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Bis(diethyldithiocarbamato)(iodo)(4-methoxyphenyl)tellurium
 p -MeOC₆H₄Te(Et₂NCS₂)₂I, and its
Isomorphous Partially Bromine-Replaced
Analogue, p -MeOC₆H₄Te(Et₂NCS₂)₂Br_{0.41}I_{0.59}

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**Bis(diethyldithiocarbamato)(iodo)-
(4-methoxyphenyl)tellurium(IV), *p*-
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logue, *p*-MeOC₆H₄Te(Et₂NCS₂)₂Br_{0.41}I_{0.59}**

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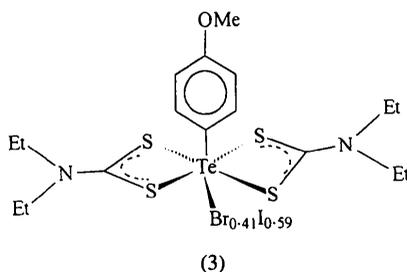
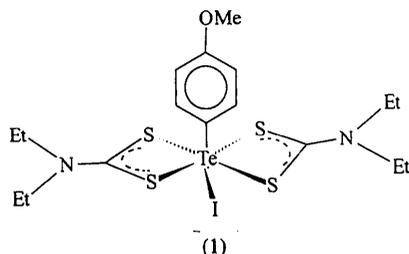
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Abstract

The Te^{IV} complexes *p*-MeOC₆H₄Te(Et₂NCS₂)₂I, (1), and *p*-MeOC₆H₄Te(Et₂NCS₂)₂Br_{0.41}I_{0.59}, (3), have been synthesized by reacting *p*-MeOC₆H₄Te(Et₂NCS₂)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.



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, 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

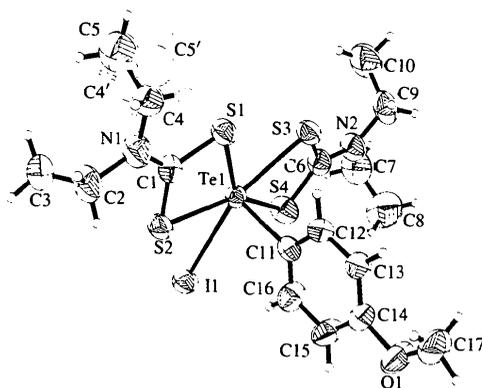


Fig. 1. Perspective view of (1) showing the labelling of non-H atoms. The minor component of the disordered ethyl group is shown by dashed lines. The displacement ellipsoids are drawn at the 50% probability level.

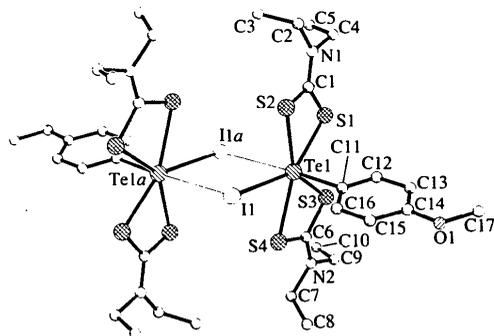


Fig. 2. Perspective view of the centrosymmetric dimer of (1). Disordered groups and H atoms are removed for clarity. Secondary intermolecular bonds are shown by thin lines.

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(Et₂NCS₂)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 non-bonded 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).

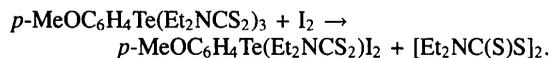
On the other hand, in the less sterically extended Me derivative (5), the I and four S atoms are in the plane within 0.02 Å. The Te atom is shifted outside, not towards but away from the Me group by 0.122 Å. This might be considered as a result of larger localization of the Te lone electron pair and 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 Csp²—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.

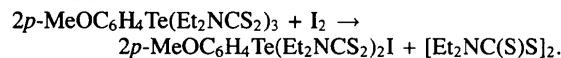
The role of the lone electron pair in the investigated structures is not very clear. The relatively strong secondary Te··I interaction here gives a roughly 0.5 Å shorter intermolecular contact than the sum of the respective van der Waals radii (Bondi, 1964) in the direction of the 'empty' axial position 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*-MeOC₆H₄Te(Et₂NCS₂)₂I₂ by the following reaction:



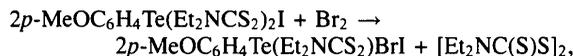
However, our structural investigation shows that, in reality, the following process takes place:



The compound PhTe(Et₂NCS₂)₂I, (2) (Husebye & Maartmann-Moe, 1994), has been obtained in our laboratory (Bergen)

using this reaction. Moreover, there is evidence that PhTe(Et₂NCS₂)Cl₂ gave PhTe(Et₂NCS₂)₂Cl on recrystallization (Dakternieks, Di Giacomo, Gable & Hoskins, 1988). It is noteworthy that the compound Te(Et₂NCS₂)₂I₂ 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:



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*-MeOC₆H₄Te(Et₂NCS₂)(Br_{0.4}I_{0.6})₂ (Husebye, Kudis, Lindeman & Strauch, 1995).

Compound (1)

Crystal data

C₁₇H₂₇IN₂OS₄Te
M_r = 658.15
 Monoclinic
*P*2₁/*n*
a = 10.069 (3) Å
b = 14.545 (2) Å
c = 16.784 (2) Å
 β = 90.59 (2)°
V = 2458.0 (9) Å³
Z = 4
D_x = 1.779 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 24 reflections
 θ = 12.4–15.1°
 μ = 2.816 mm⁻¹
T = 293 (2) K
 Well formed prism
 0.5 × 0.2 × 0.15 mm
 Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/0.7\theta$ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
 T_{\min} = 0.167, T_{\max} = 0.381
 6746 measured reflections
 6420 independent reflections

5101 observed reflections
 $[I > 2\sigma(I)]$
 R_{int} = 0.0247
 θ_{\max} = 29.96°
 h = -14 → 14
 k = 0 → 20
 l = 0 → 23
 3 standard reflections
 frequency: 120 min
 intensity decay: 6.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.0321
 $wR(F^2)$ = 0.0878
 S = 1.055
 6420 reflections
 238 parameters
 H atoms: riding and rotating model with fixed U_{iso}
 $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.2739P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = -0.103
 $\Delta\rho_{\max}$ = 0.778 e Å⁻³
 $\Delta\rho_{\min}$ = -0.957 e Å⁻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 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

| $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ | | | | |
|---|---------------|-------------|-------------|-----------------|
| | x | y | z | U_{eq} |
| Te1 | 0.07661 (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 (\AA , $^\circ$) for (I)

| | | | |
|-------------------------|------------|-------------|-----------|
| 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) |
| S1—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* $\text{C}_{17}\text{H}_{27}\text{Br}_{0.41}\text{I}_{0.59}\text{N}_2\text{O}_5\text{S}_4\text{Te}$ $M_r = 638.88$

Monoclinic

 $P2_1/n$ $a = 10.060 (1) \text{\AA}$ $b = 14.363 (2) \text{\AA}$ $c = 16.705 (4) \text{\AA}$ $\beta = 90.63 (1)^\circ$ $V = 2413.5 (7) \text{\AA}^3$ $Z = 4$ $D_x = 1.758 \text{ Mg m}^{-3}$ *Data collection*

Enraf-Nonius CAD-4 diffractometer

 $\omega/1.3\theta$ scans

Absorption correction: numerical (Gaussian method)

 $T_{\text{min}} = 0.270, T_{\text{max}} = 0.527$

7362 measured reflections

7003 independent reflections

*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 $P = (F_o^2 + 2F_c^2)/3$ Mo $K\alpha$ radiation $\lambda = 0.71069 \text{\AA}$

Cell parameters from 24 reflections

 $\theta = 12.3\text{--}15.2^\circ$ $\mu = 3.022 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Well formed prism

 $0.34 \times 0.30 \times 0.22 \text{ mm}$

Orange

4946 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.0295$ $\theta_{\text{max}} = 29.97^\circ$ $h = -14 \rightarrow 14$ $k = 0 \rightarrow 20$ $l = 0 \rightarrow 23$

3 standard reflections

frequency: 120 min

intensity decay: 9.0%

 $(\Delta/\sigma)_{\text{max}} = 0.015$ $\Delta\rho_{\text{max}} = 0.795 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.702 \text{ e \AA}^{-3}$

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'; $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ for all others.

| | x | y | z | $U_{\text{eq}}/U_{\text{iso}}$ |
|------|---------------|--------------|--------------|--------------------------------|
| 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) |
| S1—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: $U_{\text{iso}}(\text{Br}) = U_{\text{iso}}(\text{I})$, $g(\text{Br}) + g(\text{I}) = 1$ and $\text{Te—I} = 3.169 (1) \text{\AA}$ [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).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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 C4ⁱ 3.751(3) Å, C7—Te \cdots C4ⁱ 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 C4ⁱ are nearly equidistant from the neighbouring (original) Te1 atom [Te \cdots S3ⁱ 4.164(1), Te \cdots S4ⁱ 4.017(1) and Te \cdots N2ⁱ 4.025(3) Å] and the C4ⁱ atom itself is shifted by 0.044(3) Å towards this Te atom from the equatorial coordination plane of its 'own' Te1ⁱ 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).