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Bromobis(dimethyldithiocarbamato)(4-methoxyphenyl)tellurium
Dichloromethane Hemisolvate, *p*-
 $\text{MeOC}_6\text{H}_4\text{Te}(\text{Me}_2\text{NCS}_2)_2\text{Br}\cdot 0.5\text{CH}_2\text{Cl}_2$

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**Bromobis(dimethyldithiocarbamato)-
(4-methoxyphenyl)tellurium(IV)
Dichloromethane Hemisolvate,
p-MeOC₆H₄Te(Me₂NCS₂)₂Br·0.5CH₂Cl₂**

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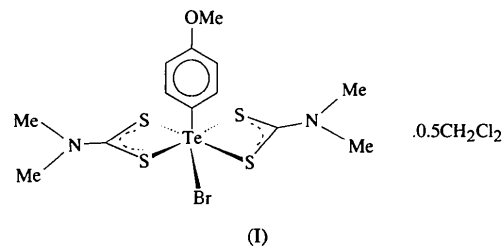
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Abstract

The structure of the title Te^{IV} complex, C₁₃H₁₉BrN₂OS₄Te·0.45(CH₂Cl₂), is pentagonal bipyramidal with four S atoms [Te—S 2.623 (1)–2.717 (1) Å] and the Br atom [Te—Br 2.890 (1) Å] in equatorial positions. The *p*-methoxyphenyl group is axial [Te—C 2.145 (3) Å] and the second axial position seems to be occupied by a dithiocarbamate group of a neighbouring molecule acting as a π ligand [Te···C 3.751 (3) Å, C—Te···C 170.2 (1)°], so that molecules are joined into centrosymmetric associations by this secondary coordination.

Comment

The Te atom in bromobis(dimethyldithiocarbamato-*S,S'*)(4-methoxyphenyl)tellurium(IV) dichloromethane hemisolvate, (1), has effectively pentagonal-bipyramidal coordination with two bidentate dithiocarbamate ligands and a Br atom in the equatorial plane. There is an aryl



Generally, secondary bonding interactions are rather common for aryl-substituted Te^{IV} complexes. Additional intermolecular coordination has been found in earlier investigated analogues of (1). Thus, in the structure of iodobis(diethyldithiocarbamato)phenyltellurium(IV), (2) (Husebye & Maartmann-Moe, 1994), two symmetrically independent molecules are paired off with Te···S distances of 3.597 (1) and 3.832 (1) Å [respective C—Te···S angles of 166.2 (1) and 154.9 (1)°], and in the structure of chlorobis(diethyldithiocarbamato)(4-

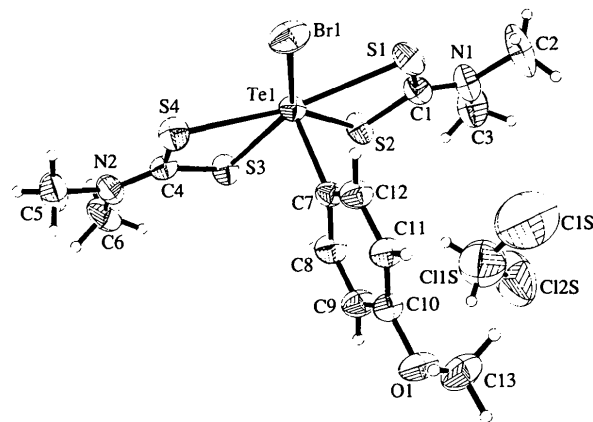


Fig. 1. Perspective view of complex (1) showing the labelling of non-H atoms and 50% probability displacement ellipsoids. Only one possible position of disordered CH₂Cl₂ is shown.

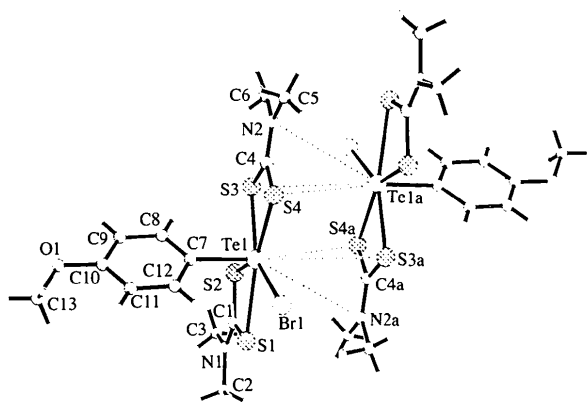


Fig. 2. Perspective view of the centrosymmetric associate of (1) in the crystal. Short intermolecular Te...C contacts are shown by dashed lines, others are indicated by dotted lines.

ethoxyphenyl)tellurium(IV), (3) (Husebye, Maartmann-Moe & Steffensen, 1990), two symmetrically independent complex units are connected into centrosymmetric 'dimers' by additional Te...S contacts of 3.705 (1) and 3.739 (1) Å [respective C—Te...S angles of 162.3 (1) and 161.7 (1)°].

There is an example of much stronger intermolecular C—Te...I coordination in the structure of bis(diethylthiocarbamato)iodo(4-methoxyphenyl)tellurium(IV), (4) (Husebye, Kudis & Lindeman, 1996), where molecules are connected into centrosymmetrical dimers by Te...I contacts of 3.569 (1) Å [C—Te...I 176.7 (1)°]. Such short contacts between the Te atom and the electron-pair donor atoms and groups would be impossible if the lone electron pair of the Te atom was stereochemically active (it occupies the axial position). Apparently, in aryl-substituted Te^{IV} complexes, the lone electron pair is sufficiently inert (*e.g.* localized in an *s* orbital of Te) due to the strong negative σ -inductive effect of the aryl group. This may be confirmed by the elongation (loosening) of the Te—C_{aryl} bond in complexes (1) and (2)–(4) to 2.145 (3) and 2.139 (2)–2.211 (2) Å, respectively, in comparison to the Te—C_{alkyl} bond length of 2.115 (5) Å found in the molecule of bis(diethylthiocarbamato)iodomethyltellurium(IV), (5) (Dakternieks, Di Giacomo, Gable & Hoskins, 1988), in spite of the larger covalent radius of the *sp*³-hybridized C atom. In complex (5), the strong positive σ -inductive effect of the methyl group seems to result in an increase of the spatially active role of the Te lone electron pair. No short intermolecular contacts were found for the Te atom [the shortest being a Te...I contact of 4.299 Å *cf.* the sum of the van der Waals radii of 4.04 Å (Bondi; 1964); C—Te...I 153.6°].

The *p*-methoxyphenyl ligand in (1) has the usual planar π -conjugated structure; the torsion angle C—C—O—C is only 9.1 (5)° [the mean deviation of the aromatic C atoms from their mean plane is 0.009 (3) Å]. Both dithiocarbamate ligands are quite symmetrically

coordinated to the Te atom, but the S atoms in quasi-*trans* positions to the Br ligand are nearer the Te atom than the atoms in quasi-*cis* positions; Te—S2 and Te—S3 distances are 2.629 (1) and 2.623 (1) Å, respectively, with corresponding Br—Te—S angles of 142.15 (3) and 142.15 (2)°, while the Te—S1 and Te—S4 distances are 2.717 (1) and 2.710 (1) Å, respectively, with corresponding Br—Te—S angles of 75.63 (3) and 75.45 (3)°. As a result, the corresponding C—S bond lengths and C—S—Te bond angles inside the chelate cycles are also slightly different: 1.724 (4) and 1.727 (4) Å, and 89.2 (1) and 89.1 (1)° for the '*trans*'-S atoms *versus* 1.711 (4) and 1.716 (4) Å, and 86.6 (1) and 86.5 (1)° for the '*cis*'-S atoms. A similar distribution of bond lengths was found in the complexes (2)–(5). Evidently, this feature is the result of a *trans* influence of the halogen substituent in the equatorial plane.

The presence of the comparatively large anisometric aryl substituent in an axial position in complex (1) results in substantial non-coplanarity of the equatorial substituents. Atoms Br1 and S3, eclipsed by the aryl *ortho*-CH groups [torsion angles X—Te—C—CH are -14.8 (3) and 26.6 (3)°, respectively], are displaced out of the mean equatorial plane by 0.078 (1) and 0.047 (1) Å away from the aryl group.

The non-bonded CH...Br and CH...S distances are 2.636 (4) and 2.769 (4) Å, respectively. The same distortions were found in the other aryl complexes (2)–(4), but not in the methyl derivative (5) (Husebye, Kudis & Lindeman, 1995). The dithiocarbamate ligands have a usual π -conjugated structure [the C_{sp²}—N bond distances are 1.319 (4) and 1.322 (4) Å, and the twists along these bonds are 0.8 (3) and 1.9 (3)°, respectively]. The configuration of the N atoms is planar within 0.008 (5) and 0.017 (5) Å.

Experimental

The title compound (1) was obtained by adding excess elemental bromine to *p*-MeOC₆H₄Te(Me₂NCS₂)₃ (as solutions in CCl₄ and CH₂Cl₂, respectively) and recrystallized in 66% yield by precipitation from a mixture of ethanol, CH₂Cl₂ and toluene (3:2:1 by volume).

Crystal data

C₁₃H₁₉BrN₂OS₄Te·
0.45(CH₂Cl₂)

M_r = 593.27

Monoclinic

*P*2₁/*c*

a = 9.156 (5) Å

b = 13.324 (2) Å

c = 17.564 (2) Å

β = 90.96 (3)°

V = 2142.5 (11) Å³

Z = 4

D_x = 1.839 Mg m⁻³

Mo *K* α radiation

λ = 0.71069 Å

Cell parameters from 24
reflections

θ = 10.86–13.59°

μ = 3.760 mm⁻¹

T = 293 (2) K

Prisms

0.60 × 0.19 × 0.14 mm

Yellow

<i>Data collection</i>	
Enraf-Nonius CAD-4 diffractometer	3922 observed reflections
$\omega/2\theta$ scans	$[I > 2\sigma(I)]$
Absorption correction: numerical (Gaussian method)	$R_{\text{int}} = 0.0201$
$T_{\text{min}} = 0.480$, $T_{\text{max}} = 0.642$	$\theta_{\text{max}} = 29.96^\circ$
6554 measured reflections	$h = -12 \rightarrow 12$
6217 independent reflections	$k = 0 \rightarrow 18$
	$l = 0 \rightarrow 24$
	3 standard reflections
	frequency: 120 min
	intensity decay: 6.2%
<i>Refinement</i>	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2]$
$R(F) = 0.0368$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.0958$	$(\Delta/\sigma)_{\text{max}} = 0.126$
$S = 1.144$	$\Delta\rho_{\text{max}} = 0.660 \text{ e } \text{\AA}^{-3}$
6194 reflections	$\Delta\rho_{\text{min}} = -0.546 \text{ e } \text{\AA}^{-3}$
233 parameters	Atomic scattering factors
H atoms refined as riding using a rotating model with U_{iso} refined by groups	from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Te1	0.07939 (2)	0.65796 (2)	0.03915 (1)	0.03147 (6)
Br1	-0.18557 (4)	0.70638 (3)	0.11841 (2)	0.05136 (12)
S1	-0.00501 (11)	0.83763 (8)	-0.02002 (5)	0.0451 (2)
S2	0.24766 (11)	0.72099 (7)	-0.07089 (5)	0.0420 (2)
S3	0.27780 (10)	0.51728 (7)	0.02616 (5)	0.0394 (2)
S4	0.04842 (11)	0.50729 (7)	0.14125 (5)	0.0430 (2)
O1	0.4678 (3)	0.9184 (2)	0.2608 (2)	0.0518 (7)
N1	0.1694 (4)	0.8951 (2)	-0.1317 (2)	0.0492 (8)
N2	0.2430 (4)	0.3622 (2)	0.1187 (2)	0.0430 (7)
C1	0.1398 (4)	0.8265 (3)	-0.0798 (2)	0.0391 (8)
C2	0.0817 (7)	0.9861 (4)	-0.1396 (3)	0.082 (2)
C3	0.2922 (6)	0.8866 (4)	-0.1836 (2)	0.0650 (13)
C4	0.1948 (4)	0.4517 (3)	0.0984 (2)	0.0344 (7)
C5	0.1798 (6)	0.3064 (3)	0.1819 (2)	0.0606 (12)
C6	0.3666 (5)	0.3144 (3)	0.0815 (3)	0.0581 (11)
C7	0.2098 (3)	0.7413 (2)	0.1196 (2)	0.0309 (7)
C8	0.3618 (4)	0.7340 (3)	0.1202 (2)	0.0408 (8)
C9	0.4433 (4)	0.7927 (3)	0.1689 (2)	0.0437 (9)
C10	0.3761 (4)	0.8614 (3)	0.2167 (2)	0.0372 (8)
C11	0.2262 (4)	0.8669 (3)	0.2176 (2)	0.0394 (8)
C12	0.1438 (4)	0.8076 (3)	0.1687 (2)	0.0397 (8)
C13	0.4053 (5)	0.9988 (3)	0.3030 (3)	0.0608 (12)
C15†	0.5090 (14)	0.9506 (13)	0.0171 (9)	0.115 (5)
C15†	0.3662 (13)	1.0286 (8)	0.0223 (8)	0.181 (5)
C125†	0.6330 (13)	0.9867 (8)	-0.0461 (7)	0.141 (4)

† Partial occupancy (see below).

Table 2. Selected geometric parameters (\AA , $^\circ$)

Te1—C7	2.145 (3)	O1—C13	1.427 (5)
Te1—S3	2.623 (1)	N1—C1	1.322 (4)
Te1—S2	2.629 (1)	N1—C2	1.459 (5)
Te1—S4	2.710 (1)	N1—C3	1.464 (5)
Te1—S1	2.717 (1)	N2—C4	1.319 (4)
Te1—Br1	2.8897 (9)	N2—C6	1.461 (5)
Te1—C4 ⁱ	3.751 (3)	N2—C5	1.464 (5)
Te1—S4 ⁱ	4.017 (1)	C7—C12	1.381 (4)
Te1—N2 ⁱ	4.025 (3)	C7—C8	1.396 (4)
Te1—S3 ⁱ	4.164 (1)	C8—C9	1.370 (5)

S1—C1	1.711 (4)	C9—C10	1.392 (5)
S2—C1	1.724 (4)	C10—C11	1.375 (5)
S3—C4	1.727 (3)	C11—C12	1.381 (5)
S4—C4	1.716 (3)	C15—C12S	1.67 (1)
O1—C10	1.364 (4)	C15—C11S	1.67 (1)
C7—Te1—S3	92.79 (9)	C1—N1—C2	121.5 (4)
C7—Te1—S2	89.57 (9)	C1—N1—C3	122.9 (3)
S3—Te1—S2	75.48 (3)	C2—N1—C3	115.6 (3)
C7—Te1—S4	90.61 (9)	C4—N2—C6	122.1 (3)
S3—Te1—S4	66.94 (3)	C4—N2—C5	121.9 (3)
S2—Te1—S4	142.38 (3)	C6—N2—C5	115.9 (3)
C7—Te1—S1	87.00 (9)	N1—C1—S1	122.2 (3)
S3—Te1—S1	142.13 (3)	N1—C1—S2	120.2 (3)
S2—Te1—S1	66.66 (3)	S1—C1—S2	117.6 (2)
S4—Te1—S1	150.89 (3)	N2—C4—S4	122.2 (3)
C7—Te1—Br1	91.69 (8)	N2—C4—S3	120.5 (3)
S3—Te1—Br1	142.15 (2)	S4—C4—S3	117.4 (2)
S2—Te1—Br1	142.15 (3)	C12—C7—C8	119.1 (3)
S4—Te1—Br1	75.45 (3)	C12—C7—Te1	119.9 (2)
S1—Te1—Br1	75.63 (3)	C8—C7—Te1	120.9 (2)
C7—Te1—C4 ⁱ	170.2 (1)	C9—C8—C7	119.8 (3)
C7—Te1—S4 ⁱ	162.82 (8)	C8—C9—C10	120.7 (3)
C7—Te1—N2 ⁱ	151.92 (9)	O1—C10—C11	124.7 (3)
C7—Te1—S3 ⁱ	153.89 (9)	O1—C10—C9	115.8 (3)
C1—S1—Te1	86.6 (1)	C11—C10—C9	119.5 (3)
C1—S2—Te1	89.2 (1)	C10—C11—C12	119.9 (3)
C4—S3—Te1	89.1 (1)	C11—C12—C7	120.9 (3)
C4—S4—Te1	86.5 (1)	C12S—C1S—C11S	113 (1)
C10—O1—C13	117.7 (3)		
S2—Te1—S1—C1	0.2 (1)	S3—Te1—C7—C12	-157.2 (3)
S1—Te1—S2—C1	-0.2 (1)	S2—Te1—C7—C12	127.4 (3)
S4—Te1—S3—C4	2.0 (1)	S4—Te1—C7—C12	-90.3 (3)
S3—Te1—S4—C4	-2.0 (1)	S1—Te1—C7—C12	60.7 (3)
C2—N1—C1—S1	1.6 (6)	Br1—Te1—C7—C12	-14.8 (3)
C3—N1—C1—S2	-0.1 (6)	S3—Te1—C7—C8	26.6 (3)
Te1—S1—C1—S2	-0.3 (2)	S2—Te1—C7—C8	-48.8 (3)
Te1—S2—C1—S1	0.3 (2)	S4—Te1—C7—C8	93.6 (3)
C5—N2—C4—S4	-3.3 (5)	S1—Te1—C7—C8	-115.4 (3)
C6—N2—C4—S3	-0.4 (5)	Br1—Te1—C7—C8	169.0 (3)
Te1—S4—C4—S3	3.2 (2)	C13—O1—C10—C11	-9.1 (5)
Te1—S3—C4—S4	-3.3 (2)		

Symmetry codes: (i) $-x, 1 - y, -z$.

The absorption correction was made assuming that the crystal contained a stoichiometric ratio (2:1) of complex (1) and dichloromethane solvent molecules. The CH_2Cl_2 solvent molecule was located by a difference Fourier synthesis (disordered on the centre of symmetry with partial population; the occupancy factor of 0.45 instead of 0.5 for the symmetrically independent position was adjusted empirically) and refined by a least-squares method with the restriction $d(\text{C—C11}) = d(\text{C—C12}) = d$ (d was refined as an independent parameter).

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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