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### CHALCOGENOLATES AND THEIR DERIVATIVES, XIII<sup>1</sup> COMPLEXES OF TELLURIUM WITH HALIDE AND DITHIO LIGANDS. Crystal and Molecular Structure of Bromo-Bis(Dimethyldithiocarbamato-S,S')Tellurium(IV) Tetrabromo-(Dimethyldithiocarbamato-S,S') Tellurate(IV) Dioxane Solvate

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# CHALCOGENOLATES AND THEIR DERIVATIVES, XIII<sup>1</sup> COMPLEXES OF TELLURIUM WITH HALIDE AND DITHIO LIGANDS

## Crystal and Molecular Structure of Bromo-Bis(Dimethyldithiocarbamato-S,S')Tellurium(IV) Tetrabromo-(Dimethyldithiocarbamato-S,S')Tellurate(IV) Dioxane Solvate

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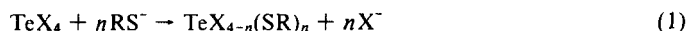
(Received March 29, 1982)

Starting from tellurium(IV) chloride and bromide the mixed ligand complexes  $\text{cis-}[\text{TeCl}_2(\text{S}_2\text{CNMe}_2)_2]$  (**8**),  $\text{cis-}[\text{TeBr}_2(\text{S}_2\text{CNEt}_2)_2]$  (**11**),  $[\text{TeCl}(\text{S}_2\text{CNEt}_2)_3]$  (**10**),  $[\text{TeBr}(\text{S}_2\text{CNMe}_2)_3][\text{TeBr}_4(\text{S}_2\text{CNMe}_2)]$  (**9**),  $[\text{TeBr}(\text{S}_2\text{COEt})_2]_2$  (**12**) and  $[\text{TeCl}(\text{S}_2\text{CPh})_2]_2$  (**13**) are formed by reaction with the corresponding dithio ligands in dioxane or ethanol as solvents. The X-ray crystal structure of **9** has been determined and shows the lone pair of tellurium(IV) to be stereochemically active in both ions of the compound. The structures of the cation and the anion of **9** can be derived from octahedral and pentagonal bipyramidal coordinations respectively.

Tellurium in oxidation states +2 and +4 occurs in a variety of complexes with coordination numbers 4 to 8 and stereochemically active or inactive lone pairs, thus allowing a broadly based study of the structural features of compounds of the main group elements. For instance, with halide and thio ligands ( $\text{X}^- = \text{Cl}^-, \text{Br}^-$ ;  $\text{L} = \text{thiourea}$  and derivatives including benzimidazole-thione, benzthiazole-thione) the square planar  $[\text{TeL}_4]^{2+}$  (**1**)<sup>2-4</sup> and  $\text{cis}$  or  $\text{trans}$   $[\text{TeX}_2\text{L}_2]$  (**2**)<sup>5-7</sup> as well as the octahedral  $[\text{TeX}_6]^{2-}$  (**3**)<sup>8,9</sup> and  $\text{cis}$  or  $\text{trans}$   $[\text{TeX}_4\text{L}_2]$  (**4**)<sup>10-12</sup> are formed. With dithio ligands ( $\text{L-L}^- = \text{dithiocarbamate}$ , xanthate) the trapezoidal  $[\text{Te}(\text{L-L})_2]$  (**5**)<sup>13-17</sup> the pentagonal planar  $[\text{Te}(\text{L-L})_3]^-$  (**6**)<sup>18</sup> and the bitrapezoidal  $[\text{Te}(\text{L-L})_4]$  (**7**)<sup>19</sup> are known. However, no heteroleptic compounds with halide and dithio ligands had been fully characterized when we started our investigations on these mixed ligand complexes of tellurium in order to look for new coordination modes and to get further information on the stereochemical effects of lone pairs.

## SYNTHESIS OF THE MIXED LIGAND COMPLEXES

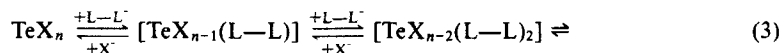
Two types of reactions may occur when dithio ligands ( $\text{RS}^- = \text{dithiocarbamate}$ , xanthate) are added to tellurium(IV) halides ( $\text{TeX}_4$ ,  $\text{X} = \text{Cl}, \text{Br}$ ), namely substitution (Eq. 1) or oxidation-reduction (Eq. 2).<sup>20-22</sup>



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Although dithiocarbamates give mixed ligand complexes of tellurium(IV), xanthates and dithiobenzoate reduce tellurium(IV) to give tellurium(II) compounds. The compositions of the products isolated apparently do not depend on the molar ratio of the reactants but seem to be controlled by the relative solubilities of the possible products which can be formed according to Eq. 3.



Although all of the mixed ligand complexes of tellurium(IV) and tellurium(II) have not yet been reported in the literature, the tellurium(II) xanthates **5a** and **5b** have already been prepared in a different way from telluropentathionate and the corresponding xanthates.<sup>25</sup>

TABLE I  
Reaction products of tellurium(IV) halides and dithio ligands

dithio ligand (L—L <sup>-</sup> )	tellurium(IV) halide	molar ratio	solvent	reaction product
dimethyl dithiocarbamate	TeCl <sub>4</sub>	2:1	dioxane	[TeCl <sub>2</sub> (L—L) <sub>2</sub> ] ( <b>8</b> )
	TeBr <sub>4</sub>	1:1	dioxane	[Te <sub>2</sub> Br <sub>5</sub> (L—L) <sub>3</sub> ]·dioxane ( <b>9</b> )
diethyl dithiocarbamate	TeCl <sub>4</sub>	2:1	dioxane ethanol	[TeCl(L—L) <sub>3</sub> ]·dioxane ( <b>10a</b> ) <sup>23,24</sup> [TeCl(L—L) <sub>3</sub> ] ( <b>10b</b> )
	TeBr <sub>4</sub>	1:1	dioxane	[TeBr <sub>2</sub> (L—L) <sub>2</sub> ]·dioxane ( <b>11</b> )
methyl xanthate	TeCl <sub>4</sub>	3:1	ethanol	[Te(L—L) <sub>2</sub> ] ( <b>5a</b> )
ethyl xanthate	TeCl <sub>4</sub>	3:1	ethanol	[Te(L—L) <sub>2</sub> ] ( <b>5b</b> )
	TeBr <sub>4</sub>	3:1	dioxane	[TeBr(L—L)] ( <b>12</b> )
dithio benzoate	TeCl <sub>4</sub>	2:1	dioxane	[TeCl(L—L)] ( <b>13</b> )

## STRUCTURES OF THE MIXED LIGAND COMPLEXES

For the tellurium(II) derivatives with analytical compositions [TeBr(S<sub>2</sub>COEt)] (**12**) and [TeCl(S<sub>2</sub>CPh)] (**13**) we propose dimeric structures in which the halide ions act as bridging ligands in analogy to the structure described for di(μ-bromo)bis[di(ethylenethiourea)tellurium(II)] bromide.<sup>26</sup> Unfortunately, no proof of the structures by measurement of the molecular weights was possible since no solvent was found in which the compounds could be dissolved without decomposition.

The structures of the tellurium(IV) derivatives, however, are better established. An X-ray analysis of [TeBr<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] (**11**) which has been reported elsewhere<sup>1</sup> shows the tellurium(IV) in an octahedral environment, the two bromo ligands being in cis positions (Figure 1). A corresponding structure can be deduced for [TeCl<sub>2</sub>(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>] (**8**) from the similarity of the IR spectra of **8** and **11** (differences should only be seen below 300 cm<sup>-1</sup> in the regions of the ν<sub>TeCl</sub> and ν<sub>TeBr</sub> vibrations).

Further, a crystal structure determination of  $[\text{TeCl}(\text{S}_2\text{CNEt}_2)_3] \cdot \text{dioxane}$  (**10a**)<sup>24</sup> revealed a pentagonal bipyramidal geometry for tellurium(IV) with the chloro ligand occupying an axial position (Figure 1).

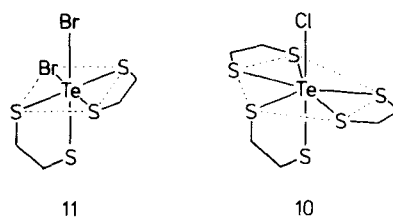


FIGURE 1 Simplified molecular structures of  $[\text{TeBr}_2(\text{S}_2\text{CNEt}_2)_2]$  (**11**)<sup>1</sup> and  $[\text{TeCl}(\text{S}_2\text{CNEt}_2)_3]$  (**10**)<sup>24</sup> in each of which the lone pair of tellurium(IV) is stereochemically inactive.

The structure of **9** with the unusual stoichiometric composition  $[\text{Te}_2\text{Br}_5(\text{S}_2\text{CNMe}_2)_3]$  could only be elucidated by an X-ray analysis. The results of this structure determination by which all non-hydrogen atoms could be located are given in Tables II and III. The crystal structure of **9** is built from  $[\text{TeBr}(\text{S}_2\text{CNMe}_2)_2]^+$  and  $[\text{TeBr}_4(\text{S}_2\text{CNMe}_2)]^-$  ions and includes also solvate dioxane. There is a weak contact between cation and anion ( $\text{Te1} \cdots \text{Br21} = 331 \text{ pm}$ ).

TABLE II  
Crystal data of **9**

crystal system: monoclinic C	
space group: C2/c	
$a = 4122(4) \text{ pm}$	$Z = 8$
$b = 998(2) \text{ pm}$	$V = 6793.9 \times 10^6 \text{ pm}^3$
$c = 1681(1) \text{ pm}$	$M = 1103.5$
$\beta = 100.66(6)^\circ$	$\rho = 2.16 \text{ g/cm}^3$

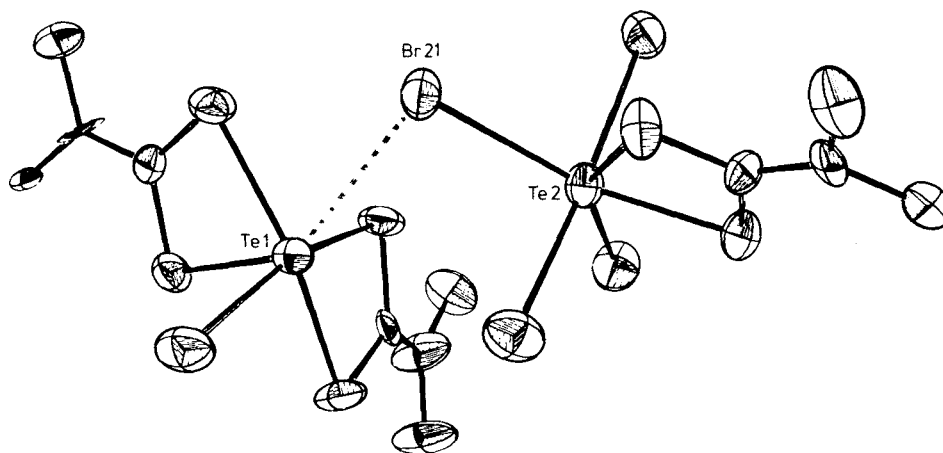


FIGURE 2 Relative orientation of the cation and the anion of **9**.

TABLE III

Final positional and thermal parameters for 9. The anisotropic temperature factor is defined as  $\exp[-2\pi^2(U_1h^2a^{*2} + U_2k^2b^{*2} + U_3l^2c^{*2} + 2U_{12}h^*k^* + 2U_{13}h^*l^*c^* + 2U_{23}k^*l^*c^*)]$

Atom	X/a (σ)	Y/b (σ)	Z/c (σ)	U <sub>11</sub> (σ)	U <sub>22</sub> (σ)	U <sub>33</sub> (σ)	U <sub>23</sub> (σ)	U <sub>13</sub> (σ)	U <sub>12</sub> (σ)
Te1	0.1837(1)	0.3498(3)	-0.0529(2)	0.0554(18)	0.0370(17)	0.0474(17)	0.0043(15)	0.0166(14)	0.0081(16)
Br11	0.2224(1)	0.5727(5)	-0.0284(3)	0.0728(34)	0.0412(29)	0.0814(36)	-0.0091(27)	0.0097(28)	-0.0018(26)
Si1	0.1865(3)	0.3721(11)	-0.1964(6)	0.0673(69)	0.0416(65)	0.0409(58)	0.0054(55)	0.0190(52)	0.0004(58)
Si2	0.2227(3)	0.1663(12)	-0.0910(6)	0.0604(67)	0.0483(67)	0.0445(60)	0.0127(56)	0.0064(51)	0.0176(61)
C11	0.214(1)	0.236(4)	-0.182(2)	0.031(15)	0.048(15)	0.055(15)	0.010(14)	0.017(14)	0.002(14)
N11	0.228(1)	0.196(3)	-0.245(2)	0.041(14)	0.037(14)	0.096(15)	-0.013(14)	0.027(13)	0.029(13)
C111	0.250(1)	0.086(4)	-0.236(2)	0.055(15)	0.042(15)	0.062(15)	-0.015(14)	0.009(14)	0.013(14)
C112	0.218(1)	0.253(4)	-0.336(3)	0.064(15)	0.055(15)	0.108(16)	0.053(15)	0.062(14)	0.048(14)
Si3	0.1299(3)	0.4895(12)	-0.1021(8)	0.0601(73)	0.0390(67)	0.0822(82)	-0.0035(61)	0.0135(65)	0.0216(58)
Si4	0.1345(3)	0.1915(11)	-0.0984(8)	0.0522(70)	0.0265(65)	0.1025(88)	0.0095(61)	0.0182(65)	0.0050(53)
C12	0.110(1)	0.336(4)	-0.122(2)	0.096(16)	0.023(14)	0.043(14)	0.001(14)	0.052(13)	-0.005(15)
N12	0.080(1)	0.327(4)	-0.154(3)	0.030(13)	0.064(15)	0.133(16)	-0.023(15)	-0.006(14)	0.007(14)
C121	0.065(1)	0.189(4)	-0.173(3)	0.081(16)	0.055(16)	0.084(16)	-0.005(15)	-0.004(15)	-0.026(15)
C122	0.060(1)	0.449(4)	-0.173(4)	0.046(15)	0.030(15)	0.216(18)	-0.030(16)	0.014(16)	-0.010(15)
Te2	0.1358(1)	0.1609(3)	0.1426(2)	0.0472(17)	0.0515(18)	0.0357(16)	-0.0041(15)	0.0093(13)	-0.0031(16)
Br21	0.2003(1)	0.1318(5)	0.0973(3)	0.0481(26)	0.0697(33)	0.0480(25)	0.0050(26)	0.0161(21)	0.0019(26)
Br22	0.0721(1)	0.1706(6)	0.0474(3)	0.0599(31)	0.0928(41)	0.0612(30)	0.0031(31)	0.0041(24)	0.0087(30)
Br23	0.1452(1)	0.4253(5)	0.1273(3)	0.1000(42)	0.0561(33)	0.0747(37)	-0.0066(29)	0.0063(31)	-0.0040(30)
Br24	0.1319(1)	-0.1060(5)	0.1602(3)	0.0836(37)	0.0537(31)	0.0647(31)	0.0046(25)	0.0277(28)	-0.0000(26)
S21	0.1731(3)	0.1630(14)	0.2804(6)	0.0512(65)	0.0851(83)	0.0446(63)	0.0046(66)	0.0135(52)	-0.0109(68)
S22	0.1011(3)	0.1897(12)	0.2471(7)	0.0423(62)	0.0648(79)	0.0544(66)	-0.0054(59)	0.0154(52)	-0.0071(56)
C21	0.139(1)	0.169(4)	0.318(2)	0.058(15)	0.041(15)	0.038(15)	-0.008(15)	0.021(14)	0.005(14)
N21	0.137(1)	0.161(3)	0.397(2)	0.075(14)	0.019(12)	0.040(13)	-0.003(12)	0.023(12)	-0.021(13)
C211	0.167(1)	0.139(4)	0.454(2)	0.091(16)	0.065(15)	0.007(12)	-0.001(14)	0.014(13)	-0.048(15)
C212	0.104(1)	0.168(5)	0.434(3)	0.096(16)	0.055(16)	0.090(16)	0.026(15)	0.046(15)	0.015(15)
O1	0.030(1)	0.643(5)	0.145(3)	0.135(11)					
C2	0.050(2)	0.532(7)	0.108(4)	0.139(14)					
C3	0.064(2)	0.574(8)	0.046(5)	0.160(15)					
O4	0.047(1)	0.681(4)	-0.001(2)	0.123(10)					
C5	0.036(2)	0.791(7)	0.045(4)	0.140(14)					
C6	0.014(2)	0.746(8)	0.108(5)	0.163(15)					

The cation (**9, A**) can be described as a square pyramid (or an octahedron with one edge unoccupied) the anion (**9, B**) as a distorted octahedron (or a pentagonal bipyramid with an equatorial position unoccupied) as shown in Figure 3. The relative orientation of cation and anion in the crystal is shown in Figure 2; the relevant bond distances and angles are given in Table IV.

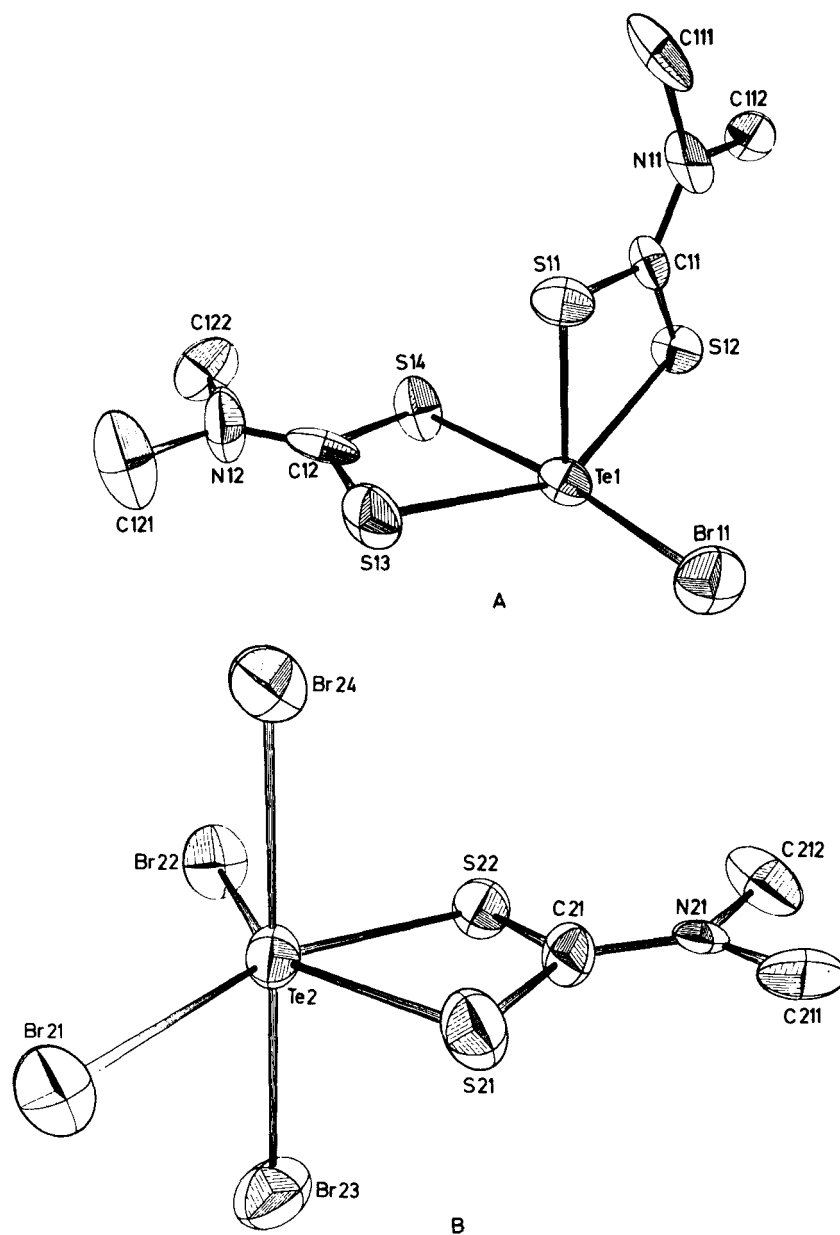


FIGURE 3 Molecular structure of the cation (A) and the anion (B) of **9**. ORTEP-plot and numbering scheme of atoms; the asymmetric unit also contains a dioxane molecule (O1, C2, C3, O4, C5, C6).

TABLE IV  
 Relevant distances (pm) and angles (°) in **9**

distances (pm)			
Te1-Br11	272.5(6)	Te1-S11	244.5(11)
Te2-Br21	291.1(5)	Te1-S12	259.4(12)
Te2-Br22	281.3(5)	Te1-S13	262.0(12)
Te2-Br23	268.6(6)	Te1-S14	257.1(11)
Te2-Br24	268.9(6)	Te2-S21	253.1(10)
Te1...Br21	330.7	Te2-S22	248.1(12)
S11-C11	175(4)	N11-C111	143(5)
S12-C11	166(4)	N11-C112	161(6)
S13-C12	175(4)	N12-C121	151(6)
S14-C12	177(4)	N12-C122	148(6)
S21-C21	166(4)	N21-C211	145(5)
S22-C21	178(4)	N21-C212	160(6)
N11-C11	134(6)		
N12-C12	125(6)		
N21-C21	134(5)		
angles(°)			
Br11-Te1-S14	162.6(3)	S12-Te1-S13	145.6(4)
Br11-Te1-S12	103.9(3)	S11-Te1-Br11	86.6(3)
S12-Te1-S14	89.0(4)	S11-Te1-S12	71.1(4)
S14-Te1-S13	70.1(4)	S11-Te1-S14	86.7(4)
S13-Te1-Br11	93.0(3)	S11-Te1-S13	80.4(4)
Br21-Te2-S22	150.6(3)		
S21-Te2-Br22	149.8(3)	Br23-Te2-Br24	175.3(2)
Br21-Te2-S21	79.1(3)	S22-Te2-Br22	78.3(3)
S21-Te2-S22	71.5(4)	Br22-Te2-Br21	131.0(2)
Br23-Te2-Br21	85.3(2)	Br24-Te2-Br21	90.4(2)
Br23-Te2-S21	90.3(3)	Br24-Te2-S21	86.9(3)
Br23-Te2-S22	93.8(3)	Br24-Te2-S22	89.0(3)
Br23-Te2-Br22	92.8(2)	Br24-Te2-Br22	91.6(2)
Te1-S11-C11	86.7(14)	Te1-S12-C11	83.6(15)
Te1-S13-C12	86.5(15)	Te1-S14-C12	87.5(14)
Te2-S21-C21	86.2(13)	Te2-S22-C21	85.2(14)
S11-C11-S12	119(3)	C11-N11-C111	121(4)
S11-C11-N11	119(3)	C11-N11-C112	125(3)
S12-C11-N11	123(3)	C111-N11-C112	113(3)
S13-C12-S14	116(2)	C12-N12-C121	118(4)
S13-C12-N12	123(3)	C12-N12-C122	120(4)
S14-C12-N12	121(3)	C121-N12-C122	122(3)
S21-C21-S22	116(2)	C21-N21-C211	118(3)
S21-C21-N21	126(3)	C21-N21-C212	127(3)
S22-C21-N21	117(3)	C211-N21-C212	116(3)

## DISCUSSION OF THE RESULTS

Any discussion should start from the structures of tellurium(II) compounds. Figure 4 shows the known coordination modes (**Ia-IVa**), all being planar arrangements with coordination numbers 2 (angular), 4 (square planar or trapezoidal), and 5 (pentagonal planar). The orbitals of the central atom oriented perpendicular to the molecular plane ( $p_z$ ,  $d_{z^2}$ ) can be used to bind further ligands in corresponding tellurium(IV) derivatives leading to two different series of compounds, one with two axial ligands above and below the original plane (**Ib-IVb**) and a second one with

only one axial ligand (**Ic**, **IIc**); examples of the possible structures **IIIc** and **IVc** have not yet been reported.

The structures of the new mixed ligand compounds **8–11** fit well into the scheme of Figure 4. Especially the anion **9B** is the first example of the hitherto unknown type **IIIb**.

A closer look at the structural details of the tellurium(IV) compounds reveals intermediate forms to exist indicating transitions between **Ib** and **IIb** or **IIIb/IVb** respectively. This is shown in Figures 5 and 6.











Te(II)				
	Ia	IIa	IIIa	IVa
Te(IV)				
	Ib	IIb	IIIb	IVb
				
	Ic	IIc		

FIGURE 4 Synopsis of the known structures of mononuclear tellurium(II) and tellurium(IV) compounds. Examples of types **Ia**:  $\text{TeX}_2$ ,<sup>27</sup>  $\text{R}_2\text{Te}$ ,<sup>28</sup> **Ib**:  $\text{R}_2\text{TeX}_2$ ,<sup>29,30</sup> **Ic**:  $[\text{TeX}_3]^+$ ,<sup>31,32</sup>  $[\text{R}_3\text{Te}]^+$ ,<sup>33,34</sup> **IIa**:  $[\text{Te}(\text{tu})_4]^{2+}$  (**1**),<sup>2-4</sup>  $\text{TeX}_2(\text{tu})_2$  (**2**),<sup>5-7</sup> **IIb**:  $[\text{TeX}_6]^{2-}$  (**3**),<sup>8,9</sup>  $\text{TeX}_4(\text{tu})_2$  (**4**),<sup>10-12</sup> **IIc**:  $[\text{TeX}_5]^-$ ,<sup>35,36</sup>  $[\text{RTeX}_4]^-$ ,<sup>33</sup> **IIIa**:  $\text{Te}(\text{dte})_2$  (**5**),<sup>13-17</sup> **IIIb**: **9B** (this investigation); **IVa**:  $[\text{Te}(\text{dte})_3]^-$  (**6**),<sup>18</sup> **IVb**: **10**<sup>24</sup> ( $\text{R}$  = alkyl, aryl;  $\text{X}$  = halide,  $\text{tu}$  = thiourea and related compounds;  $\text{dte}$  = dithiocarbamate and related compounds).

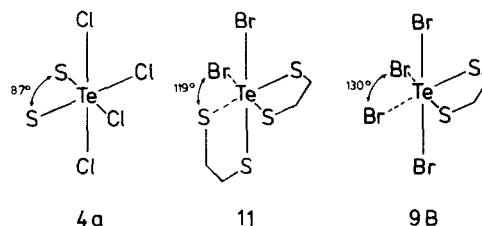


FIGURE 5 Increase of bond angle  $\text{XTeY}$  in  $\text{cis}[\text{TeCl}_4(\text{benzimidazole-thione-S})_2]$  (**4a**),<sup>10</sup>  $\text{cis}[\text{TeBr}_2(\text{S}_2\text{CNET}_2)_2]$  (**11**)<sup>1</sup> and  $[\text{TeBr}_4(\text{S}_2\text{CNMe}_2)]^-$  (**9B**) according to transitions between structures **IIb** and **IIIb**. The accompanying bond lengthening is indicated by broken lines.

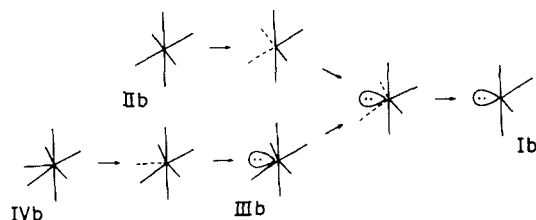


FIGURE 6 Relations between different structural forms of tellurium(IV) compounds. Weaker bonds are indicated by broken lines.



An interesting feature of structures **Ib/c** and **IIb/c** are the Te(IV)—X bond lengths. Two significantly different distances are found and can be explained by a simple model which puts the two electrons of tellurium(IV) into a sterically inactive *s*-orbital and uses only *p*-orbitals to bind the ligands X. Each *p*-orbital can interact either with only one ligand (giving normal, relatively short Te(IV)—X bonds) or with two ligands (leading to longer, hypervalent bonds<sup>37</sup> in linear X—Te(IV)—X or X—Te(IV)—Y units).

Taking mean values of normal Te(IV)—X bond lengths in compounds **Ic** and **Iic** from the literature (cited in the legend of Figure 4) and assuming the usual single bond radii of the ligand X,<sup>38</sup> different bond radii of tellurium(IV) are obtained depending on the electronegativity of X (see Figure 7). No example with a normal Te(IV)—Br bond is known; but with  $EN_{Br} = 3.0$  the bond radius  $r_{Te(Br)} = 133$  pm can be taken from Figure 7. Thus, the "normal" bond distance  $d_{Te(IV)-Br} = 247$  pm would be, as is to be expected, slightly shorter than  $d_{Te(II)-Br} = 251$  pm.<sup>27</sup>

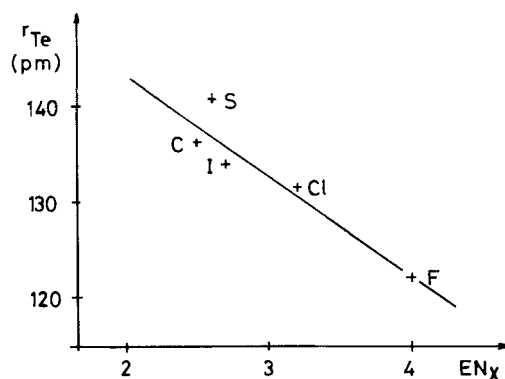


FIGURE 7 Correlation of tellurium(IV) bond radii  $r_{Te} = d_{TeX} - r_X$  and Pauling's electronegativities of different ligands X for normal Te(IV)—X bonds in compounds **Ib/c** and **Iic**.

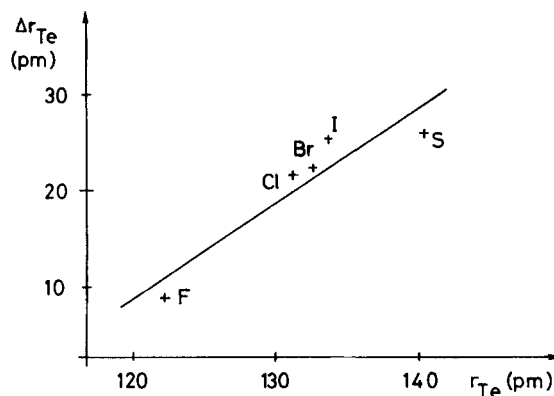


FIGURE 8 Increase of tellurium(IV) bond radii  $\Delta r_{Te} = r_{Te}(TeX) - r_{Te}(XTeX)$  (in X—Te(IV)—X relative to Te(IV)—X units) in relation to the tellurium(IV) bond radii in corresponding normal Te(IV)—X bonds in compounds **Ib/c** and **IIb/c**.

The addition of a further ligand X to a normal Te(IV)—X arrangement leads to a linear X—Te(IV)—X unit with longer TeX bonds. If no change in the single bond radii of ligands X is considered the effective bond radius of tellurium(IV) must be enlarged. The amount of increase correlates with the corresponding bond radius of tellurium(IV) in normal TeX bonds (Figure 8).

When a ligand Y is added to a Te(IV)—X arrangement the two ligands of the Y—Te(IV)—X unit formed compete for the *p*-orbital of the central tellurium(IV), and the more loosely one ligand is bonded the more tightly bonded is the other. In this case two different effective bond radii of tellurium(IV) are found in Y—Te(IV)—X units, each being enlarged relative to the radii in normal Te(IV)—Y and Te(IV)—X bonds. The corresponding amounts of increase for  $\Delta r_{\text{Te}}(\text{X})$  and  $\Delta r_{\text{Te}}(\text{Y})$  depend on each other as can be seen from Figure 9.

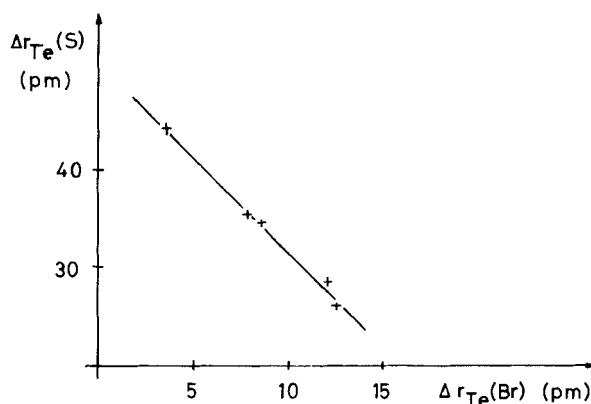


FIGURE 9 Correlation of  $\Delta r_{\text{Te}}(\text{S}) = r_{\text{Te}}(\text{STeBr}) - r_{\text{Te}}(\text{TeS})$  and  $\Delta r_{\text{Te}}(\text{Br}) = r_{\text{Te}}(\text{STeBr}) - r_{\text{Te}}(\text{TeBr})$  for different linear or nearly linear S—Te(IV)—Br units in compounds **9** and **11**.

## EXPERIMENTAL

All preparations were carried out under nitrogen and exclusion of moisture.

**Derivatives of dithiocarbamates.** *General procedure:* Using dioxane or ethanol as solvents the solution of tellurium(IV) halide was added dropwise to the solution of alkali dithiocarbamate at room temperature. The reaction mixture was allowed to stand overnight, then heated to ca. 50°C to dissolve the product and filtered from the alkali halide. After having covered the solution with a layer of petroleum ether the product gradually crystallized in the course of a few days.

**Dichloro-bis(dimethyldithiocarbamato-S,S')tellurium(IV) (8).** 1.34 g (5 mmole) tellurium(IV) chloride/100 ml dioxane, 1.79 g (10 mmole) sodium dimethyldithiocarbamate dihydrate/50 ml dioxane. Yield: 1.18 g (54%), yellow crystals (from methylene chloride), m.p. 165–168°C.  $\text{C}_6\text{H}_{12}\text{Cl}_2\text{N}_4\text{S}_4\text{Te}$  (438.9). Calc.: C, 16.41; H, 2.76; Cl, 16.15; N, 6.38; S, 29.22; Te, 29.07. Found: C, 17.01; H, 3.01; Cl, 15.82; N, 6.32; S, 29.00; Te, 28.85.

**Bromo-bis(dimethyldithiocarbamato-S,S')tellurium(IV) tetrabromo(dimethyldithiocarbamato-S,S')tellurate(IV)—dioxane (1/1) (9).** 1.79 g (4 mmole) tellurium(IV) bromide/100 ml dioxane, 0.72 g (4 mmole) sodium dimethyldithiocarbamate dihydrate/50 ml dioxane. Yield: 0.75 g (51%), yellow needles, m.p. 170–173°C.  $\text{C}_{13}\text{H}_{26}\text{Br}_3\text{N}_3\text{O}_2\text{S}_6\text{Te}_2$  (1103.5). Calc.: C, 14.15; H, 2.38; Br, 36.21; N, 3.81; Te, 23.13. Found: C, 13.86; H, 2.33; Br, 36.25; N, 3.60; Te, 23.98.

**Chloro-tris(diethyldithiocarbamato-S,S')tellurium(IV) (10b).** 0.67 g (2.5 mmole) tellurium(IV) chloride/100 ml ethanol, 1.3 g (5 mmole) sodium diethyldithiocarbamate trihydrate/50 ml ethanol. Yield:

0.74 g (73%), yellow needles (from ethanol), m.p. 136°C.  $C_{15}H_{30}ClN_3S_6Te$  (607.8). Calc.: C, 29.64; H, 4.97; Cl, 5.83; N, 6.91; Te, 20.99. Found: C, 29.61; H, 5.04; Cl, 6.55; N, 6.92; Te, 21.00.

**cis-Dibromo-bis(diethyldithiocarbamato-S,S')tellurium(IV)—dioxane (1/1) (11).** 1.79 g (4 mmole) tellurium(IV) bromide/100 ml dioxane, 0.90 g (4 mmole) sodium diethyldithiocarbamate trihydrate/50 ml dioxane. Yield: 0.60 g (45%), ruby red crystals, m.p. 84°C.  $C_{14}H_{28}Br_2N_2O_2S_4Te$  (672.1). Calc.: C, 25.02; H, 4.19; Br, 23.78; N, 4.16; Te, 18.98. Found: C, 24.88; H, 4.17; Br, 22.47; N, 4.13; Te, 19.30.

**Derivatives of xanthates.** *General procedure:* The solutions of the reactants were combined in the dark with cooling, the precipitates of alkali halide and eventually of metallic tellurium were separated by filtration, the solution kept at  $-20^\circ\text{C}$  in the refrigerator for a few days. The crystals formed were separated, washed with petroleum ether and dried in vacuum.

**Di(methylxanthato-S,S')tellurium(II) (5a).** 2.00 g (7.4 mmole) tellurium(IV) chloride/40 ml ethanol, 3.25 g (22.2 mmole) potassium methylxanthate/40 ml ethanol. Yield: 0.75 g (40%), red violet crystals, m.p.  $86^\circ\text{C}$  decomp. (lit.<sup>25</sup>  $89^\circ\text{C}$ ).  $C_4H_6O_2S_4Te$  (341.9). Calc.: C, 14.05; H, 1.77; Te, 37.32. Found: C, 14.00; H, 1.79; Te, 37.40.

**Di(ethylxanthato-S,S')tellurium(II) (5b).** 2.56 g (9.5 mmole) tellurium(IV) chloride/50 ml ethanol, 4.80 g (29.5 mmole) potassium ethylxanthate/50 ml ethanol. Yield: 0.15 g (6%), red needles, m.p.  $84^\circ\text{C}$  decomp. (lit.<sup>25</sup>  $86^\circ\text{C}$ ).  $C_6H_{10}O_2S_4Te$  (370.0). Calc.: C, 19.47; H, 2.72; Te, 34.48. Found: C, 19.27; H, 2.67; Te, 34.80.

**Bromo(ethylxanthato)tellurium(II) (12).** 0.80 g (1.8 mmole) tellurium(IV) bromide/50 ml dioxane, 0.86 g (5.4 mmole) potassium ethylxanthate/50 ml dioxane. Yield: 0.15 g (25%), red needles, m.p.  $106^\circ\text{C}$  decomp.  $C_3H_5BrOS_2Te$  (328.7). Calc.: C, 11.05; H, 1.53; Te, 38.81. Found: C, 10.97; H, 1.52; Te, 38.54.

**Derivative of dithiobenzoate. Chloro-(dithiobenzoato)tellurium(II) (13).** A solution of 0.38 g (1.5 mmole) tellurium(IV) chloride in 50 ml dioxane was added to a solution of 0.44 g (3 mmole) dithiobenzoic acid<sup>39</sup> in 50 ml dioxane. After having been covered with a layer of petroleum ether the red reaction mixture precipitated red needles (m.p.  $126^\circ\text{C}$ , decomp.). Yield: 0.25 g (79%).  $C_7H_5ClS_2Te$  (316.3). Calc.: C, 26.65; H, 1.59; Cl, 11.20; Te, 40.34. Found: C, 26.80; H, 1.65; Cl, 11.22; Te, 40.00.

**Structure determination.** X-ray data collection was made on a Syntex P2<sub>1</sub> four-circle diffractometer using the  $\omega$ -scan technique and Mo-K $\alpha$  radiation ( $\lambda = 71.069$  pm). 3693 independent reflections with  $2 < 2\theta < 40^\circ$  were collected by standard procedures, the check reflections showing no significant variation in intensity, and corrected for Lorentz and polarized factors. No absorption correction was made. The structure was solved by direct methods (MULTAN 74,<sup>40</sup> SHEL 76<sup>41</sup>) which gave the positions of the heavy atoms. On this basis, successive difference Fourier syntheses gradually allowed all non-hydrogen atoms of the compound to be located as well as showing the presence of a solvate dioxane molecule. Block-diagonal anisotropic least-squares refinement (SHEL 76<sup>41</sup>) led to a final  $R = 0.087$  for 1832 reflections having  $|F_o| > 3\sigma(|F_o|)$ .

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