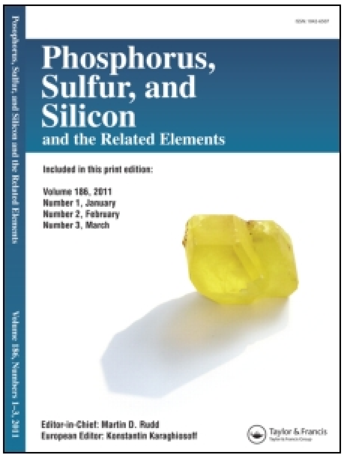

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CHALCOGENOLATES AND THEIR DERIVATIVES, IX[1] CRYSTAL AND MOLECULAR STRUCTURE OF CHLORO-TRIS(DIETHYLDITHIOCARBAMATO-S,S')-TELLURIUM (IV) - DIOXANE (1/1)

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CHALCOGENOLATES AND THEIR DERIVATIVES, IX[1] CRYSTAL AND MOLECULAR STRUCTURE OF CHLORO-TRIS(DIETHYLDITHIOCARBAMATO-S,S′)-TELLURIUM (IV) — DIOXANE (1/1)

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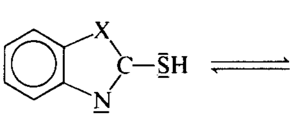
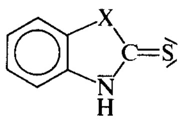
The reaction of sodium N,N-diethyldithiocarbamate with tellurium (IV) chloride in 2:1 molar ratio in dioxane yields the title compound $[Cl(Et_2NCS_2)_3Te]\cdot C_4H_8O_2$ (**5**), the X-ray crystal structure of which has been determined. Tellurium has a distorted pentagonal-bipyramidal coordination with the lone pair showing only slight stereochemical activity.

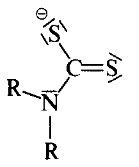
Using dioxane as solvent mercaptobenzothiazole **1** (X=S) and mercaptobenzimidazole **1** (X=NH) react with tellurium (IV) chloride to give 2:1 addition compounds of their thione forms **1b** of general composition $[Cl_4L_2Te]$ in which tellurium is octahedrally coordinated: in the case of X=S the trans-complex **2** is obtained,[2] while for X=NH the *cis*-complex **3** forms.[3]



1a



1b



4

These results prompted us to react dithiocarbamate **4** under analogous conditions in 2:1 molar ratio with tellurium (IV) chloride. However, no addition is observed, but instead partial substitution of chloro ligands by dithiocarbamate takes place. While in accord with the employed molar ratio sodium dimethyldithiocarbamate yields a complex of composition

$[Cl_2(Me_2NCS_2)_2Te]$,[4]

the reaction of sodium diethyldithiocarbamate gives a complex of composition $[Cl(Et_2NCS_2)_3Te]$ (**5**).[1] Analogous compounds of general composition $[X(R_2NCS_2)_3M]$, in which the central atom M is seven-coordinate, have been reported for titanium (**6**, R=CH_3, X=Cl)[5] and ruthenium (**7**, R=C_2H_5, X=Cl);[6] in the case of tellurium such compounds have only been obtained either if the X position is blocked by a covalently bonded substituent like phenyl (**8**, R=C_2H_5, X=C_6H_5)[7] or for X=Cl if one of the groups R carries an additional function, e.g. R=CH_2CH_2OH.[8] In these complexes the coordination around M is more or less distorted pentagonalbipyramidal, but significant differences are observed. We therefore were interested whether these differences are mainly due to the central atom M, particularly in view of the stereochemical role of the lone pair on tellurium, or whether they depend on the ligand X. An X-ray structure investigation was undertaken to elucidate this question.

STRUCTURE DETERMINATION

All measurements were made on a Syntex $P2_1$ four-circle diffractometer using Mo-K_α(λ = 71.069 pm) radiation. A crystal of approximate dimensions $0.4 \times 0.4 \times 0.7$ mm^3 was sealed in a Lindeman capillary. From a rotation Photograph 15 reflections of varying intensity were selected for lattice constants determination giving monoclinic P with dimensions $a = 854.0(5)$, $b = 2752.4(15)$, $c = 1797.6(7)$ pm, $\beta = 118.09°$; space group $P2_1/c$; $Z = 4$, $V = 3727.6 \times 10^6$ pm^3. 4526 independent reflections with $1 < 2\theta < 44°$ were collected by

TABLE I

Final positional and thermal parameters for **5**

Atom	$X/a(\sigma)$	$Y/b(\sigma)$	$Z/c(\sigma)$	$U_{11}(\sigma)$	$U_{22}(\sigma)$	$U_{33}(\sigma)$	$U_{12}(\sigma)$	$U_{13}(\sigma)$	$U_{23}(\sigma)$
Te	−0.0094(1)	0.1741(1)	0.2510(1)	0.0410(4)	0.0571(5)	0.0317(4)	−0.0003(4)	0.0127(3)	0.0006(4)
Cl	−0.3070(4)	0.2042(2)	0.2525(2)	0.0499(19)	0.1363(37)	0.0431(18)	0.0032(20)	0.0181(15)	−0.0095(20)
S11	0.2710(4)	0.1472(1)	0.2503(2)	0.0474(18)	0.0699(25)	0.0636(21)	0.0025(16)	0.0258(16)	0.0022(19)
S12	0.0254(5)	0.0703(1)	0.2498(3)	0.0594(21)	0.0683(23)	0.0766(23)	−0.0065(19)	0.0312(18)	−0.0035(22)
C1	0.2221(16)	0.0875(5)	0.2543(8)	0.0474(73)	0.0778(105)	0.0506(73)	0.0063(69)	0.0167(60)	0.0014(70)
N1	0.3427(15)	0.0529(5)	0.2650(8)	0.0588(75)	0.0953(109)	0.0911(94)	0.0070(71)	0.0282(68)	−0.0010(79)
C11	0.5295(20)	0.0691(7)	0.2719(16)	0.0466(98)	0.1068(144)	0.1656(232)	0.0123(90)	0.0349(127)	0.0305(149)
C12	0.3157(26)	0.0000(7)	0.2677(15)	0.1260(152)	0.0584(115)	0.1872(212)	0.0157(104)	0.0973(155)	0.0166(127)
C13	0.5287(27)	0.0696(8)	0.1910(15)	0.1186(158)	0.1213(191)	0.1393(189)	0.0016(128)	0.0836(151)	−0.0006(147)
C14	0.3777(29)	−0.0182(10)	0.3566(21)	0.1000(156)	0.1614(253)	0.2673(321)	0.0335(153)	0.0669(185)	0.1176(243)
S21	0.1432(5)	0.1485(1)	0.4199(2)	0.0687(22)	0.0717(26)	0.0436(18)	−0.0082(18)	0.0170(16)	0.0054(17)
S22	0.1759(4)	0.2434(1)	0.3533(2)	0.0591(19)	0.0676(24)	0.0328(16)	−0.0070(17)	0.0121(14)	0.0004(15)
C2	0.2250(14)	0.2051(5)	0.4399(7)	0.0401(65)	0.0813(103)	0.0332(68)	−0.0007(63)	0.0140(56)	−0.0029(64)
N2	0.3222(12)	0.2230(5)	0.5168(6)	0.0455(57)	0.1009(97)	0.0304(57)	−0.0004(59)	−0.0095(46)	−0.0022(58)
C21	0.3512(20)	0.1942(6)	0.5924(8)	0.0959(109)	0.1034(129)	0.0344(71)	−0.0037(92)	0.0238(72)	0.0146(75)
C22	0.4018(16)	0.2739(6)	0.5314(8)	0.0465(73)	0.0873(116)	0.0444(73)	−0.0179(75)	0.0064(60)	−0.0146(73)
C23	0.5261(22)	0.1642(7)	0.6236(10)	0.0906(114)	0.1168(171)	0.0636(100)	0.0221(109)	0.0196(86)	0.0238(102)
C24	0.2810(23)	0.3100(7)	0.5398(11)	0.0964(121)	0.0914(140)	0.0991(130)	−0.0060(100)	0.0427(104)	−0.0326(105)
S31	−0.1987(4)	0.1505(1)	0.0819(2)	0.0611(20)	0.0740(25)	0.0398(18)	−0.0064(18)	0.0159(15)	−0.0077(17)
S32	−0.0248(4)	0.2442(1)	0.1514(2)	0.0594(19)	0.0696(25)	0.0336(16)	−0.0029(17)	0.0131(14)	0.0015(16)
C3	−0.1524(14)	0.2074(5)	0.0644(7)	0.0394(63)	0.0849(105)	0.0272(62)	0.0104(62)	0.0112(51)	0.0049(62)
N3	−0.2086(12)	0.2265(5)	−0.0114(6)	0.0428(57)	0.1019(102)	0.0402(62)	0.0056(59)	0.0126(48)	−0.0020(61)
C31	−0.3315(18)	0.1975(7)	−0.0899(8)	0.0600(87)	0.1198(143)	0.0401(76)	−0.0094(86)	0.0041(67)	−0.0129(83)
C32	−0.1546(18)	0.2763(6)	−0.0267(8)	0.0664(89)	0.0967(125)	0.0496(82)	−0.0085(84)	0.0259(71)	0.0115(80)
C33	−0.2177(21)	0.1696(7)	−0.1224(9)	0.0886(107)	0.1172(145)	0.0620(91)	−0.0101(99)	0.0352(83)	−0.0318(94)
C34	−0.2890(21)	0.3156(6)	−0.0350(10)	0.0882(110)	0.0835(128)	0.0829(104)	0.0084(91)	0.0367(89)	0.0142(88)
O1	0.1760(27)	0.0101(11)	0.0424(16)	0.1433(168)	0.2139(260)	0.2746(265)	−0.0244(170)	0.0187(161)	−0.1070(218)
CO1	0.0320(61)	0.0479(11)	0.0092(30)	0.2067(351)	0.0741(212)	0.4116(531)	0.0253(230)	0.1398(383)	−0.0050(260)
CO2	−0.1359(58)	0.0324(13)	−0.0020(33)	0.2010(363)	0.1438(313)	0.4224(641)	−0.0447(259)	0.1010(398)	−0.1597(366)
O2	0.1541(29)	0.5045(14)	0.0584(21)	0.1374(188)	0.3292(391)	0.4190(401)	0.0363(214)	−0.0102(201)	−0.2709(352)
CO3	0.1141(43)	0.4676(17)	0.0101(35)	0.1070(215)	0.2762(525)	0.3585(569)	0.0584(249)	−0.0063(271)	−0.1947(457)
CO4	0.0285(62)	0.5349(17)	0.0482(29)	0.1651(323)	0.3517(555)	0.3627(531)	0.1367(367)	−0.0622(336)	−0.2755(467)

standard procedures, the check reflections showing no significant variation in intensity, and corrected for Lorentz and polarisation factors. The initial solution of the structure proceeded by the combination of direct methods[9] and Patterson map investigation, which allowed the position of tellurium and four sulfur atoms to be unambiguously located. All other atoms were then found from successive difference Fourier maps coupled with block-diagonal least-squares anisotropic refinement with unit weights used throughout. In the later stages only those reflections having $F_0 > 3\sigma$ were retained, eliminating 869 reflections. Careful inspection of the F_0/F_c tables showed that there were unreasonable deviations particularly in the range of $\theta < 5°$ as well as systematic errors in the range of small $|F_c|$ values so that it was decided to exclude a total of 189 reflections (including all with $\theta < 5°$) from the last stages of refinement. Since the hydrogen atoms positions were irrelevant for the structure no attempt was made to locate them. Refinement with all atoms anisotropic led to a final conventional R = 0.064.

The final positional and thermal parameters can be found in Table I.

RESULTS AND DISCUSSION

The solid state structure of **5** consists of discrete molecules $[Cl(Et_2NCS_2)_3Te]$. Figure 1 shows the molecular structure, the relevant interatomic distances and angles are given in Table II.

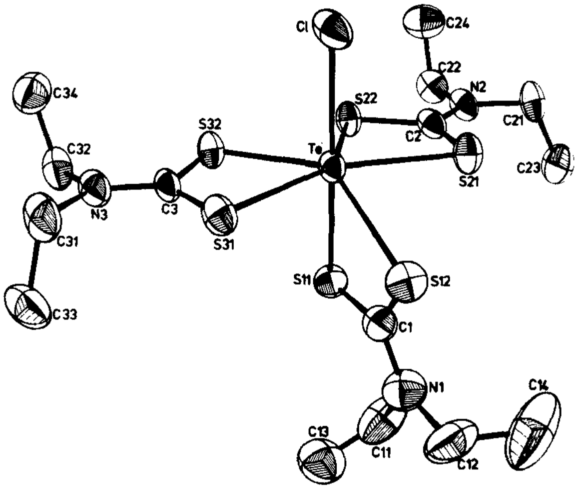


FIGURE 1 ORTEP-plot[10] of **5** and numbering scheme of atoms; in addition the asymmetric unit also contains two half molecules of dioxane (O1, CO1, CO2, and O2, CO3, CO4).

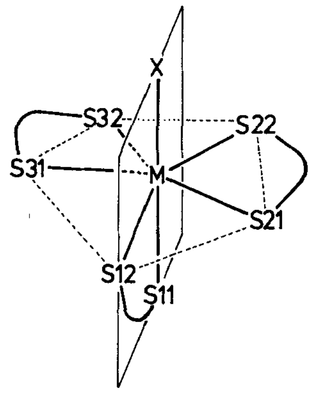


FIGURE 2 Simplified ideal structure of the compounds **5**–**8** with composition $[X(R_2NCS_2)_3M]$.

The crystal structure of **5** is thus comparable with that of compounds **6**–**8**, all having the general composition $[X(R_2NCS_2)_3M]$. To a first approximation each central atom *M* is seven-coordinate with a pentagonal-bipyramidal geometry of donor atoms, the dithiocarbamato ligands being bidentate (Figure 2). The axial positions are occupied by X and S11 of dithiocarbamato ligand 1, while the other sulfur atom S12 of this ligand takes up one of the equatorial positions. The other four equatorial sites are occupied by the sulfur atoms of dithiocarbamato ligands 2 and 3. X, M, S11, and S12 form an approximate mirror plane perpendicular to the equatorial plane; the latter is best defined in terms of M and the sulfur atoms of ligands 2 and 3 only, since S12 of ligand 1 is variable in its position relative to what would be considered the equatorial plane depending upon the specific compound in question (Table II).

In the tellurium compounds **5** and **8** the Te-S bonds are not all equivalent; in each case there are three shorter and three longer distances, which are fundamentally different in their relative orientation in the two compounds. This difference is dependent upon the ligand X. If one assumes as a limiting case only the three sulfur atoms with the shorter Te-S distance to be bonded as ligands and the other three to be displaced by the lone pair on tellurium (IV) the resulting coordination geometry derives from the trigonal-bypyramid in accord with the VSEPR model.[11] The lone pair then occupies an equatorial position, as expected, the electronegative substituent X=Cl in **5** takes up an axial position, while in **8** the less electronegative substituent $X = C_6H_5$ is in an equatorial

TABLE II

Relevant distances (pm) and angles (°) in **5** and in comparable compounds **6**^{5}, **7**^{6}, and **8**^{7} all of composition $[\mathrm{X(S_2CNR_2)_3M}]$, standard deviations

	$[\mathrm{Cl(S_2CNEt_2)_3Te}]$ (**5**)	$[\mathrm{Ph(S_2CNEt_2)_3Te}]$ (**8**)	$[\mathrm{Cl(S_2CNMe_2)_3Ti}]$ (**6**)	$[\mathrm{Cl(S_2CNEt_2)_3Ru}]$ (**7**)
distances (pm)				
M-X	268.6(4)	212.4	230.5	244.8
M-S11	251.2(4)	322.8	247.7	235.2
M-S12	287.4(4)	260.6	257.7	239.7
M-S21	277.3(3)	265.7	251.6	242.8
M-S22	260.5(3)	281.6	247.3	242.5
M-S31	276.5(3)	270.1	253.3	240.7
M-S32	259.4(4)	279.7	249.6	242.3
C1-S11	170.4(15)	167.2	171.2	170
C1-S12	171.0(15)	172.5	171.7	174
C2-S21	167.7(14)	172.2	169.9	169
C2-S22	175.9(13)	172.1	173.6	169
C3-S31	168.2(15)	174.8	172.2	178
C3-S32	174.7(11)	168.9	170.9	171
C1-N1	134.9(20)	138.9	133	135
C2-N2	132.7(14)	132.7	131	134
C3-N3	132.1(16)	133.6	131	133
S11—S12	297.8	294.6	289.8	282.1
S21—S22	294.2	294.5	288.4	276.8
S31—S32	294.6	298.6	283.6	274.7
S11—S21	369.2	389.0	340.6	336.7
S11—S22	353.7	515.1	365.3	363.7
S11—S31	371.8	407.1	346.6	360.9
S11—S32	352.8	511.0	351.9	334.7
S12—S21	347.9	339.6	308.8	294.0
S12—S31	349.3	334.2	295.1	302.0
S22—S32	320.2	330.6	301.1	289.5
angles°				
X—M—S11	179.1(1)	144.6	165.0	173.0
X—M—S12	114.1(1)	84.2	95.1	100.3
X—M—S21	91.5(1)	87.5	89.5	87.0
X—M—S22	91.7(1)	93.7	96.7	85.3
X—M—S31	91.0(1)	91.4	88.7	81.4
X—M—S32	92.1(1)	89.8	102.2	97.4
S11—M—S12	66.7(1)	60.5	69.9	72.9
S21—M—S22	66.3(1)	65.0	69.5	69.5
S31—M—S32	66.6(1)	64.8	68.7	69.3
S12—M—S21	76.0(1)	78.8	74.6	75.1
S12—M—S31	76.5(1)	79.6	74.2	78.0
S22—M—S32	76.0(1)	72.2	72.9	73.3
S11—M—S21	88.5(1)	87.0	86.0	89.5
S11—M—S22	87.5(1)	115.3	95.1	99.2
S11—M—S31	89.5(1)	81.5	87.8	98.6
S11—M—S32	87.4(1)	117.3	90.1	89.0
S11—C1—S12	121.4(9)	123.0	115.4	110
S21—C2—S22	117.8(6)	117.6	111.7	110
S31—C3—S32	118.4(7)	118.0	111.5	108
max. deviations (pm) from				
plane M/X/S11/S12	0.4(Te)	1.9(Te)	0.7(Ti)	2.4(Ru)
plane M/S21/S22/S31/S32	5.1(Te)	11.1(S32)	10.4(S32)	25.7(S22)
	116.1(S12)	15.7(S12)	61.4(S12)	80.5(S12)
angles (°) *between*				
planes M/X/S11/S12 and M/S21/S22/S31/S32	90.2	88.6	89.3	90.1
plane M/S21/S22/S31/S32				
and Te—X	89.2	87.6	80.0	84.0
and Te—S11	88.3	57.9	85.0	88.7

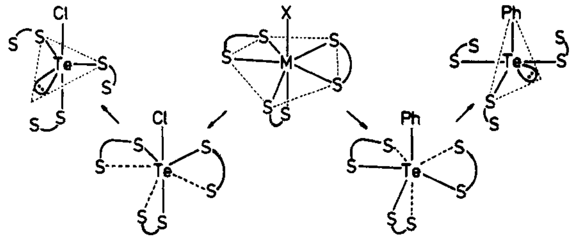


FIGURE 3 Distortion of the ideal structure of [X(R$_2$NCS$_2$)$_3$M] by the lone pair of tellurium (IV) in compounds **5** and **8** depending on X.

position (Figure 3). Overall, the lone pair in **5** causes less distortion than in **8**, presumably because the strongly electronegative Cl ligand removes electron density from tellurium, thus contracting the lone pair; consequently, the structure of **5** is similar to that of **6** and **7**, in which there is either no lone pair or no stereochemically active lone pairs to be considered.

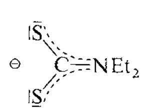
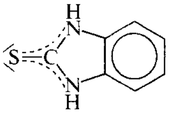
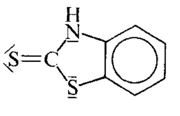
In **5** as in the other complexes the dithiocarbamato ligands are essentially planar (except for the methyl groups for R=C$_2$H$_5$). This is indicative of π-delocalization within the S$_2$CN-moiety. Accordingly, the mean C—S bond lengths of 171 pm and the C—N bond lengths of 133 pm are intermediate between those of single and double bonds ($d_{C-S} = 181$, $d_{C=S} = 160$, $d_{C-N} = 147$, $d_{C=N} = 127$ pm).[12] Some of the dithio ligands show chemically non-relevant, although statistically significant, differences in C—S distances; here, the shorter bond with more double bond character is to the sulfur atom further from tellurium and vice versa.

The bite of the chelate ligands is comparable in all cases. In contrast, inter-ligand S-S distances are significantly different. Due to the larger atomic radius of tellurium there is no crowding of ligands in **5**, which in **6** leads to distances much smaller than the sum of the van der Waals radii (Table II).

The tellurium compounds show a marked contrast in the axial configuration X-Te-S11. There is a large deviation from linearity in **8** (145°) and the Te-S11 distance of 323 pm is rather long indicating a very weak, if any, bond. In **5** the X-Te-S11 grouping is virtually linear with the Te-S11 bond length being the shortest of all Te-S interactions in the complex. We attribute this to the influence of the chloro ligand and its ability to withdraw electron density from tellurium. This is evident by comparison with other linear X-Te-S and Cl-Te-Y groups. Taking *cis-bis*(benzimidazolethione-S)tetrachlorotellurium (IV) (**3**) and trans-*bis*(benzothiazolethione-*S*)tetrachlorotellurium (IV) (**2**) for comparison, Table 3 shows that the Te-S bond lengths are shorter, the more electronegative the trans-substituents X are and the higher the effective charge of the sulfur ligand and consequently its polarizability is. Te-Cl bond lengths are shorter for more electronegative Y and increase with increasing polarizability (effective negative charge) of the trans-sulfur atom.

TABLE III

Distances (pm) in linear units X—Te—S and Cl—Te—Y of tellurium compounds **2**, **3**, and **5**

Compound	Ligand L	d_{Te-S}	d_{Te-Cl}
[ClL$_3$Te] (**5**)		251 (X=Cl)	269 (Y=S)
cis-[Cl$_4$L$_2$Te] (**3**)		263 (X=Cl)	256 (Y=S) 253 (Y=Cl)
trans-[Cl$_4$L$_2$Te] (**2**)		270 (X=S)	251 (Y=Cl)

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