The Crystal Structure of Tris(dimethyldithiocarbamato)-4-methoxyphenyltellurium(IV) Chloroform Solvate, $[Te(Me_2NCS_2)_3(MeOPh)] \cdot CHCl_3$

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The yellow crystals of the title compound are monoclinic, a = 13.172(1), b = 9.240(1), c = 23.532(2) Å, β = 90.97(1)°, Z = 4, space group $P2_1/c$ and R = 0.049 for 4264 unique observed reflections. The structure was determined by Patterson and Fourier methods. The coordination sphere of the central tellurium atom can be described as distorted pentagonal bipyramidal with the aromatic ligand axial and *trans* to a weakly bonded sulfur atom. The bond lengths involving tellurium are Te–C = 2.153(5), Te–S_{eq}(ave) = 2.721, Te–S_{ax} = 3.277(2) Å, and the angle C–Te–S_{ax} = 143.34(5)°.

During our investigations of the structural chemistry of tellurium, seven-coordinate more-or-less pentagonal bipyramidal complexes of the type $Te(IV)L_3X$ have been studied.[1] Two types of structures as depicted in Fig. 1 are found, both with X axial. Type **A** has been found with L = dialkyldithiocarbamates and X = halogens or pseudohalogens.[1,2] The structure found for **A** seems to be truly pentagonal bipyramidal with distortion largely due to the constraints imposed by the odd bidentate ligand chelating through an axial and an equatorial position in the coordination sphere. The small S–S bite causes the equatorial sulfur to be lifted out of the equatorial plane so as to maintain a nearly linear X_{ax}–Te–S_{ax} system. The lone pair of electrons in such an AB_7E complex seems to be inert.[2,3]

Complexes of the type **B** have L = dialkyldithiocarbamate,[4] but mixed compounds with one of the L groups being, for example, diethyldithiophosphate have also been studied.[5,6] In these compounds, X is always an aromatic group. The main difference from **A** is that in the **B** complexes the unique ligand has its equatorial sulfur coplanar with the other equatorial ligand atoms. Because of the small bite, the axial sulfur is pulled away from an ideal axial position so that the sequence X_{ax}–Te–X_{ax} makes an angle of between 140 and 150°.[1] Also the Te–S_{ax} bond is very long and weak, ca. 0.5 Å shorter than the sum of the van der Waals radii.[7] This may be due to the strong, well-known *trans* influence of aromatic ligands. Alternatively, the complex may be considered distorted ψ-dodecahedral with the lone pair stereochemically active and located near S_{ax}.[5]

Since only two structures of type **B** are known, it was decided to investigate such structures further.

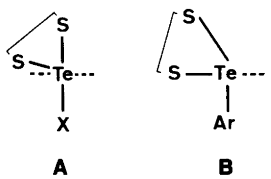

Fig. 1. The two configurations found for $Te(IV)L_3X$ compounds. The equatorial coordination plane is indicated by a dotted line.

Experimental

Preparation of complex. The complex was prepared according to published procedures.[8] Recrystallization from chloroform gave yellow crystals of $[Te(Me_2NCS)_3(MeOPh)] \cdot CHCl_3$, **1**, m.p. 163.0 °C.

X-Ray data. Reflection intensities were measured with an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Data were measured at room temperature and Mo $K\alpha$ radiation (λ = 0.71069 Å) was used. Unit cell paramters were calculated from setting angles of 25 general reflections.

Reflection intensities were recorded using the ω-scan technique and the scan rate varied between 1.25 and 6.67° min^{-1}. The standard reflections were re-measured every 2 h, and they showed no significant intensity variation during the course of measurements. For further information on unit cell and intensity data, see Table 1. The intensities were corrected for Lorentz and polarization effects and for

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Table 1. Crystallographic parameters of the title compound.

Compound	$[Te(Me_2NCS_2)_3(MeOPh)] \cdot CHCl_3$
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo *Kα*
Wavelength/Å	0.71069
Crystal system	Monoclinic
a/Å	13.172(1)
b/Å	9.240(1)
c/Å	23.532(2)
β/°	90.97(1)
V/Å^3	2863.5
Space group	$P2_1/c$ (No. 14)
F.W.	714.8
Z	4
D_{calc}/g cm^{-3}	1.658
μ(Mo *Kα*)/cm^{-1}	17.60
Crystal dimensions/mm	0.09×0.12×0.30
Scan mode/θ_{max}/°	ω-scan/2θ
Fudge factor	0.04
Scale factor	1.0482
No. of independent measurements	6885
No. with $I>2\sigma(I)$	4264
Transmission factors	0.757–0.891
$R=\Sigma\|F_o - F_c\|/\Sigma F_o$	0.049
$Rw=[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{0.5}$	0.047
$S=[\Sigma w(\Delta F)^2/N-n]^{0.5}$	1.237

absorption. Computer programs were supplied by Enraf-Nonius (SDP-Vax 1985 and CAD 4 1985).

Structure determination

The structure was solved by means of a Patterson map, and refined by least-squares methods. The function minimized is $\Sigma w(\Delta F)^2$. A weighting scheme with $w = 4F_o^2/\sigma(F_o^2)^2$ where $\sigma(F_o^2) = [\sigma(I)^2 + (0.03I)^2]^{1/2}$ was used. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were given constant isotropic temperature factors of 1.3 times those of the parent carbon atoms. Hydrogens were kept riding on the parent carbons at a fixed C–H distance of 0.95 Å. Refinement results are shown in Table 1. A final difference map showed a maximum of 1.06 e Å^{-3} (near the tellurium position) and a minimum of −0.72 e Å^{-3}.

Results and discussion

Atomic parameters are listed in Table 2, interatomic distances and angles in Tables 3 and 4 and molecular planes in Table 5. Tables of observed and calculated structure factors, anisotropic temperature factors and hydrogen atom parameters are available from one of the authors (K.M-M.) on request. The crystals are built up of monomeric tris(dimethyldithiocarbamato)-4-methoxyphenyltellurium(IV), **1**, molecules and separate $CHCl_3$ molecules in the ratio 1:1 as seen in Fig. 2. Fig. 3 illustrates the coordination around the central tellurium atom. It may be described as distorted pentagonal bipyramidal, with tellurium bonded to the

Table 2. Positional parameters with estimated standard deviations.

Atom	*x*	*y*	*z*	*B*/Å^2
Te	−0.29046(3)	0.21468(4)	0.08267(2)	2.792(6)
Cl1	0.2940(2)	0.1873(3)	0.1421(1)	9.74(8)
Cl2	0.1216(2)	0.0226(4)	0.1064(1)	9.88(9)
Cl3	0.2590(4)	−0.0845(4)	0.1912(1)	13.4(1)
S11	−0.1036(1)	0.2421(2)	0.05175(6)	3.66(3)
S12	−0.2389(1)	0.3570(2)	−0.04107(7)	4.62(4)
S21	−0.4542(1)	0.0244(2)	0.09078(7)	4.06(4)
S22	−0.2725(1)	−0.0252(2)	0.02227(7)	3.79(3)
S31	−0.4464(1)	0.3473(2)	0.14848(7)	3.82(3)
S32	−0.2419(1)	0.4699(2)	0.13254(7)	3.81(3)
O	−0.0930(4)	−0.0983(5)	0.2939(2)	5.1(1)
N1	−0.0391(4)	0.3396(6)	−0.0461(2)	3.6(1)
N2	−0.4185(4)	−0.2191(6)	0.0348(2)	4.1(1)
N3	−0.3899(4)	0.6060(6)	0.1861(2)	4.1(1)
C	0.2465(6)	0.016(1)	0.1296(3)	6.2(2)
C1	−0.2249(4)	0.1039(6)	0.1549(2)	2.9(1)
C2	−0.1465(4)	0.0057(7)	0.1464(2)	3.3(1)
C3	−0.1014(4)	−0.0635(7)	0.1919(2)	3.4(1)
C4	−0.1327(5)	−0.0363(7)	0.2466(2)	3.4(1)
C5	−0.2109(5)	0.0619(7)	0.2554(2)	4.0(1)
C6	−0.2570(5)	0.1306(7)	0.2094(3)	3.5(1)
C7	−0.0121(7)	−0.199(1)	0.2879(3)	7.0(2)
C10	−0.1223(4)	0.3164(6)	−0.0161(2)	3.2(1)
C11	−0.0456(6)	0.4034(9)	−0.1031(3)	5.2(2)
C12	0.0624(5)	0.3000(9)	−0.0255(3)	5.3(2)
C20	−0.3875(4)	−0.0875(7)	0.0478(2)	3.3(1)
C21	−0.5163(6)	−0.2729(9)	0.0526(4)	6.4(2)
C22	−0.3606(6)	−0.3181(8)	−0.0009(3)	5.6(2)
C30	−0.3627(5)	0.4870(6)	0.1589(2)	3.3(1)
C31	−0.3200(7)	0.7274(8)	0.1945(4)	6.5(2)
C32	−0.4898(6)	0.6196(9)	0.2124(4)	6.6(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: (4/3) $[a^2B(1.1) + b^2B(2.2) + c^2B(3.3) + ab(\cos\gamma)B(1.2) + ac(\cos\beta)B(1.3) + bc(\cos\alpha)B(2.3)]$.

methoxyphenyl group and all six sulfur atoms of the molecule. It is clearly seen (Fig. 3a) that the molecule has the structure *B* in Fig. 1, i.e. the same type, **(B)**, as found in analogous tris(diethyldithiocarbamatophenyltellurium-(IV), **2**,[4] and bis(diethyldithiocarbamato)diethyldithiophosphatophenyltellurium(IV), **3**.[5]

The lone pair of electrons may occupy the eighth coordination position in a distorted dodecahedral structure,[5] i.e. near the Te–C1 axis and *"trans"* to the aryl group. However, the strong *trans* influence of the axial phenyl group may push the axial sulfur of the unique (axial–equatorial) dimethyldithiocarbamate ligand away from the central tellurium atom and thus account for most of the deviation from pentagonal bipyramidal geometry. In addition the small ligand bite of the dimethyldithiocarbamate will also contribute in this respect. Thus, the lone pair may possibly be stereochemically inert after all.[4]

The equatorial plane is at nearly right angles to the plane through Te, S11, S12 and C1 (or the unique ligand). The latter plane is an approximate mirror plane for the molecule except for the 4-methoxyphenyl group. While C1 is in

Table 3. Bond lengths (Å) with standard deviations.

Te	S11	2.591(1)
Te	S12	3.277(2)
Te	S21	2.792(2)
Te	S22	2.646(2)
Te	S31	2.868(2)
Te	S32	2.706(2)
Te	C1	2.153(5)
S11	C10	1.752(5)
S12	C10	1.677(5)
S21	C20	1.701(6)
S22	C20	1.737(6)
S31	C30	1.712(6)
S32	C30	1.725(6)
O	C4	1.350(6)
O	C7	1.422(8)
N1	C10	1.331(6)
N1	C11	1.467(7)
N1	C12	1.461(7)
N2	C20	1.317(7)
N2	C21	1.449(8)
N2	C22	1.465(8)
N3	C30	1.325(7)
N3	C31	1.462(8)
N3	C32	1.469(8)
C1	C2	1.391(7)
C1	C6	1.380(7)
C2	C3	1.373(7)
C3	C4	1.380(7)
C4	C5	1.391(8)
C5	C6	1.385(7)
C	Cl1	1.728(8)
C	Cl2	1.726(8)
C	Cl3	1.725(8)

the plane, the phenyl group makes an angle of 44.2° with it. The phenyl plane intersects the equatorial S11–Te–S22 angle, but eclipses the longest equatorial Te–S bond, Te–S31. A similar arrangement is found in the other $ArTeL_3$ (L = dithiolate) complexes.[4,5]

The equatorial Te–S bond lengths lie in the range from 2.591 to 2.868 Å, with an average value of 2.721 Å. This may be compared with 2.71 and 2.69 Å found in the analogous complexes **2** and **3**. The Te–C1 bond length of 2.153(5) Å is in the upper range for a Te–C(aryl) bond.[9] The weak

Table 5. Least-squares planes in the complex.

Atoms included in plane	Max. atomic dev. from plane/Å	Interplanar angles/°
Te,S11,S21,S22,S31,S32	0.15(S21)	1.2 94.0(1)
S11,S12,C10,N1,C11,C12	0.02(C12)	1.3 7.7(6)
S21,S22,C20,N2,C21,C22	0.04(C21)	1.4 4.0(1.1)
S31,S32,C30,N3,C31,C32	0.04(C32)	1.5 92.5(1)
C1,C2,C3,C4,C5,C6	0.005(C6)	1.6 92.0(1)
Te,S11,S12,C1	0.07(Te)	3.4 8.5(7)
		2.6 4.8(8)
		5.6 44.2(2)

Table 4. Bond angles (°) with standard deviations.

S11	Te	S12	59.93(4)
S11	Te	S21	145.03(5)
S11	Te	S22	80.63(5)
S11	Te	S31	143.34(5)
S11	Te	S32	79.52(5)
S12	Te	S21	119.04(5)
S12	Te	S22	80.61(5)
S12	Te	S31	118.00(5)
S12	Te	S32	89.13(5)
S21	Te	S22	65.49(5)
S21	Te	S31	70.81(4)
S21	Te	S32	134.14(5)
S22	Te	S31	136.00(5)
S22	Te	S32	160.14(5)
S31	Te	S32	63.86(4)
S11	Te	C1	84.1(1)
S12	Te	C1	143.7(1)
S21	Te	C1	86.9(1)
S22	Te	C1	89.3(1)
S31	Te	C1	93.3(1)
S31	Te	C1	93.3(1)
S32	Te	C1	89.0(1)
Te	S11	C10	100.0(2)
Te	S12	C10	78.5(2)
Te	S21	C20	86.3(2)
Te	S22	C20	90.3(2)
Te	S31	C30	86.2(2)
Te	S32	C30	91.3(2)
Te	C1	C2	119.0(4)
Te	C1	C6	121.6(4)
S11	C10	S12	121.4(3)
S11	C10	N1	116.2(4)
S12	C10	N1	122.4(4)
S21	C20	S22	117.8(3)
S21	C20	N2	122.5(4)
S22	C20	N2	119.7(4)
S31	C30	S32	118.3(3)
S31	C30	N3	121.1(4)
S32	C30	N3	120.5(4)
C10	N1	C11	120.9(5)
C10	N1	C12	122.8(5)
C11	N1	C12	116.3(5)
C20	N2	C21	121.6(6)
C20	N2	C22	123.1(5)
C21	N2	C22	115.2(5)
C30	N3	C31	121.9(5)
C30	N3	C32	121.7(5)
C31	N3	C32	116.3(5)
C2	C1	C6	119.4(5)
C1	C2	C3	120.2(5)
C2	C3	C4	120.6(5)
C3	C4	C5	119.4(5)
C4	C5	C6	120.0(5)
C1	C6	C5	120.4(5)
C4	O	C7	118.5(5)
O	C4	C3	125.0(5)
O	C4	C5	115.6(5)
Cl1	C	Cl2	111.1(5)
Cl1	C	Cl3	108.7(5)
Cl2	C	Cl3	111.3(5)

Te···S6 bond has a length of 3.277(2) Å. This is significantly longer than the 3.228(4) Å found in **2** but also shorter than 3.436(5) Å found in **3**, and the sum of the van der Waals

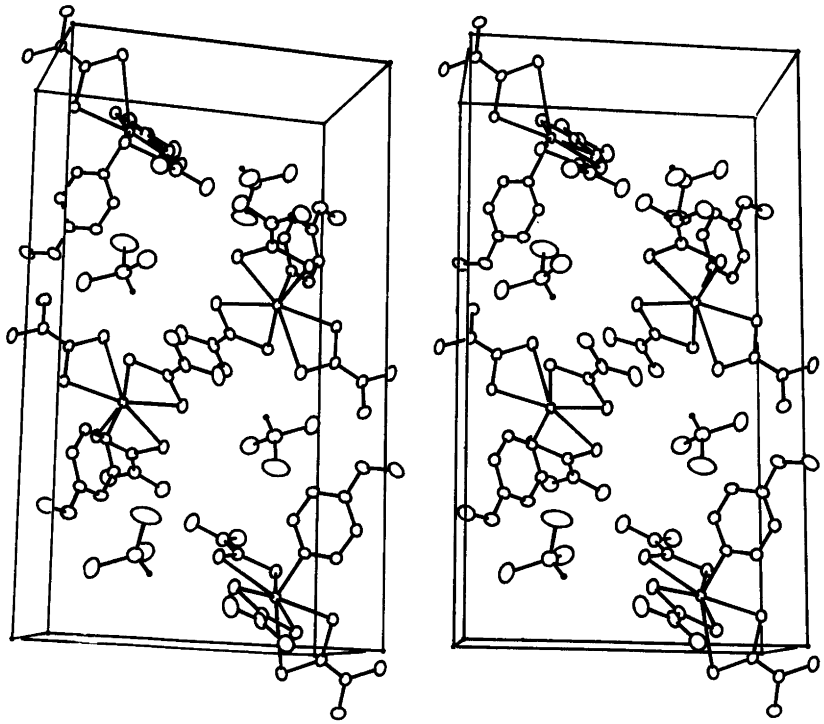

Fig. 2. A stereoscopic view of the molecular packing in the unit cell.

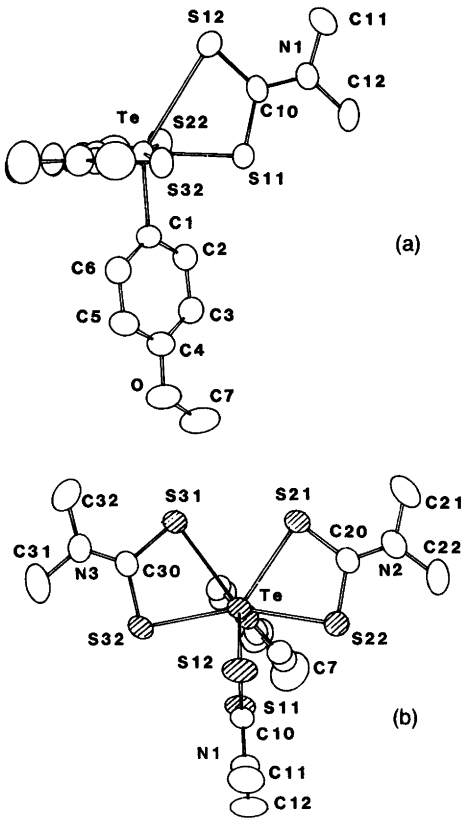

Fig. 3. The structure of the complex molecule as seen (a) along the normal to the axial–equatorial ligand and (b) along the normal to the equatorial plane. In (b), Te and atoms bonded to it are shaded.

radii of 3.86 Å.[7] It is interesting to note that the weaker nucleophile, diethyldithiophosphate, is the unique ligand in **3**, where the other two dithiolate ligands are diethyldithiocarbamates. This may account for the extra long Te···S bond. Also, this ligand has a greater S···S bite than the diethyldithiocarbamate ligand and this is reflected in a significantly larger C–Te···S angle in **3** as compared with **1** and **2** (148.0(4) as compared with 143.34(5) and 144.6(2)°). For further discussion of structure and bonding in such compounds, see Refs. 1, 2, 4 and 6.

The dimethyldithiocarbamate ligands are esentially planar except for the hydrogen atoms. This agrees well with the mesomeric shift of electron density from nitrogen to sulfur. Average S–C, C···N and N–C bond lengths in the ligands are normal, being 1.717, 1.324 and 1.462 Å, respectively.

Packing in the unit cell. The packing of the $[Te(Me_2NCS_2)_3(MeOPh)]$ and $CHCl_3$ molecules in the unit cell is shown in Fig. 2. The complex molecules lie in pairs across centres of symmetry, with $CHCl_3$ molecules in a zig-zag pattern in between. There are no particularly short intermolecular distances.

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