Bonding and Packing of Molecules

Hydrogen bonds are listed in Table III, C-H···X interactions have not been considered. There are intra- and intermolecular hydrogen bonds between halide ligands and NH groups of the thiourea ligands. In addition there are hydrogen bonds between the oxygen of the solvated DMF molecule and the N2 (NH) atom in **3**. In all four complexes there are two intramolecular N-H···X bonds, one from each X to one of the two thioureas *cis* to it so that the two X ligands are bound to different thioureas. In **1** (Figure 3) the intermolecular N-H···Br bonds connect the complex molecules into layers in the *bc*-plane. In **2** (Figure 4) the same type of hydrogen bonds as in **1** connects the molecules into chains parallel to *a*. The only intermolecular hydrogen bonds in **3** (Figure 5) are of the type N-H···O connecting two DMF molecules to each complex molecule. Finally in **4** (Figure 6) very weak intermolecular N-H···I bonds connect the molecules into chains parallel to *a*. For **1** and **2** the N···Br distances in the hydrogen bonds varies between 3.320(2) and 3.726(2) Å, while the corresponding variation in the N···I distances for **3** and **4** is 3.723(2) to 3.755(2) Å. The N···O distance in the intermolecular hydrogen bond in **3** is 2.881(2) Å. Apart from the hydrogen bonds, there are no especially short contacts between molecules in the four complexes.

EXPERIMENTAL

The complexes were prepared according to a modified literature method.[13,14]

Cis-dibromobis(N,N′-diisopropylthiourea)tellurium(II), 1

A hot solution of 6.4 g (40 mmol) N,N′-diisopropylthiourea in 20 ml methanol was added to 1.6 g (40 mmol) TeO_2 dissolved in 5 ml hot, concentrated HCl, under stirring. The resulting solution was filtered hot to remove an oil-like product. To the filtrate 20 ml of 47% aqueous HBr was added dropwise with stirring, and the solution was then stored in a refrigerator for 2 days to complete crystallization. The yellow crystals were recrystallized from DMF after adding an equal amount of methanol, and cooling in a refrigerator for 2–3 days. After filtration and washing with diethyl ether containing a little N,N′-diisopropylthiourea, the yield was 3.3 g (47.3%), m.p. 161–162°C. Anal. Calcd. for $C_{14}H_{32}S_2N_4Br_2Te$: C, 27.63; H, 5.31; Br, 26.28; S, 10.53%. Found: C, 27.60; H, 5.32; Br, 26.32; S, 10.51%.

Cis-dibromobis(N,N′-diisobutylthiourea)tellurium(II), 2

The same procedure as that described above was followed. Yield of yellow crystals, 3.6 g (47.5%), m.p. 166°C. Anal. Calcd for $C_{18}H_{40}S_2N_4Br_2Te$: C, 32.53; H, 6.07%. Found: C, 32.53; H, 6.02%.

Trans-diiodobis(N,N′-diisopropylthiourea)tellurium(II), 3

A solution of 3.2 g (20 mmol) and N,N′-diisopropyl thiourea in 50 ml DMF was added to a large excess of 1.6 g (10 mmol) of TeO_2 dissolved in 5 ml hot, concentrated HCl with stirring. Then a mixture of 10 ml of 57% aqueous HI and 50 ml methanol was added to this solution with stirring. The resulting solution was stored in the dark at r.t. for 48 h. Brownish crystals formed, consisting of a DMF disolvate, **3** · 2DMF. The precipitate was recrystallized from DMF containing a little HI upon addition of methanol. Yield 2.9 g (82.7%) based on N,N′-isopropylthiourea, m.p. 81–82°C. Anal. Calcd. for $C_{20}H_{46}S_2N_6I_2O_2Te$: C, 28.32; H, 5.47; N, 9.90; S, 7.55%. Found: C, 28.39; H, 5.36; N, 9.99, S, 7.50%.

Trans-diidobis(N,N′-diisobutylthiourea)tellurium(II), 4

Here, the same procedure used to prepare **3** was used. The yield of red crystals was 3.1 g (85.0% based on the thiourea used), m.p. 154–155°C (dec). Anal. Calcd. for $C_{18}H_{40}S_2N_4I_2Te$: C, 28.49; H, 5.32%. Found: C, 27.97; H, 4.95%.

IR Spectra

IR spectra of the two thiourea ligands and of the complexes **1**–**4** were recorded in nujol mulls and some assignments made for absorptions in the range 800–200 cm^{-1}: $\nu(CS) = 733$ ($(^{i}PrNH)_2CS$), 732 ($(^{i}BuNH)_2CS$), 672 (**1**), 676 (**2**), 665 (**3**), 672 (**4**) cm^{-1}; ν_{asym} (Te-S) = 285 (**1**), 295 (**2**), 245 (**3**), 235 (**4**) cm^{-1}.

Structure Determination

The X-ray data were collected on a Bruker-AXS SMART 2K CCD diffractometer. A full sphere of reflections using Mo*Kα* radiation was collected for all four complexes. Data were collected, reduced and the structures solved using the programs SMART, SAINT, and SHELXTL.[15,16] Numerical absorption correction was applied in all cases. All nonhydrogen

TABLE IV Crystal Data

Compound	Complex **1**	Complex **2**	Complex **3**·2DMF	Complex **4**
Empirical formula	$C_{14}H_{32}Br_2N_4S_2Te$	$C_{18}H_{40}Br_2N_4S_2Te$	$C_{14}H_{32}I_2N_4S_2Te \cdot (C_3H_7NO)_2$	$C_{18}H_{40}I_2N_4S_2Te$
Formula weight, g mol^{-1}	607.98	664.08	848.15	758.06
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group (No.)	P1 (1)	P1 (1)	Pbca (61)	P-1 (2)
a, Å	8.4282(6)	7.8042(4)	9.6218(4)	8.3472(2)
b, Å	10.2836(7)	9.6185(5)	16.0589(6)	9.7428(3)
c, Å	14.7854(1)	9.7861(5)	21.3006(8)	9.7720(3)
α,°	73.275(1)	82.103(1)	90	87.839(1)
β,°	80.440(1)	80.715(1)	90	68.158(1)
γ,°	87.414(1)	70.560(1)	90	72.989(1)
V, Å^3	1210.2(1)	680.87(6)	3291.3(2)	703.12(3)
Z	2	1	4	1
D_{calc} Mg m^{-3}	1.668	1.620	1.712	1.790
μ, mm^{-1}	4.707	4.191	2.932	3.413
Crystal size, mm	0.09 × 0.28 × 0.38	0.17 × 0.20 × 0.29	0.05 × 0.09 × 0.35	0.06 × 0.13 × 0.30
Transmission coeff., min, max	0.2017, 0.6684	0.3885, 0.5291	0.5197, 0.8771	0.3576, 0.8306
Temperature, K	173(2)	173(2)	173(2)	173(2)
Reflections measured	23393	13302	52384	13772
Indep. reflections (Rint)	16718 (0.0138)	9468 (0.0127)	4809 (0.0324)	5056 (0.0223)
θ range, °, completeness, %	2.45–32.65, 98.0	2.25–32.60, 98.0	1.91–30.01, 100.0	2.19–32.57, 98.4
Max diff. peak/hole, eÅ^{-3}	0.60/−0.50	0.52/−0.49	0.41/−0.34	1.08/−0.89
R1 (all data)	0.0316	0.0192	0.0289	0.0318
R1 [I > 2σ(I)]	0.0274	0.0186	0.0177	0.0231
WR2 (all data)	0.0584	0.0442	0.0414	0.0586
Goodness of fit on F^2	0.999	1.024	1.078	1.051

Complex **1**: Flack parameter 0.003(3).

Complex **2**: Racemic twin, major component is 0.552(3).
One thiourea group (N2 through C9) is two-fold disordered, residue ratio is 0.56/0.44.

atoms were refined anisotropically and the hydrogen atoms were assigned isotropic displacement parameters equal to 1.5 times the equivalent isotropic displacement parameter of the parent C, N, and O atoms. All hydrogen atoms were located in their geometrically optimised positions. One of the $-NHCH_2CH(CH_3)_2$ groups (N2) of **2** was disordered with an approximate mirror plane symmetry between the two components for atoms N2 through C9. Only atomic positions of the main component (56%) were used in calculating bonds and angles and in the figures. Crystallographic and structure refinement data are shown in Table IV.

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