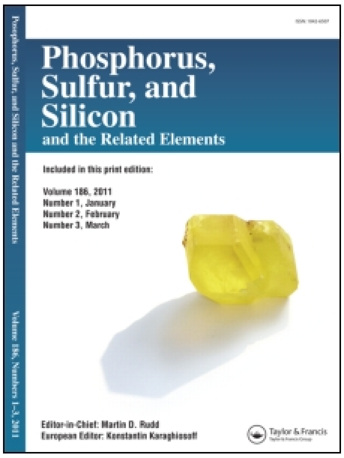

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

TAUTOMERIC CONVERSION OF A THIOUREA LIGAND UPON FORMATION OF A HYPERVALENT TELLURIUM (II) COMPLEX. SYNTHESIS, AND X-RAY STRUCTURAL STUDIES OF N-PHENYL-N'-(1,3-THIAZOL-2-YL)-THIOUREA AND BROMOPHENYL [1-PHENYL-3-(1',3'-THIAZOL-3'-IUM-2'-YL)-ISOTHIOUREIDATO]TELLURIUM(II)

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To cite this Article Rudd, Martin D. , Lindeman, Sergey V. and Husebye, Steinar(1997) 'TAUTOMERIC CONVERSION OF A THIOUREA LIGAND UPON FORMATION OF A HYPERVALENT TELLURIUM (II) COMPLEX. SYNTHESIS, AND X-RAY STRUCTURAL STUDIES OF N-PHENYL-N'-(1,3-THIAZOL-2-YL)-THIOUREA AND BROMOPHENYL [1-PHENYL-3-(1',3'-THIAZOL-3'-IUM-2'-YL)-ISOTHIOUREIDATO]TELLURIUM(II)', Phosphorus, Sulfur, and Silicon and the Related Elements, 123: 1, 313 — 327

To link to this Article: DOI: 10.1080/10426509708044219

URL: http://dx.doi.org/10.1080/10426509708044219

Phosphorus, Sulfur, and Silicon, 1997, Vol. 123, pp. 313-327
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TAUTOMERIC CONVERSION OF A THIOUREA LIGAND UPON FORMATION OF A HYPERVALENT TELLURIUM (II) COMPLEX. SYNTHESIS, AND X-RAY STRUCTURAL STUDIES OF N-PHENYL-N'-(1,3-THIAZOL-2-YL)-THIOUREA AND BROMOPHENYL [1-PHENYL-3-(1',3'-THIAZOL-3'-IUM-2'-YL)-ISOTHIOUREIDATO]TELLURIUM(II)*

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(Received 21 January 1997; In final form 6 May 1997)

The divalent tellurium title complex (II) has been synthesized by addition of Ph_2Te_2 and Br_2 to the ligand 1-phenyl-3-(2-thiazolyl)-2-thiourea (I).The molecular structures of I and II were subsequently determined by X-ray crystallographic methods. As a result, it was found that upon complexation, the ligand had undergone a transition from a thiourea to to an isomeric isothiourea, involving a transfer of a thiourea proton to the thiazolyl ring. This does not seem to influence the bonding properties of the ligand, and the reasons for this are discussed. The central tellurium atom is three-coordinate and its coordination sphere is T-shaped with a linear S-Te-Br sequence with bond lengths Te(1)-S(1) and Te(1)-Br(1) equal to 2.548(1) and 2.883(1) Å, respectively, and ∠ S(1)-Te(1)-Br(1)=174.49(2)°. At nearly right angles to this sequence, there is a Te(1)-C(11)(phenyl) bond of 2.127(3) Å.

Keywords: Tellurium (II) complex; T-shaped structure; proton transfer; tautomeric conversion of thiourea ligand

INTRODUCTION

Recently, we reviewed hypervalent complexes of divalent three-coordinated tellurium with a general formula L=Y–Te(Ar)—X, where X is a halogen ligand, Y is a double-bonded chalcogen atom from a neutral organic or phosphorus-con-

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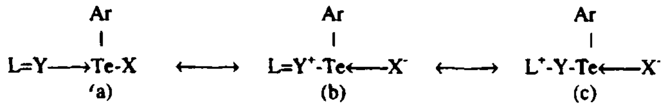
* Dedicated to Professor Robert Wolf on the occasion of his 70th birthday

taining ligand (the remainder of the ligand is marked as L) and Ar is usually Ph.[1] We considered them in a framework of a 3-center,4-electron (3c,4e) bonding scheme. In summary, this scheme (also known as 'hypervalent bonding' or 'secondary bonding') considers a linear 3-center group of atoms A--B--C comprising, for instance, a σ-bonded covalent A-B molecule and an additional, 'secondary' ligand C donating its lone electron pair onto the A-B σ-antibonding orbital and inducing the weakening of the A-B bond (or vice versa).[2]

In the case of the Te complexes studied, it is possible to represent this by the following resonance forms:



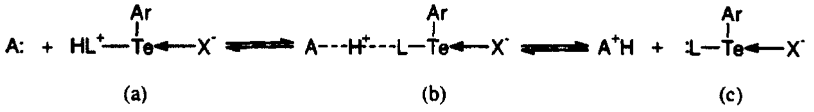
$$\underset{\text{(a)}}{\mathrm{L{=}Y{\longrightarrow}\overset{\overset{Ar}{|}}{Te}{-}X}} \quad\longleftrightarrow\quad \underset{\text{(b)}}{\mathrm{L{=}Y^{+}{-}\overset{\overset{Ar}{|}}{Te}{\longleftarrow}X^{-}}} \quad\longleftrightarrow\quad \underset{\text{(c)}}{\mathrm{L^{+}{-}Y{-}\overset{\overset{Ar}{|}}{Te}{\longleftarrow}X^{-}}}$$

SCHEME 1

We are using the symbol '→' not in its conventional meaning of a coordination bond, but to designate a lone electron pair of a ligand only initially oriented toward the molecular σ*-orbital of the central atom bond with another ligand. This oriented lone pair becomes a convenient σ-bond expelling the electrons of the opposite, initially σ-bonded ligand, from the valence shell of the central atom. Then the second ligand in turn becomes an oriented 2-electron donor. In practice, the central atom always has a complete 8-electron sp-shell, and both the opposite hypervalent bonds (designated here by the symbol '– –' as distinguished from usual single bond designated as '–') have bond orders less than 1 and their comparative 'strength' (a 'primary' character) or 'weakness' (a 'secondary' character) is dependent on the trans-influence[3] of the corresponding ligands. Now, among the halogens, iodine has a larger *trans*-influence than bromine, which again has a larger *trans*-influence than chlorine. In the same manner, the *trans*-influence decreases in the order Se > S > O for chalcogens.

In our previous work[1], we suggested that the ability of the rest of the ligand, L, to accept (to delocalize) additional positive charge [see Scheme 1(b,c)] can modify the trans-influence of the chalcogen atom in these complexes. We have confirmed this conclusion from a literature survey of a large variety of organic ligands containing in most cases the moiety $(H/R)_2N\text{-}C(=Y)\text{-}N(H/R')_2$, where Y=O,S,Se.[1]

Hauge and Vikane,[4] who investigated the majority of these structures, have suggested that the relative trans-influence of thione ligands in this group is: thiourea (tu) ≈ ethylenethiourea (etu) > trimethylenethiourea (trtu) > tetramethylthiourea (tmtu), but did not give any explanation for these differences. Now we propose that the larger *trans*-influence of proton-containing ligands may be caused by an opportunity to get rid of the accepted positive charge [and thereby stabilize the resonance form (c), Scheme 1] by a partial [H-bonding, Scheme 2(b)] or complete [dissociation, Scheme 2(c)] elimination of H^+:



SCHEME 2

Indeed, all the known structures[4,5,6,7,8] of complexes with thiourea-derived ligands containing active hydrogens (i.e. NH or NH_2 groups) are obviously H-bonded even though in many cases the hydrogen atoms were not located accurately.[4,5,8] However, still no evidence of a complete proton transfer has been found in such complexes.

In this paper, we report the syntheses and results of X-ray structural investigations of the thiourea-derived ligand, N-phenyl-N'-thiazolylthiourea (**I**), and its hypervalent complex (**II**) with PhTeBr, where such proton transfer occurs intramolecularly upon complexation.

EXPERIMENTAL

Materials: Diphenylditelluride, 1-phenyl-3-(2-thiazolyl)-2-thiourea (**I**) and bromine were used as supplied commercially(Aldrich). Acetonitrile was stored over 4 Å molecular sieves prior to use. **I** was recrystallized from acetonitile to give large pale yellow blocks suitable for X-ray crystallographic studies.

Synthesis of **II. I** (0.294g, 1.25 mmol) was dissolved in methanol (15 cm^3) and added to a rapidly stirred solution of diphenylditelluride (0.256g, 0.625 mmol) in the same solvent (15 cm^3). Bromine (0,10g, 0.625 mmol) in methanol (5 cm^3) was added and the reaction was allowed to stir at room temperature for an hour. The solvent was removed under reduced pressure and the oily residue was washed with hexane and recrystallised from hot tetrahydrofuran by slow cooling to -10 °C to give orange-red block crystals.

M.p. 165-8 °C(dec.) Yield 0.45g, 82%. Reaction: PhTeTePh + 2 **I**+ Br_2 -----> 2 **II**

Structure determinations. Crystal data are given in Table I, together with some data collection and refinement details. Data for both crystals were collected with MoKα radiation at low temperature using an Enraf-Nonius CAD4 diffractometer. The unit cell parameters and orientation matrices were obtained by a least-squares fit of 25 randomly oriented intense reflections in both cases. The diffracted intensities were collected using a variable scan speed.

Three standard reflections were measured at regular intervals. All corrections needed (including empirical psi-scan absorption correction for **II**) were made using Blessing's program package.[9] The structures were solved using direct methods with the SHELXS86 program.[10]All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found in difference Fourier maps and refined isotropically. Refinement was undertaken with SHELXL93[11] on a MicroVax 2000 computer.

Positional and thermal parameters of atoms of the structures **I** and **II** are given in Tables II and III. Bond distances and angles, and selected torsion angles are listed in Tables IV and V. Molecular structures of **I** and **II** are shown in Figures 1 and 2. Additional material, available from the Cambridge Crystallographic Data Centre, comprises anisotropic thermal parameters of non-hydrogen atoms, remaining geometrical parameters and tables of structure factors.

TABLE I Crystal data and structure refinement parameters for compounds **I** and **II**

Compound	*I*	*II*
Empirical Formula	$C_{10}H_9N_3S_2$	$C_{16}H_{14}BrN_3S_2Te$
M	235.32	519.93
Crystal System	Triclinic	Monoclinic
Space Group	P-1	$P2_1/c$
a/Å	8.229(2)	10.723(2)
b/Å	8.733(2)	11.347(2)
c/Å	9.115(2)	15.454(3)
α/°	62.68(3)	90
β/°	78.39(3)	108.19(3)
γ/°	68.62(3)	90
Temp./K	103(2)	103(2)
V/Å^3	541.5(2)	1786.4(6)
Z	2	4
D_c/mg.m^{-3}	1.443	1.933
μ/mm^{-1}	0.459	4.137
F(000)	244	1000
Crystal size (mm)	0.15x0.2x0.2	0.1x0.1x0.12
θ range/°	2.0-36.0	2.5-30.0
hkl ranges	0/13, -13/14, -14/15	0/15,0/15, -21/20
Total no of reflections	5119	5398
Crystal decay correction	0.986-1.000	0.971-1.000
Transmission coeff.	1.0	0.645-0.720

TABLE I Crystal data and structure refinement parameters for compounds I and II (continued)

Compound	*I*	*II*
Independent reflections I>2σ(I) (R_{int})	3873 (0)	3506 (0.035)
Data (all) / parameters	5106/172	5148/264
Goodness of fit on F^2 (obs / all data)	1.064/1.032	1.103 / 0.988
Final R indices:		
R_1 (obs / all data)	0.0274/0.0521	0.0298 / 0.0697
wR_2 (obs / all data)	0.0748 / 0.0873	0.0748 / 0.0840
Largest difference peak and hole/e.Å^{-3}	0.502, -0.512	1.910, -0.678

TABLE II Atomic coordinates (× 10^4; for H × 10^3) and equivalent isotropic (for H - isotropic) temperature factors (x 10^4; for H × 10^3) for compound I

Atom	*x*	*y*	*z*	$U_{iso/eq}{}^a/U_{iso}$
S(1)	2304.8(3)	3327.4(3)	6421.2(3)	208.9(5)
S(2)	-2844.0(3)	9403.4(3)	5579.2(3)	212.5(5)
N(1)	2441.1(9)	5500.7(9)	7695.2(9)	166(1)
N(2)	6.6(9)	6434.7(9)	6230.0(9)	167(1)
N(3)	-191.8(10)	8631.2(10)	7184.1(9)	192(1)
C(1)	4055(1)	4294(1)	8468(1)	145(1)
C(2)	4137(1)	2587(1)	9738(1)	180(1)
C(3)	5695(1)	1472(1)	10534(1)	210(1)
C(4)	7156(1)	2066(1)	10079(1)	224(2)
C(5)	7061(1)	3769(1)	8819(1)	232(2)
C(6)	5508(1)	4891(1)	8003(1)	193(1)
C(7)	1580(1)	5176(1)	6825(1)	147(1)
C(8)	-815(1)	8033(1)	6413(1)	159(1)
C(9)	-2843(1)	10895(1)	6327(1)	228(2)
C(10)	-1357(1)	10270(1)	7126(1)	215(2)
H(1n)	203(2)	649(2)	778(2)	30(4)
H(2n)	-50(2)	629(2)	561(2)	32(4)
H(2)	311(2)	216(2)	1008(2)	26(3)
H(3)	581(2)	22(2)	1135(2)	28(4)
H(4)	819(2)	130(2)	1063(2)	38(4)
H(5)	804(2)	425(2)	846(2)	34(4)
H(6)	540(2)	608(2)	715(2)	28(4)
H(9)	-382(2)	1203(2)	615(2)	29(4)
H(10)	-110(2)	1091(2)	758(2)	33(4)

a $U_{iso/eq} = (1/3)\ \Sigma_i\Sigma_j U_{ij} a_i{}^* a_j{}^* \mathbf{a}_i \mathbf{a}_j$.

TABLE III Atomic coordinates (x 10^4; for H x 10^3) and equivalent isotropic (for H isotropic) temperature factors (x 10^4; for H x 10^3) for compound **II**

Atom	*x*	*y*	*z*	$U_{iso}/_{eq}{}^{a}/U_{iso}$
Te(1)	2955.7(2)	410.2(2)	-35.5(1)	287.6(6)
Br(1)	3197.0(3)	-1884.0(3)	-769.7(2)	324.4(8)
S(1)	2507.4(8)	2426.4(7)	530.4(5)	322(2)
S(2)	1284.0(8)	4508.6(7)	1129.8(6)	339(2)
N(1)	3828(3)	3151(2)	-572(2)	321(5)
N(2)	2694(2)	4626(2)	-127(2)	282(5)
N(3)	1867(3)	6279(2)	354(2)	335(6)
C(1)	4350(3)	3752(3)	-1182(2)	319(6)
C(2)	4374(3)	4973(3)	-1269(2)	320(6)
C(3)	4914(4)	5452(3)	-1896(2)	383(7)
C(4)	5441(4)	4746(3)	-2423(2)	409(8)
C(5)	5467(5)	3550(4)	-2314(3)	496(10)
C(6)	4914(4)	3041(3)	-1690(3)	440(8)
C(7)	3026(3)	3500(3)	-98(2)	288(6)
C(8)	2029(3)	5108(3)	376(2)	290(6)
C(9)	827(4)	5892(3)	1388(3)	390(7)
C(10)	1211(4)	6733(3)	920(3)	381(7)
C(11)	1170(3)	565(3)	-1126(2)	309(6)
C(12)	122(3)	-179(3)	-1181(2)	345(6)
C(13)	-1061(3)	-41(4)	-1896(2)	384(7)
C(14)	-1187(4)	850(3)	-2532(2)	386(7)
C(15)	-148(3)	1587(3)	-2480(2)	340(6)
C(16)	1045(3)	1447(3)	-1781(2)	323(6)
H(1n)	415(4)	246(4)	-43(3)	33(10)
H(3n)	228(4)	666(4)	6(3)	33(10)
H(2)	407(3)	541(3)	-93(2)	24(8)
H(3)	506(5)	635(5)	-187(4)	70(16)
H(4)	588(5)	499(5)	-283(3)	56(13)
H(5)	594(5)	298(4)	-261(3)	53(13)
H(6)	497(5)	218(4)	-155(3)	50(12)
H(9)	23(5)	597(5)	171(3)	59(14)
H(10)	107(5)	750(5)	102(4)	69(15)
H(12)	20(4)	-77(3)	-77(3)	31(9)
H(13)	-177(4)	-53(3)	-193(3)	33(10)
H(14)	-191(5)	99(4)	-299(3)	52(12)
H(15)	-21(4)	223(4)	-291(3)	47(12)
H(16)	179(4)	194(3)	-174(3)	35(10)

[a] See Table 2.

TABLE IV Bond lengths (*d*/Å) and angles (ω/°), and selected torsion angles (τ/°) in molecule I

Bond	*d*	*Bond*	*d*
S(1)-C(7)	1.689(1)	N(3)-C(8)	1.306(1)
S(2)-C(8)	1.737(1)	N(3)-C(10)	1.386(1)
S(2)-C(9)	1.726(1)	C(1)-C(6)	1.389(1)
N(1)-C(1)	1.431(1)	C(1)-C(2)	1.393(1)
N(1)-C(7)	1.338(1)	C(2)-C(3)	1.390(1)
N(1)-H(1n)	0.84(2)	C(3)-C(4)	1.394(1)
N(2)-C(7)	1.370(1)	C(4)-C(5)	1.386(2)
N(2)-C(8)	1.383(1)	C(5)-C(6)	1.396(1)
N(2)-H(2n)	0.84(2)	C(9)-C(10)	1.353(1)
Angle	ω	*Angle*	ω
C(8)-S(2)-C(9)	88.8(1)	C(2)-C(3)-C(4)	120.3(1)
C(1)-N(1)-C(7)	124.6(1)	C(3)-C(4)-C(5)	119.9(1)
C(1)-N(1)-H(1n)	117(1)	C(4)-C(5)-C(6)	120.2(1)
C(7)-N(1)-H(1n)	118(1)	C(1)-C(6)-C(5)	119.6(1)
C(7)-N(2)-C(8)	127.6(1)	S(1)-C(7)-N(1)	124.3(1)
C(7)-N(2)-H(2n)	118(1)	S(1)-C(7)-N(2)	118.3(1)
C(8)-N(2)-H(2n)	114(1)	N(1)-C(7)-N(2)	117.3(1)
C(8)-N(3)-C(10)	109.7(1)	S(2)-C(8)-N(2)	119.4(1)
N(1)-C(1)-C(2)	120.3(1)	S(2)-C(8)-N(3)	115.3(1)
N(1)-C(1)-C(6)	119.0(1)	N(2)-C(8)-N(3)	125.3(1)
C(2)-C(1)-C(6)	120.6(1)	S(2)-C(9)-C(10)	110.0(1)
C(1)-C(2)-C(3)	119.4(1)	N(3)-C(10)-C(9)	116.1(1)
Angle	τ	*Angle*	τ
C(7)-N(1)-C(1)-C(2)	-63.8(1)	C(8)-N(2)-C(7)-S(1)	-179.7(1)
C(7)-N(1)-C(1)-C(6)	120.1(1)	C(8)-N(2)-C(7)-N(1)	0.3(1)
C(1)-N(1)-C(7)-S(1)	-3.0(1)	C(7)-N(2)-C(8)-S(2)	-178.7(1)
C(1)-N(1)-C(7)-N(2)	177.0(1)	C(7)-N(2)-C(8)-N(3)	1.2(1)

TABLE V Bond lengths (d/Å) and angles (ω/°), and selected torsion angles (τ/°) in molecule **II**

Bond	*d*	*Bond*	*d*
Te(1)-Br(1)	2.883(1)	C(1)-C(2)	1.393(5)
Te(1)-S(1)	2.548(1)	C(1)-C(6)	1.389(5)
Te(1)-C(11)	2.127(3)	C(2)-C(3)	1.385(5)
S(1)-C(7)	1.753(3)	C(3)-C(4)	1.382(5)
S(2)-C(8)	1.743(3)	C(4)-C(5)	1.368(6)
S(2)-C(9)	1.728(4)	C(5)-C(6)	1.404(5)
N(1)-C(1)	1.413(4)	C(9)-C(10)	1.339(5)
N(1)-C(7)	1.351(4)	C(11)-C(12)	1.386(5)
N(1)-H(1n)	0.85(4)	C(11)-C(16)	1.400(4)
N(2)-C(7)	1.324(4)	C(12)-C(13)	1.406(5)
N(2)-C(8)	1.325(4)	C(13)-C(14)	1.387(5)
N(3)-C(8)	1.340(4)	C(14)-C(15)	1.376(5)
N(3)-C(10)	1.380(4)	C(15)-C(16)	1.402(5)
N(3)-H(3n)	0.84(4)		

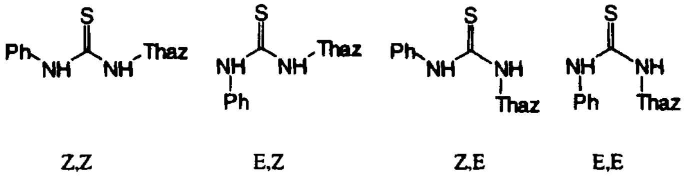
Angle	ω	*Angle*	ω
Br(1)-Te(1)-S(1)	174.49(2)	C(4)-C(5)-C(6)	119.7(4)
Br(1)-Te(1)-C(11)	86.1(1)	C(1)-C(6)-C(5)	120.1(4)
S(1)-Te(1)-C(11)	88.7(1)	S(1)-C(7)-N(1)	117.5(2)
Te(1)-S(1)-C(7)	107.9(1)	S(1)-C(7)-N(2)	124.1(2)
C(8)-S(2)-C(9)	91.3(2)	N(1)-C(7)-N(2)	118.3(3)
C(1)-N(1)-C(7)	132.2(3)	S(2)-C(8)-N(2)	132.4(2)
C(1)-N(1)-H(1n)	113(3)	S(2)-C(8)-N(3)	108.7(2)
C(7)-N(1)-H(1n)	114(3)	N(2)-C(8)-N(3)	119.0(3)
C(7)-N(2)-C(8)	124.5(3)	S(2)-C(9)-C(10)	111.4(3)
C(8)-N(3)-C(10)	116.3(3)	N(3)-C(10)-C(9)	112.3(3)
C(8)-N(3)-H(3n)	116(3)	Te(1)-C(11)-C(12)	120.7(2)
C(10)-N(3)-H(3n)	127(3)	Te(1)-C(11)-C(16)	119.4(2)
N(1)-C(1)-C(2)	124.6(3)	C(12)-C(11)-C(16)	119.9(3)
N(1)-C(1)-C(6)	115.5(3)	C(11)-C(12)-C(13)	119.7(3)
C(2)-C(1)-C(6)	119.9(3)	C(12)-C(13)-C(14)	120.1(3)

TABLE V Bond lengths (d/Å) and angles (ω/°), and selected torsion angles (τ/°) in molecule **II** (Continued)

Bond	*d*	*Bond*	*d*
C(1)-C(2)-C(3)	118.8(3)	C(13)-C(14)-C(15)	120.2(3)
C(2)-C(3)-C(4)	121.5(3)	C(14)-C(15)-C(16)	120.3(3)
C(3)-C(4)-C(5)	119.9(3)	C(11)-C(16)-C(15)	119.8(3)
Angle	τ	*Angle*	τ
C(11)-Te(1)-S(1)-C(7)	-82.4(1)	Te(1)-S(1)-C(7)-N(2)	164.9(2)
C(7)-N(1)-C(1)-C(2)	15.9(6)	C(7)-N(2)-C(8)-S(2)	-5.5(5)
C(7)-N(1)-C(1)-C(6)-	166.7(4)	C(7)-N(2)-C(8)-N(3)	173.2(3)
C(8)-N(2)-C(7)-S(1)	6.4(4)	Br(1)-Te(1)-C(11)-C(12)	64.5(3)
C(8)-N(2)-C(7)-N(1)	-172.8(3)	Br(1)-Te(1)-C(11)-C(16)	-116.9(2)
C(1)-N(1)-C(7)-S(1)	175.3(3)	S(1)-Te(1)-C(11)-C(12)	-113.5(3)
C(1)-N(1)-C(7)-N(2)	-5.4(5)	S(1)-Te(1)-C(11)-C(16)	65.0(2)
Te(1)-S(1)-C(7)-N(1)	-15.9(3)		

RESULTS AND DISCUSSION

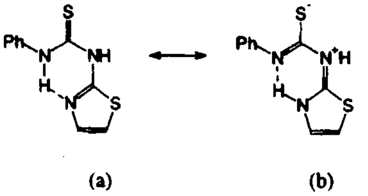
Molecular structures. Molecule **I**, with the exception of the phenyl group, has an essentially planar structure in the crystal. The phenyl ring forms an angle with the planar remainder of the ligand of ca. 60° (Figure 1, Table III), probably due to sterical hindrances. Theoretically, molecule **I** can exist (e.g. in solution) as four isomers (though with comparatively low potential energy barriers of interconversion):



Z,Z E,Z Z,E E,E

SCHEME 3

Z,Z-and *E,E*-configurations should be the most sterically hindered because of repulsion between the thione sulfur and the substituents or between the substituents themselves, respectively. A thiazolyl ring is less bulky than a phenyl ring, therefore the *E,Z*-configuration should be preferred. However, the *Z,E*-configuration found in the crystals of **I** allows for an additional stabilizing factor - an intramolecular H-bond N(1)-H(1n)...N(3) [N...N 2.703(1) Å, N...H 2.03(2) Å, ∠ N-H...N 137(3)°] forming a planar six-membered ring (Figure 1). This interaction is comparatively strong since it influences the bond lengths in the thiourea ligand owing to resonance as shown in Scheme 4.



SCHEME 4

Indeed, the N(1)-C(7) bond [1.338(1) Å] is much shorter than the normally equivalent bond, N(2)-C(7) [1.370(1) Å], and the non-conjugated N(1)-C(1) bond [1.431(1) Å] is much longer than its formal equivalent, the N(2)-C(8) bond [1.383(1) Å]. However, both the average (S)Csp^2-N bond length (1.356 Å) and C=S bond length [1.689(1) Å] are close to the corresponding standard values for thioureas [1.35(2) and 1.68(2) Å, respectively].[12]

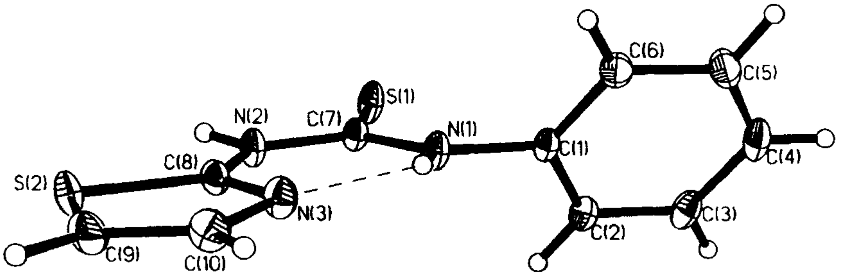
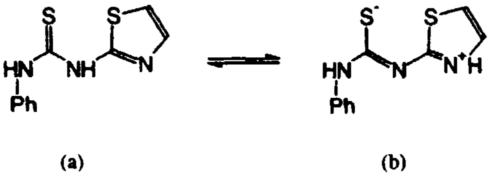


FIGURE 1 Perspective projection of the molecule I with numbering of the atoms. Intermolecular H-bond N-H...N is shown by a dashed line. The thermal displacement ellipsoids are given at 50% probability level

It is very interesting that in complex **II** the transition from a thiourea [Scheme 4(a)] to an isothiourea structure [Scheme 4(b)] of the ligand actually takes place, but now as a true tautomeric conversion :



SCHEME 5

The resulting bipolar structure (b) is expected to be preferable for complexation in such a hypervalent complex, even though its occurrence is a bit surprising.

The aforementioned considerations on the relative stability of the different configurations of the N,N'-diarylthiourea structure (Scheme 3) are valid for the ligand in **II**. Absence of an intramolecular H-bond favors the *E,Z*-isomer for steric reasons and it consequently occurs in the crystals of **II** (Figure 2) as a largely planar (Table V) unstrained conjugated structure.

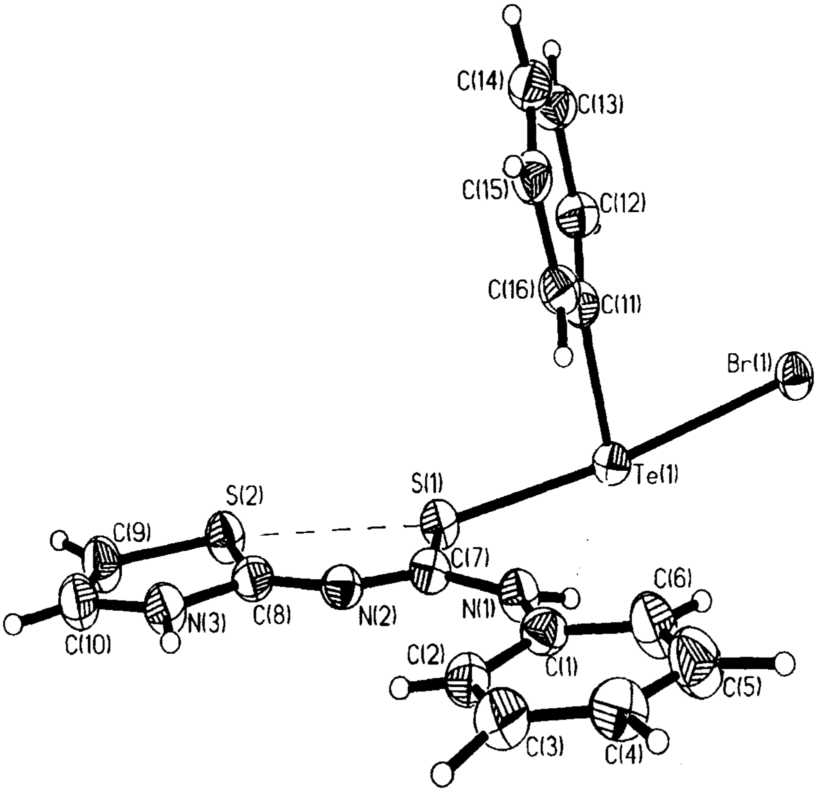
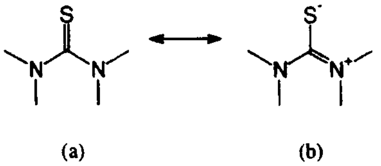


FIGURE 2 Perspective projection of the molecule **II** (in the same orientation of the thio ligand as in Fig. 1) with numbering of the atoms. The secondary interaction S...S is shown by a dashed line and the short agostic contact N-H...Te by a dotted line. The thermal displacement ellipsoids are given at the 50% probability level

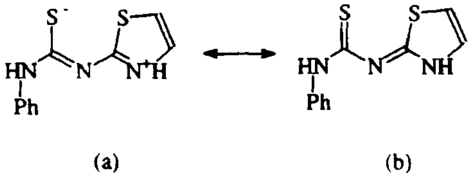
However, we can not affirm that the complexing ability (and also the trans-influence) of the resulting isothioureidate ligand is greater than that of conventional thiourea ligands in hypervalent complexes of this type. Geometrical parameters (Table V) of the linear Br--Te--S 3c,4e moiety [∠BrTeS 174.49(2)°] are quite normal: bond distance Br--Te 2.883(1) Å is of medium length [larger than 2.833(1) Å found in the tetramethylthiourea analog[13] and 2.835(1) Å observed in one of the crystalline modifications of the ethylenethiourea analog,[6] but smaller than 2.904(1) Å found in the related trimethylenethiourea complex,[4] or 2.969(1) Å found in the second crystalline modification of the ethylenethiourea analog[6] and 3.11(1) Å found in the complex of thiourea itself[5]]. The same holds for the Te--S distance of 2.548(1) Å [2.50(2)-2.589(2) in the analogous thiourea-derived complexes[4-6,13]].

The reason for the moderate trans-influence of the isothioureidate ligand may be due to the resonance between thiourea and isothiourea structures like that shown in Scheme 4. This resonance increases the trans-influence of the ligands with a normal thiourea structure:



SCHEME 6

owing to the contribution of the (b) form, but it decreases the trans-influence of the ligand with an isothiourea structure just the other way around:



SCHEME 7

Indeed, the bond lengths N(2)-C(7) and N(2)-C(8) in the coordinated ligand are identical within the estimated error: 1.324(4) and 1.325(4) Å, respectively. It means that contributions of resonance forms (a) and (b) (Scheme 7) are almost equal.

Another possible reason for the reduced trans-influence of the ligand **I** may be the short intramolecular contact S(1)...S(2) (Fig. 2) of 2.987(1) Å. Its geometrical features are quite favorable for secondary bonding between S(1) and S(2). [∠ Te(1)S(1)S(2) 164.8°, ∠ S(1)S(2)C(9) 166.9°].

Another interesting short intramolecular contact in molecule **II** is N(1)-H(1n)...Te(1) of only 2.82(2) Å (the sum of van der Waals radii of Te and H is 3.26 Å).[14] It occurs very close to the plane perpendicular to the Te-Ph bond [the pseudotorsion angle C(11)-Te(1)-S(1)...H(1n) is -99(2)°], this may correspond to an attractive (agostic) interaction of the NH-group with a lone electron pair of Te.

Crystal packing and intermolecular interactions. In the crystal, molecules of **I** are linked into centrosymmetric pairs [through the (0 ½ ½) inversion centre for the reference molecule] by pairs of intermolecular H-bonds S(1)...H(2n')-N(2') (S...N 3.256(1) Å, S...H 2.43(1) Å). Geometrical conditions are favourable for such interaction: it happens just in the direction of a lone electron pair of the sulfur atom [∠C(7)=S(1)...H(2n') 110(1)°, ∠S...H(2n')-N(2') 166(3)° ; the N(2')-H(2n') vector is inclined only 4.5° relative to the mean plane of the thiourea moiety]. In addition, there are shortened contacts S...S both inside the pair [S(1)...S(2') of 3.479(1) Å] and between pairs [S(2)...S(2") of 3.549(1) Å through the (–½ 1 ½) inversion centre for the reference molecule], see Figure 3. However, we can not consider these as bonding interactions. They are rather a consequence of a van der Waals asphericity of the sulfur atoms because these contacts happen just in the directions of σ*-orbitals of the corresponding groups [∠ C(7)=S(1)...S(2') 159.6(1)°, ∠C(8)-S(2)...S(2") 158.8(1)°, ∠C(9)-S(2)...S(1') 170.2(1)°]. We may also mention a weak intermolecular C(3"')-H(3"')...S(1) interaction [S...H 2.85(1) Å, ∠C-H...S 154(1)°].

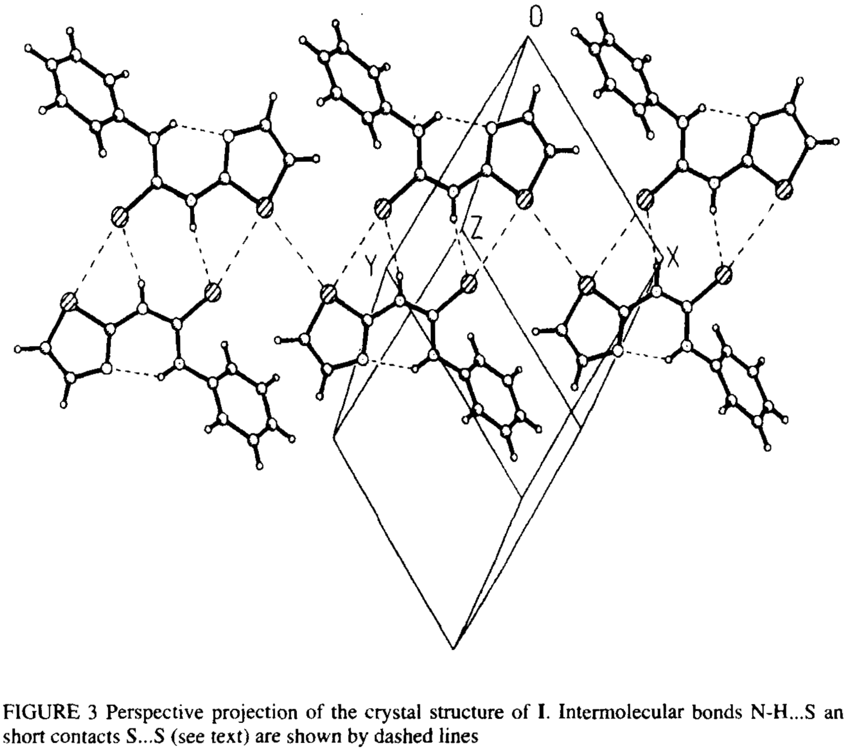


FIGURE 3 Perspective projection of the crystal structure of I. Intermolecular bonds N-H...S and short contacts S...S (see text) are shown by dashed lines

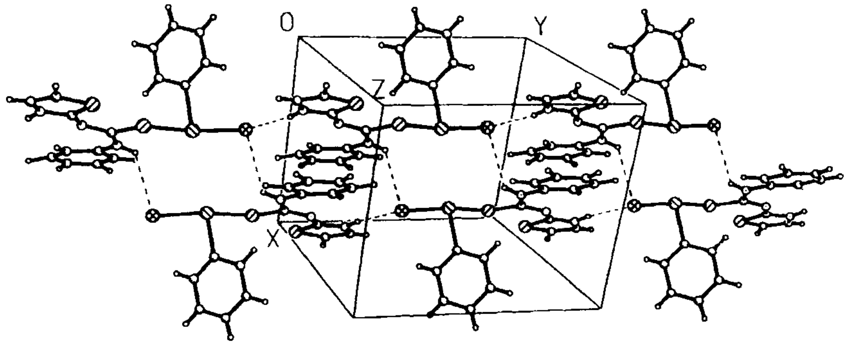


FIGURE 4 Perspective projection of the crystal structure of **II**. Intermolecular bonds N-H...Br are shown by dashed lines

Molecules of **II** are linked by H-bonds N(3)-H(3n)...Br(1') in chains along the y-axis in the crystal [N...Br 3.308(2) Å, H...Br 2.48(3) Å, ∠N-H...Br 168(6)°], see Figure 4. There are weaker H-bonds N(1)-H(1n)...Br(1") [through the (½ 00) inversion centre for the reference molecule] between these chains [N...Br 3.524(2) Å, H...Br 2.95(3) Å, ∠N-H...Br 127(6)°] which may explain the aforementioned deviation of the N(1)-H group from the coordination plane of Te (the hydrogen atom is moved toward the bromine atom of the neighbouring molecule). In addition, there is a weak intermolecular C(5"')-H(5"')...Br(1) interaction [H...Br 2.93(3) Å, ∠C-H...Br 134(7)°]. It is not unexpected that all the Br...H interactions happen in the equatorial plane of the bromine atom [bond angles Te-Br...H are 98, 107 and 118(1)° for H(1"), H(3') and H(5"'), respectively] occupied by its lone *p*-electron pairs.

Acknowledgements

Martin D. Rudd would like to thank the Royal Society for a European science Exchange Programme Post-doctoral Fellowship. Sergey V. Lindeman thanks the University of Bergen for financial support.

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