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Bis(diethyldithiocarbamato)(iodo)(4-methoxyphenyl)telluri p-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_2$I, and its Isomorphous Partially Bromine-Replaced Analogue, p-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_2$Br$_{0.41}$I$_{0.59}$

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Bis(diethyldithiocarbamato)(iodo)-(4-methoxyphenyl)tellurium(IV), p-MeOC6H4Te(Et2NCS2)2I, and its Isomorphous Partially Bromine-Replaced Analogue, p-MeOC6H4Te(Et2NCS2)2Br0.41I0.59

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Abstract

The Te^{IV} complexes $p\text{-MeOC}_6H_4Te(Et_2NCS_2)_2I$, (1), and $p\text{-MeOC}_6H_4Te(Et_2NCS_2)_2Br_{0.41}I_{0.59}$, (3), have been synthesized by reacting $p\text{-MeOC}_6H_4Te(Et_2NCS_2)_3$ with the elementary halogens. The crystals of (1) and (3) are isomorphous with the I atom position in (3) partially replaced by a Br atom. The structures are pentagonal bipyramidal with four S atoms [Te—S 2.624 (1)–2.733 (1) Å] and the halogen atom [Te—I 3.169 (1) and 3.164 (1), Te—Br 2.904 (3) Å] in equatorial positions. The p-methoxyphenyl group is axial [Te—C 2.211 (3) and 2.151 (4) Å] and the second axial position is occupied by a halogen atom of a neighbouring molecule [Te···I 3.569 (1) and 3.558 (4), Te···Br 3.476 (9) Å, bond angles C—Te···I 176.7 (1) and 174.9 (4), C—Te···Br 176.3 (2)°] so that the molecules are joined into centrosymmetric pairs by this secondary coordination.

Comment

The structure of the isomorphous mixed Br/I complex (3) is quite similar to the structure of the pure iodine complex (1), therefore the discussion will focus on (1) and the corresponding structural parameters for (3) will be given in brackets, where necessary, with the exceptions of those peculiarities, which are an effect of the halogen-atom replacement.

OMe

(1)

OMe

(3)
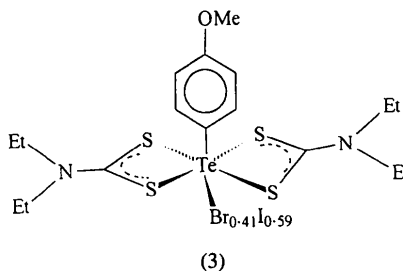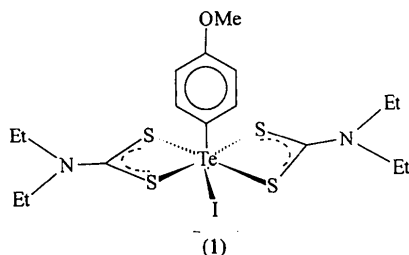
The Te atom in the crystal (1) has pentagonal-bipyramidal coordination with two bidentate chelating dithiocarbamate ligands, an I atom in the equatorial plane, and an aryl group in an axial position (Fig. 1). The second axial site is comparatively weakly coordinated by the I atom of a neighbouring complex unit, symmetrically related to the first one by an inversion centre [(0, $\frac{1}{2}$, 1) for the reference molecule], so that molecules of (1) are connected into dimers *via* two bridging iodine ligands (Fig. 2).

Such secondary bonding is rather common for Te^{IV} compounds. The Te—I and Te···I distances are
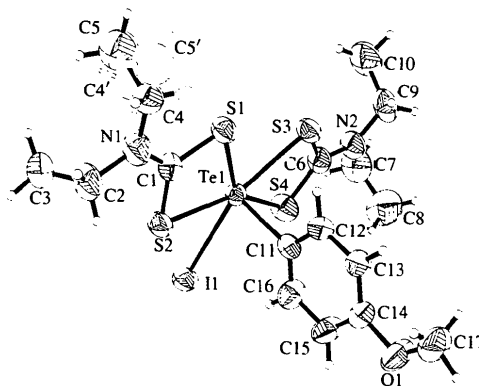

Fig. 1. Perspective view of (1) showing the labelling of non-H atoms. The minor component of the disordered ethyl group is shown by dashed lines. The displacement ellipsoids are drawn at the 50% probability level.
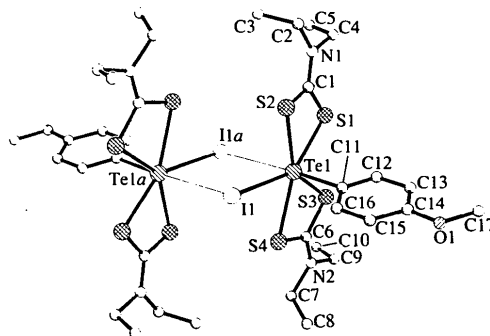

Fig. 2. Perspective view of the centrosymmetric dimer of (1). Disordered groups and H atoms are removed for clarity. Secondary intermolecular bonds are shown by thin lines.

not very different from each other {3.169 (1) and 3.569 (1) Å [3.164 (1) and 3.558 (4) Å]} with the practically 'ideal' valence angle values for C—Te···I {176.7 (1)° [174.9 (4)°]} and Te—I···Te {92.75 (1)° [89.6 (1)°]}. In the bromine-substituted complex (3) the corresponding Te—Br and Te···Br distances are 2.904 (3) and 3.476 (9) Å, and the C—Te···Br and Te—Br···Te angles are 176.3 (2) and 95.7 (2)°. The increased difference between the 'primary' and 'secondary' bond lengths in the Br analogue is in good agreement with the 'less soft' nature (weaker *trans* effect) of the Br ligand as compared with the I ligand. It is also possible that the occurrence of such dimers of (3) is a result of the isomorphous inclusion of its molecules in the crystalline matrix of (1).

In analogues of (1) investigated earlier, the secondary coordination of the Te^{IV} atom at the seventh coordination site was found to consist of weak intermolecular Te···S contacts: in (2) [the Ph analogue of (1); Husebye & Maartmann-Moe, 1994] two symmetrically independent molecules are paired off with Te···S distances 3.597 (1) and 3.832 (1) Å [*trans* angles C—Te···S 166.2 (1) and 154.9 (1)°, respectively] and in the structure of chlorobis(diethyldithiocarbamato)(4-ethoxyphenyl)tellurium(IV), (4) (Husebye, Maartmann-Moe & Steffensen, 1990), two symmetrically independent complex units are connected into centrosymmetrical 'dimers' by additional Te···S contacts of 3.705 (1) and 3.739 (1) Å [*trans* angles C—Te···S 162.3 (1) and 161.7 (1)°, respectively]. Moreover, there are some earlier examples of intramolecular C—Te···S coordination (Husebye, Maartmann-Moe & Steffensen, 1990). In the structure of bis(diethyldithiocarbamato)(iodo)methyltellurium(IV), (5) (Dakternieks, Di Giacomo, Gable & Hoskins, 1988), molecules are connected into indefinite chains *via* very weak Te···I additional contacts of 4.299 Å (*trans* angle C—Te···I 153.6° calculated using published coordinates).

The intramolecular Te—I bond length in (1) is noticeably increased as compared with those found in (2) [3.151 (1) and 3.100 (1) Å] and (5) [3.117 (1) Å; also, the Te—C(Ar) bond, which is located *trans* to the strong secondary Te···I bond in (1), is significantly longer [2.211 (3) Å], and the endocyclic valence *ipso*-angle C12—C11—C16 in the benzene ring is distinctly larger [122.9 (3)°] than the corresponding Te—C(Ar) bonds [2.148 (2) and 2.157 (2), 2.139 (2) and 2.140 (2) Å] and the C—C—C angles [119.5 (2) and 120.1 (2), 119.4 (2) and 119.1 (2)°] in (2) and (4). These features are evidence of the significance of the stronger Te···I interaction in (1). It is possible that the formation of the by-product $Te(Et_2NCS_2)I_2$ along with (1) in the reaction in question (see *Experimental*) occurs because of this weakening of the Te—Ar bond with subsequent replacement of the aryl group by a further I ligand. It is noteworthy that in (3) the Te—C(Ar) bond length [2.151 (4) Å] and the valence angle C12—

C11—C16 [119.9 (4)°] are much closer to those found in (4), evidently due to the large contribution of the more weakly 'secondary-bonded' Br-containing structure. In both cases the *p*-methoxyphenyl ligand has the usual planar π-conjugated structure; the torsion angle C—C—O—C is only 2.7 (7)° [1.6 (9)°] and the mean deviation of aromatic C atoms out of their mean plane is 0.003 Å [0.006 Å].

Both dithiocarbamate ligands are quite symmetrically coordinated to the Te atom, but the S atoms in the quasi-*trans* positions to the I atom (Br atom) are less distant from the Te atom than the atoms in the quasi-*cis* positions: Te—S1 and Te—S3 distances are 2.627 (1) and 2.626 (1) Å [2.626 (1) and 2.624 (1) Å], respectively, with corresponding I—Te—S bond angles of 141.85 (2) and 140.69 (3)° [141.9 (1) and 141.0 (1)° for I and 142.3 (2) and 140.1 (2)° for Br], while the Te—S2 and Te—S4 distances are 2.733 (1) and 2.693 (1) Å [2.728 (1) and 2.690 (1) Å], respectively, with I—Te—S angles of 76.73 (2) and 73.60 (3)° [76.7 (1) and 73.9 (1)° for I and 77.5 (2) and 73.2 (2)° for Br]. As a result, the corresponding C—S bond lengths and C—S—Te bond angles inside the chelate cycles are also slightly different: 1.734 (4) and 1.739 (4) Å [1.725 (5) and 1.731 (5) Å] and 89.1 (1) and 88.4 (1)° [89.2 (2) and 88.5 (2)°] for the '*trans*'-S, *versus* 1.699 (4) and 1.704 (4) Å [1.697 (5) and 1.704 (5) Å] and 86.4 (1) and 86.9 (1)° [86.4 (2) and 86.9 (2)°] for the '*cis*'-S.

A similar distribution of bond lengths was found in (2) [Te—S bonds are 2.626 (1)–2.661 (1) Å in quasi-*trans* positions and 2.693 (1)–2.717 (1) Å in quasi-*cis* positions to the halogen atom], in (4) [2.642 (1)–2.654 (1) Å in quasi-*trans* and 2.681 (1)–2.731 (1) Å in quasi-*cis* positions] and in (5) [2.646 (1) and 2.618 (1) Å for the quasi-*trans* and 2.725 (1) and 2.691 (1) Å for the quasi-*cis* positions]. 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 (1)–(4) results in substantial non-coplanarity of the equatorial substituents: the atoms eclipsed by the aryl *ortho*-CH groups are displaced away from the aryl group. So, in (1) [(3)], S1 and I1 [I1/Br1] are shifted away from the aryl group by 0.159 (1) Å [0.176 (1) Å] and 0.111 (1) Å [0.029 (6)/0.110(8) Å], respectively, with corresponding torsion angles S—Te—C—C and I[Br]—Te—C—C −25.8 (3) [−25.3 (4)] and 11.8 (3)° [13.4 (4)/12.6(4)°], while the other atoms are shifted towards it by up to 0.197 (1) Å [0.171 (1) Å] (S2 atom). The nonbonded distances CH···S and CH···I[Br] are 2.84 Å [2.84 Å] and 2.84 Å [2.79 and 2.75 Å]. In (2) and (4) the out-of-plane shifts of the equatorial atoms are 0.042–0.243 Å away from the aryl group when the C—C—Te—X torsion angle is less than 45°, and 0.007–0.248 Å towards it in other cases. The Te atom in (1)–(4) is shifted out of the equatorial plane towards the aryl lig-

and by 0.055 (1) Å [0.052 (1) Å] in (1) [(3)], and by 0.011–0.017 Å in (2) and (4).

On the other hand, in the less sterically extended Me derivative (5), the I and four S atoms are in the plane within 0.02 Å. The Te atom is shifted outside, not towards but away from the Me group by 0.122 Å. This might be considered as a result of larger localization of the Te lone electron pair and its repulsion with equatorial substituents.

Perhaps intramolecular repulsion between the ligands results in non-planarity of one of the dithiocarbamate chelate cycles in (1): the S1, C1, S2, Te1 cycle is folded by 12.3 (1)° [12.2 (2)°] against the aryl ligand along the S···S line, whereas the other cycle is practically planar {folding angle is 1.8 (1)° [1.6 (2)°]}. Both dithiocarbamate ligands have a usual π-conjugated structure {the Csp^2—N bond distances are 1.317 (5)–1.332 (5) Å, the twist along these bonds being no more than 5.6 (3)°; the configuration of the N atoms is planar within 0.05 Å, excluding the disordered part – for the minor component the N atom is shifted to 0.20 (1) Å [0.18 (1) Å] out of plane of surrounding atoms}. The orientation of the ethyl groups is quite different in the two dithiocarbamate ligands: anti in the S3–C10 ligand and syn in the S1–C5 ligand for the major component. The minor component of the disordered group also has an anti orientation of ethyl groups.

The role of the lone electron pair in the investigated structures is not very clear. The relatively strong secondary Te···I interaction here gives a roughly 0.5 Å shorter intermolecular contact than the sum of the respective van der Waals radii (Bondi, 1964) in the direction of the 'empty' axial position of the pentagonal-bipyramidal coordination polyhedron of Te. So it is unlikely that the lone pair occupies this position as it would have shielded the halogen from the positively charged Te central atom. However, the lone pair (even if it is stereochemically inert in the sense that it does not occupy a position in the coordination polyhedron) probably has some antibonding character. This is shown by the long average Te—S bond distances of 2.668 Å compared with the sum of the respective covalent radii of 2.41 Å (Pauling, 1960).

Experimental

Compound (1) was obtained by an attempt to synthesize p-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)I$_2$ by the following reaction:

p-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_3$ + I$_2$ →
$\quad\quad$ p-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)I$_2$ + [Et$_2$NC(S)S]$_2$.
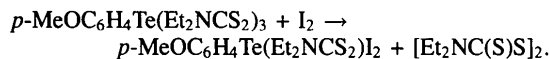
However, our structural investigation shows that, in reality, the following process takes place:

$2p$-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_3$ + I$_2$ →
$\quad\quad$ $2p$-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_2$I + [Et$_2$NC(S)S]$_2$.
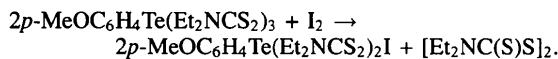
The compound PhTe(Et$_2$NCS$_2$)$_2$I, (2) (Husebye & Maartmann-Moe, 1994), has been obtained in our laboratory (Bergen)

using this reaction. Moreover, there is evidence that PhTe(Et$_2$NCS$_2$)Cl$_2$ gave PhTe(Et$_2$NCS$_2$)$_2$Cl on recrystallization (Dakternieks, Di Giacomo, Gable & Hoskins, 1988). It is noteworthy that the compound Te(Et$_2$NCS$_2$)$_2$I$_2$ is also produced, along with (1), as a by-product. The dark green regularly twinned crystals were found by us to have the same structure as that recently published (Kumar, Aravamudan, Udupa & Seshasayee, 1993).

Compound (3) was obtained from (1) in an attempt to realise the reaction:

$2p$-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)$_2$I + Br$_2$ →
$\quad\quad$ $2p$-MeOC$_6$H$_4$Te(Et$_2$NCS$_2$)BrI + [Et$_2$NC(S)S]$_2$,
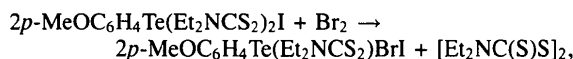
as a product of partial halogen replacement. The target product of further halogen substitution was also synthesized, but as a minor and also mixed by-product p-MeO-C$_6$H$_4$Te(Et$_2$NCS$_2$)(Br$_{0.4}$I$_{0.6}$)$_2$ (Husebye, Kudis, Lindeman & Strauch, 1995).

Compound (1)

Crystal data

$C_{17}H_{27}IN_2OS_4Te$	Mo $K\alpha$ radiation
$M_r = 658.15$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 24
$P2_1/n$	reflections
$a = 10.069$ (3) Å	$\theta = 12.4–15.1°$
$b = 14.545$ (2) Å	$\mu = 2.816$ mm^{-1}
$c = 16.784$ (2) Å	$T = 293$ (2) K
$\beta = 90.59$ (2)°	Well formed prism
$V = 2458.0$ (9) Å^3	$0.5 \times 0.2 \times 0.15$ mm
$Z = 4$	Dark red
$D_x = 1.779$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	5101 observed reflections $[I > 2\sigma(I)]$
$\omega/0.7\theta$ scans	$R_{int} = 0.0247$
Absorption correction: refined from ΔF	$\theta_{max} = 29.96°$
($DIFABS$; Walker & Stuart, 1983)	$h = -14 \rightarrow 14$
	$k = 0 \rightarrow 20$
$T_{min} = 0.167$, $T_{max} = 0.381$	$l = 0 \rightarrow 23$
6746 measured reflections	3 standard reflections frequency: 120 min
6420 independent reflections	intensity decay: 6.5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.103$
$R[F^2 > 2\sigma(F^2)] = 0.0321$	$\Delta\rho_{max} = 0.778$ e Å^{-3}
$wR(F^2) = 0.0878$	$\Delta\rho_{min} = -0.957$ e Å^{-3}
$S = 1.055$	Extinction correction: none
6420 reflections	Atomic scattering factors
238 parameters	from International Tables
H atoms: riding and rotating model with fixed U_{iso}	for Crystallography (1992, Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.2739P]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (1)*

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

	x	y	z	U_{eq}
Te1	0.07661 (2)	0.59420 (1)	0.88911 (1)	0.03667 (6)
I1	0.08866 (3)	0.38047 (2)	0.92510 (2)	0.05389 (8)
S1	0.19721 (10)	0.74969 (6)	0.92312 (6)	0.0492 (2)
S2	0.32308 (10)	0.57149 (7)	0.95592 (7)	0.0541 (2)
S3	−0.08417 (10)	0.71906 (7)	0.82925 (6)	0.0495 (2)
S4	−0.15063 (10)	0.52201 (7)	0.83068 (7)	0.0581 (3)
O1	0.3317 (4)	0.5438 (2)	0.5507 (2)	0.0720 (9)
N1	0.4212 (4)	0.7304 (2)	1.0061 (2)	0.0618 (9)
N2	−0.3140 (3)	0.6502 (3)	0.7740 (2)	0.0622 (9)
C1	0.3256 (4)	0.6876 (2)	0.9668 (2)	0.0454 (8)
C2	0.5334 (4)	0.6791 (4)	1.0432 (3)	0.0675 (12)
C3	0.5050 (6)	0.6465 (4)	1.1249 (3)	0.0790 (15)
C4	0.4335 (7)	0.8300 (4)	1.0091 (4)	0.0580 (14)
C5	0.3725 (10)	0.8668 (7)	1.0830 (6)	0.098 (3)
C4'	0.387 (2)	0.8285 (13)	1.0478 (14)	0.078 (5)
C5'	0.461 (2)	0.9007 (14)	1.0086 (13)	0.093 (6)
C6	−0.1965 (4)	0.6316 (3)	0.8074 (2)	0.0493 (8)
C7	−0.4150 (5)	0.5775 (4)	0.7632 (4)	0.084 (2)
C8	−0.3962 (6)	0.5217 (5)	0.6886 (4)	0.107 (2)
C9	−0.3517 (5)	0.7438 (4)	0.7493 (3)	0.0754 (14)
C10	−0.4262 (6)	0.7949 (5)	0.8143 (4)	0.099 (2)
C11	0.1680 (3)	0.5795 (2)	0.7706 (2)	0.0364 (6)
C12	0.2087 (4)	0.6564 (2)	0.7322 (2)	0.0449 (7)
C13	0.2652 (4)	0.6473 (3)	0.6572 (2)	0.0468 (8)
C14	0.2778 (4)	0.5619 (3)	0.6237 (2)	0.0484 (8)
C15	0.2357 (5)	0.4847 (3)	0.6652 (2)	0.0601 (11)
C16	0.1800 (5)	0.4957 (3)	0.7400 (2)	0.0554 (10)
C17	0.3840 (6)	0.6178 (4)	0.5070 (3)	0.083 (2)

Table 2. *Selected geometric parameters ($\mathring{A}$, °) for (1)*

Te1—C11	2.211 (3)	N1—C4'	1.63 (2)
Te1—S3	2.626 (1)	N2—C6	1.332 (5)
Te1—S1	2.627 (1)	N2—C9	1.472 (6)
Te1—S4	2.693 (1)	N2—C7	1.476 (7)
Te1—S2	2.733 (1)	C2—C3	1.481 (7)
Te1—I1	3.1689 (7)	C4—C5	1.49 (1)
Te1—I1^i	3.569 (1)	C4'—C5'	1.45 (3)
S1—C1	1.734 (4)	C7—C8	1.505 (8)
S2—C1	1.699 (4)	C9—C10	1.523 (8)
S3—C6	1.739 (4)	C11—C16	1.329 (5)
S4—C6	1.704 (4)	C11—C12	1.357 (5)
O1—C14	1.371 (4)	C12—C13	1.393 (5)
O1—C17	1.407 (6)	C13—C14	1.371 (5)
N1—C1	1.317 (5)	C14—C15	1.390 (6)
N1—C4	1.455 (7)	C15—C16	1.389 (6)
N1—C2	1.485 (5)		
C11—Te1—S3	89.05 (8)	C1—N1—C2	121.4 (4)
C11—Te1—S1	94.78 (8)	C4—N1—C2	115.0 (4)
S3—Te1—S1	76.67 (4)	C1—N1—C4'	118.2 (8)
C11—Te1—S4	89.68 (8)	C2—N1—C4'	115.1 (8)
S3—Te1—S4	67.18 (4)	C6—N2—C9	122.1 (4)
S1—Te1—S4	143.50 (3)	C6—N2—C7	120.9 (4)
C11—Te1—S2	88.45 (8)	C9—N2—C7	116.9 (4)
S3—Te1—S2	142.59 (3)	N1—C1—S2	122.2 (3)
S1—Te1—S2	66.36 (3)	N1—C1—S1	120.3 (3)
S4—Te1—S2	150.09 (3)	S2—C1—S1	117.5 (2)
C11—Te1—I1	93.50 (8)	N1—C2—C3	113.3 (4)
S3—Te1—I1	140.69 (3)	N1—C4—C5	110.5 (7)
S1—Te1—I1	141.85 (2)	C5'—C4'—N1	109 (2)
S4—Te1—I1	73.60 (3)	N2—C6—S4	121.6 (3)
S2—Te1—I1	76.73 (2)	N2—C6—S3	120.9 (3)
C11—Te1—I1^i	176.75 (8)	S4—C6—S3	117.5 (2)
S3—Te1—I1^i	88.38 (3)	N2—C7—C8	113.3 (5)
S1—Te1—I1^i	86.55 (3)	N2—C9—C10	112.1 (4)
S4—Te1—I1^i	87.50 (3)	C16—C11—C12	122.9 (3)
S2—Te1—I1^i	94.79 (3)	C16—C11—Te1	118.5 (2)
I1—Te1—I1^i	87.25 (1)	C12—C11—Te1	118.6 (2)
Te1—I1—Te1^i	92.75 (1)	C11—C12—C13	118.6 (3)
C1—S1—Te1	89.1 (1)	C14—C13—C12	119.8 (3)

C1—S2—Te1	86.4 (1)	O1—C14—C13	125.4 (4)
C6—S3—Te1	88.4 (1)	O1—C14—C15	114.8 (3)
C6—S4—Te1	86.9 (1)	C13—C14—C15	119.7 (3)
C14—O1—C17	118.2 (4)	C14—C15—C16	119.3 (4)
C1—N1—C4	123.3 (4)	C11—C16—C15	119.6 (4)
C11—Te1—I1—Te1^i	−176.84 (8)	C9—N2—C6—S3	3.9 (6)
S2—Te1—S1—C1	−4.7 (1)	C7—N2—C6—S3	−173.5 (4)
S1—Te1—S2—C1	4.8 (1)	Te1—S4—C6—S3	1.3 (2)
S4—Te1—S3—C6	0.8 (1)	Te1—S3—C6—S4	−1.3 (2)
S3—Te1—S4—C6	−0.8 (1)	C6—N2—C7—C8	−84.0 (6)
C4—N1—C1—S2	173.2 (4)	C6—N2—C9—C10	−92.8 (6)
C2—N1—C1—S2	0.2 (6)	S3—Te1—C11—C16	−129.0 (3)
C4'—N1—C1—S2	−152.7 (9)	S1—Te1—C11—C16	154.5 (3)
C4—N1—C1—S1	−6.2 (7)	S4—Te1—C11—C16	−61.8 (3)
C2—N1—C1—S1	−179.2 (3)	S2—Te1—C11—C16	88.4 (3)
C4'—N1—C1—S1	28 (1)	I1—Te1—C11—C16	11.8 (3)
Te1—S2—C1—S1	−7.6 (2)	S3—Te1—C11—C12	50.7 (3)
Te1—S1—C1—S2	7.8 (2)	S1—Te1—C11—C12	−25.8 (3)
C1—N1—C2—C3	−87.0 (6)	S4—Te1—C11—C12	117.9 (3)
C1—N1—C4—C5	96.5 (7)	S2—Te1—C11—C12	−91.9 (3)
C1—N1—C4'—C5'	−114 (1)	I1—Te1—C11—C12	−168.5 (3)
C9—N2—C6—S4	−176.3 (3)	C17—O1—C14—C13	2.7 (7)
C7—N2—C6—S4	6.3 (6)	C17—O1—C14—C15	−176.3 (5)

Symmetry code: (i) $-x, 1 - y, 2 - z$.

Compound (3)

Crystal data

$C_{17}H_{27}Br_{0.41}I_{0.59}N_2OS_4Te$
$M_r = 638.88$
Monoclinic
$P2_1/n$
$a = 10.060$ (1) $\mathring{A}$
$b = 14.363$ (2) $\mathring{A}$
$c = 16.705$ (4) $\mathring{A}$
$\beta = 90.63$ (1)°
$V = 2413.5$ (7) $\mathring{A}^3$
$Z = 4$
$D_x = 1.758$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ $\mathring{A}$
Cell parameters from 24 reflections
$\theta = 12.3–15.2°$
$\mu = 3.022$ mm^{-1}
$T = 293$ (2) K
Well formed prism
$0.34 \times 0.30 \times 0.22$ mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/1.3\theta$ scans
Absorption correction: numerical (Gaussian method)
$T_{min} = 0.270$, $T_{max} = 0.527$
7362 measured reflections
7003 independent reflections

4946 observed reflections
$[I > 2\sigma(I)]$
$R_{int} = 0.0295$
$\theta_{max} = 29.97°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 23$
3 standard reflections frequency: 120 min intensity decay: 9.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1337$
$S = 1.097$
6958 reflections
248 parameters
H atoms: riding and rotating model with fixed U_{iso}
$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 7.1090P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.015$
$\Delta\rho_{max} = 0.795$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.702$ e $\mathring{A}^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$) for (3)*

U_{iso} for C4 to C5'; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{eq}/U_{iso}
Te1	0.07756 (3)	0.59273 (2)	0.89269 (2)	0.03612 (8)
I1†	0.0961 (4)	0.37600 (9)	0.9248 (3)	0.0481 (3)
Br1†	0.0873 (10)	0.3944 (2)	0.9258 (6)	0.0482 (7)
S1	0.19602 (13)	0.75076 (8)	0.92758 (8)	0.0478 (3)
S2	0.32506 (14)	0.57135 (9)	0.95857 (9)	0.0526 (3)
S3	−0.08385 (12)	0.71828 (9)	0.83189 (8)	0.0483 (3)
S4	−0.14804 (13)	0.51882 (10)	0.83256 (10)	0.0557 (3)
O1	0.3343 (5)	0.5448 (3)	0.5539 (2)	0.0712 (12)
N1	0.4230 (5)	0.7324 (3)	1.0092 (3)	0.0608 (12)
N2	−0.3113 (4)	0.6486 (4)	0.7755 (3)	0.0578 (12)
C1	0.3265 (5)	0.6889 (3)	0.9691 (3)	0.0445 (10)
C2	0.5355 (6)	0.6816 (5)	1.0440 (4)	0.067 (2)
C3	0.5102 (7)	0.6468 (5)	1.1267 (4)	0.078 (2)
C4†	0.4356 (9)	0.8326 (6)	1.0117 (6)	0.059 (2)
C4'†	0.387 (2)	0.8323 (15)	1.0502 (15)	0.063 (5)
C5†	0.3775 (13)	0.8710 (10)	1.0858 (8)	0.100 (4)
C5'†	0.469 (3)	0.9056 (19)	1.0084 (16)	0.086 (7)
C6	−0.1947 (5)	0.6297 (4)	0.8093 (3)	0.0477 (11)
C7	−0.4121 (6)	0.5746 (5)	0.7650 (5)	0.075 (2)
C8	−0.3944 (8)	0.5183 (7)	0.6903 (6)	0.105 (3)
C9	−0.3484 (6)	0.7431 (5)	0.7512 (4)	0.069 (2)
C10	−0.4247 (8)	0.7928 (6)	0.8147 (5)	0.093 (2)
C11	0.1683 (4)	0.5803 (3)	0.7772 (3)	0.0388 (9)
C12	0.2113 (5)	0.6576 (3)	0.7367 (3)	0.0437 (10)
C13	0.2689 (5)	0.6488 (3)	0.6612 (3)	0.0450 (11)
C14	0.2800 (5)	0.5618 (4)	0.6274 (3)	0.0490 (11)
C15	0.2385 (7)	0.4850 (4)	0.6683 (3)	0.0614 (15)
C16	0.1807 (6)	0.4931 (4)	0.7430 (3)	0.0525 (12)
C17	0.3855 (8)	0.6203 (5)	0.5101 (4)	0.080 (2)

† Partial occupancy (see below).

Table 4. *Selected geometric parameters ($\AA$, °) for (3)*

Te1—C11	2.151 (4)	N1—C2	1.461 (7)
Te1—S3	2.624 (1)	N1—C4'	1.63 (2)
Te1—S1	2.626 (1)	N2—C6	1.325 (6)
Te1—S4	2.690 (1)	N2—C9	1.464 (8)
Te1—S2	2.728 (1)	N2—C7	1.478 (8)
Te1—Br1	2.904 (3)	C2—C3	1.494 (9)
Te1—I1	3.164 (1)	C4—C5	1.48 (1)
Te1—Br1^i	3.476 (9)	C4'—C5'	1.51 (3)
Te1—I1^i	3.558 (4)	C7—C8	1.50 (1)
S1—C1	1.725 (5)	C9—C10	1.497 (9)
S2—C1	1.697 (5)	C11—C12	1.372 (6)
S3—C6	1.731 (6)	C11—C16	1.383 (7)
S4—C6	1.704 (5)	C12—C13	1.398 (7)
O1—C14	1.371 (6)	C13—C14	1.377 (7)
O1—C17	1.409 (8)	C14—C15	1.364 (8)
N1—C1	1.329 (6)	C15—C16	1.388 (8)
N1—C4	1.45 (1)		
C11—Te1—S3	88.7 (1)	Te1—I1—Te1^i	89.58 (8)
C11—Te1—S1	94.3 (1)	Te1—Br1—Te1^i	95.7 (2)
S3—Te1—S1	76.66 (4)	C1—S1—Te1	89.2 (2)
C11—Te1—S4	89.8 (1)	C1—S2—Te1	86.4 (2)
S3—Te1—S4	67.09 (4)	C6—S3—Te1	88.5 (2)
S1—Te1—S4	143.41 (4)	C6—S4—Te1	86.9 (2)
C11—Te1—S2	87.6 (1)	C14—O1—C17	118.7 (5)
S3—Te1—S2	142.34 (4)	C1—N1—C4	123.1 (5)
S1—Te1—S2	66.29 (4)	C1—N1—C2	121.6 (5)
S4—Te1—S2	150.30 (4)	C4—N1—C2	114.7 (5)
C11—Te1—Br1	94.4 (2)	C1—N1—C4'	117.5 (9)
S3—Te1—Br1	140.1 (2)	C2—N1—C4'	116.5 (9)
S1—Te1—Br1	142.3 (2)	C6—N2—C9	122.0 (5)
S4—Te1—Br1	73.2 (2)	C6—N2—C7	120.4 (5)
S2—Te1—Br1	77.5 (2)	C9—N2—C7	117.5 (5)
C11—Te1—I1	92.6 (1)	N1—C1—S2	121.7 (4)
S3—Te1—I1	140.98 (9)	N1—C1—S1	120.6 (4)
S1—Te1—I1	141.90 (9)	S2—C1—S1	117.7 (3)
S4—Te1—I1	73.92 (9)	N1—C2—C3	113.3 (6)

S2—Te1—I1	76.65 (8)	N1—C4—C5	111.1 (9)
Br1—Te1—I1	1.9 (3)	C5'—C4'—N1	107 (2)
C11—Te1—Br1^i	176.3 (2)	N2—C6—S4	122.0 (4)
S3—Te1—Br1^i	90.1 (1)	N2—C6—S3	120.5 (4)
S1—Te1—Br1^i	88.9 (1)	S4—C6—S3	117.5 (3)
S4—Te1—Br1^i	86.4 (2)	N2—C7—C8	113.5 (6)
S2—Te1—Br1^i	95.5 (2)	N2—C9—C10	112.2 (6)
Br1—Te1—Br1^i	84.3 (2)	C12—C11—C16	119.9 (4)
I1—Te1—Br1^i	86.11 (9)	C12—C11—Te1	121.0 (3)
C11—Te1—I1^i	174.9 (1)	C16—C11—Te1	119.1 (3)
S3—Te1—I1^i	86.41 (6)	C11—C12—C13	120.5 (5)
S1—Te1—I1^i	85.79 (6)	C14—C13—C12	119.2 (5)
S4—Te1—I1^i	87.11 (8)	C15—C14—O1	115.6 (5)
S2—Te1—I1^i	97.06 (8)	C15—C14—C13	120.1 (5)
Br1—Te1—I1^i	88.6 (2)	O1—C14—C13	124.3 (5)
I1—Te1—I1^i	90.42 (8)	C14—C15—C16	121.1 (5)
Br1^i—Te1—I1^i	4.35 (6)	C11—C16—C15	119.1 (5)
C11—Te1—I1—Te1^i	−175.9 (1)	C7—N2—C6—S3	−172.7 (5)
S2—Te1—S1—C1	−4.0 (2)	Te1—S4—C6—S3	1.3 (3)
S1—Te1—S2—C1	4.1 (2)	Te1—S3—C6—S4	−1.4 (3)
S4—Te1—S3—C6	0.8 (2)	C6—N2—C7—C8	−84.9 (8)
S3—Te1—S4—C6	−0.9 (2)	C6—N2—C9—C10	−94.0 (7)
C4—N1—C1—S2	172.7 (6)	S3—Te1—C11—C12	51.2 (4)
C2—N1—C1—S2	2.2 (8)	S1—Te1—C11—C12	−25.3 (4)
C4'—N1—C1—S2	−153 (1)	S4—Te1—C11—C12	118.3 (4)
C4—N1—C1—S1	−8.6 (9)	S2—Te1—C11—C12	−91.3 (4)
C2—N1—C1—S1	−179.1 (5)	Br1—Te1—C11—C12	−168.6 (4)
C4'—N1—C1—S1	25 (1)	I1—Te1—C11—C12	−167.8 (4)
Te1—S2—C1—S1	−6.4 (3)	S3—Te1—C11—C16	−127.6 (4)
Te1—S1—C1—S2	6.6 (3)	S1—Te1—C11—C16	155.9 (4)
C1—N1—C2—C3	−87.8 (7)	S4—Te1—C11—C16	−60.5 (4)
C1—N1—C4—C5	97.9 (9)	S2—Te1—C11—C16	89.9 (4)
C1—N1—C4'—C5'	−115 (2)	Br1—Te1—C11—C16	12.6 (4)
C9—N2—C6—S4	−176.4 (4)	I1—Te1—C11—C16	13.4 (4)
C7—N2—C6—S4	6.9 (8)	C17—O1—C14—C15	−176.8 (6)
C9—N2—C6—S3	3.9 (7)	C17—O1—C14—C13	1.6 (9)

Symmetry codes: (i) $−x, 1 − y, 2 − z$.

The *DIFABS* procedure (Walker & Stuart, 1983) was applied for the absorption correction for (1) giving a sufficiently better result compared with other methods. The absorption correction was made for (3) assuming that the crystal contained an equimolar ratio of Br- and I-containing analogues. The position of the non-stoichiometric Br atom was located in a difference Fourier synthesis. The I/Br occupancy factors (g) were refined first in the isotropic approximation for these atoms with the following restrictions: U_{iso}(Br) = U_{iso}(I), g(Br) + g(I) = 1 and Te—I = 3.169 (1) $\AA$ [as was found in the pure I analog (1)], and then fixed. In both structures, one of the ethyl groups is partially disordered. The two positions C4, C5 and C4', C5' were refined isotropically (occupancy factors 0.7 and 0.3, respectively, were adjusted empirically). Refinement was on F^2 for all reflections [except for 45 flagged by us for potential systematic errors for compound (3)].

For both compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993).

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group in one axial position (Fig. 1) and the second axial site seems to be weakly π-coordinated by a dithiocarbamate ligand of a neighbouring complex unit [Te$\cdots$C4^i 3.751 (3) Å, C7—Te$\cdots$C4^i 170.2 (1)°; symmetry code: (i) $-x$, $1-y$, $-z$], symmetrically related to the original one by an inversion centre [$(0,\frac{1}{2},0)$ for the reference molecule] (Fig. 2). The atoms surrounding C4^i are nearly equidistant from the neighbouring (original) Te1 atom [Te$\cdots$S3^i 4.164 (1), Te$\cdots$S4^i 4.017 (1) and Te$\cdots$N2^i 4.025 (3) Å] and the C4^i atom itself is shifted by 0.044 (3) Å towards this Te atom from the equatorial coordination plane of its 'own' Te1^i atom [the dihedral angle between the mean plane of equatorial Te substituents and the mean plane of the C4 dithiocarbamate group is 4.8 (1)°; the other dithiocarbamate group is coplanar with the equatorial plane within 1.6 (1)°]. As a result, molecules of (1) are joined into dimeric associations in the crystal (Fig. 2).