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Bromobis(dimethyldithiocarbamato)-(4-methoxyphenyl)tellurium(IV) Dichloromethane Hemisolvate, p-MeOC$_6$H$_4$Te(Me$_2$NCS$_2$)$_2$Br.0.5CH$_2$Cl$_2$

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Abstract

The structure of the title Te^{IV} complex, C$_{13}$H$_{19}$BrN$_2$OS$_4$Te.0.45(CH$_2$Cl$_2$), 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

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···C4^i 3.751 (3) Å, C7—Te···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···S3^i 4.164 (1), Te···S4^i 4.017 (1) and Te···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).

(I)
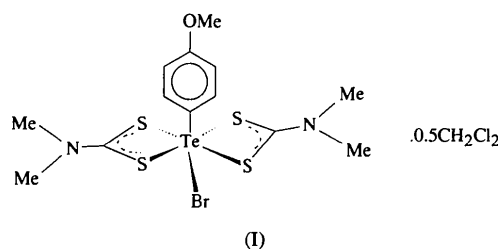
Generally, secondary bonding interactions are rather common for aryl-substituted Te^{IV} complexes. Additional intermolecular coordination has been found in earlier investigated analogues of (1). Thus, in the structure of iodobis(diethyldithiocarbamato)phenyltellurium(IV), (2) (Husebye & Maartmann-Moe, 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-
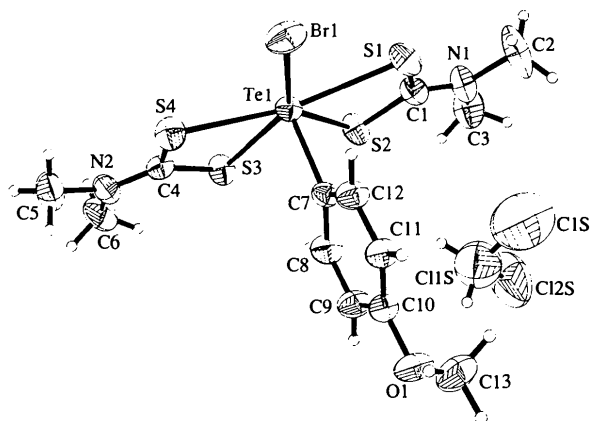

Fig. 1. Perspective view of complex (1) showing the labelling of non-H atoms and 50% probability displacement ellipsoids. Only one possible position of disordered CH$_2$Cl$_2$ is shown.
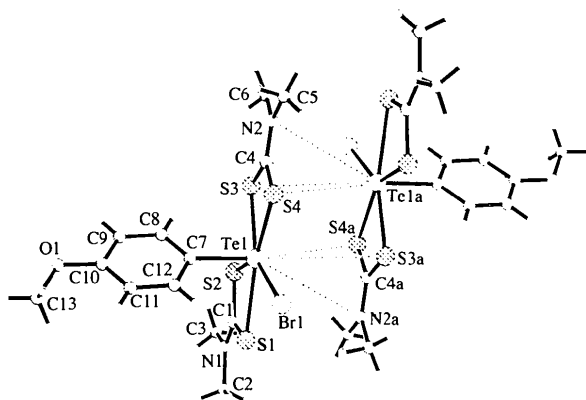
Fig. 2. Perspective view of the centrosymmetric associate of (1) in the crystal. Short intermolecular Te⋅⋅⋅C contacts are shown by dashed lines, others are indicated by dotted lines.

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(diethyldithiocarbamato)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(diethyldithiocarbamato)(iodo)methyltellurium(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$_{sp^2}$—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

Crystal data

C$_{13}$H$_{19}$BrN$_2$OS$_4$Te.- 0.45(CH$_2$Cl$_2$)	Mo Kα radiation
$M_r = 593.27$	λ = 0.71069 Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 9.156$ (5) Å	θ = 10.86–13.59°
$b = 13.324$ (2) Å	μ = 3.760 mm^{-1}
$c = 17.564$ (2) Å	T = 293 (2) K
β = 90.96 (3)°	Prisms
$V = 2142.5$ (11) Å^3	0.60 × 0.19 × 0.14 mm
$Z = 4$	Yellow
$D_x = 1.839$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	3922 observed reflections
$\omega/2\theta$ scans	$[I > 2\sigma(I)]$
Absorption correction: numerical (Gaussian method)	$R_{int} = 0.0201$
	$\theta_{max} = 29.96°$
	$h = -12 \rightarrow 12$
	$k = 0 \rightarrow 18$
$T_{min} = 0.480$, $T_{max} = 0.642$	$l = 0 \rightarrow 24$
6554 measured reflections	3 standard reflections frequency: 120 min intensity decay: 6.2%
6217 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2]$
$R(F) = 0.0368$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.0958$	$(\Delta/\sigma)_{max} = 0.126$
$S = 1.144$	$\Delta\rho_{max} = 0.660$ e Å^{-3}
6194 reflections	$\Delta\rho_{min} = -0.546$ e Å^{-3}
233 parameters	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
H atoms refined as riding using a rotating model with U_{iso} refined by groups	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
Te1	0.07939 (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)
C1S†	0.5090 (14)	0.9506 (13)	0.0171 (9)	0.115 (5)
C11S†	0.3662 (13)	1.0286 (8)	0.0223 (8)	0.181 (5)
C12S†	0.6330 (13)	0.9867 (8)	−0.0461 (7)	0.141 (4)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters (Å, °)*

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)	C1S—C12S	1.67 (1)
O1—C10	1.364 (4)	C1S—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 CH₂Cl₂ 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(C—Cl1) $= d$(C—Cl2) $= d$ (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).

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Bis(o-phénylènediammonium) cyclo-Tétraphosphate Dihydrate

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Abstract

The title compound, $2C_6H_{10}N_2^{2+}.P_4O_{12}^{4-}.2H_2O$, contains non-acidic $P_4O_{12}^{4-}$ anions connected by hydrogen bonds to water molecules and organic cations to form two-dimensional layers.

Commentaire

Au cours de ce travail, nous donnons la préparation et l'étude cristalline d'un nouveau cyclo-tétraphosphate de diamine aromatique (I). Cette structure renferme, comme c'est le cas pour les phosphates organiques que nous connaissons, une alternance de couches organiques et inorganiques. Les deux groupements organiques de l'unité asymétrique pointent dans des directions opposées. Leurs substituants —NH₃ en position *ortho* ne leur permettent de former des liaisons hydrogène qu'avec une seule couche inorganique. Il en résulte que les anions $P_4O_{12}^{4-}$ et les cations organiques qui leur sont connectés par liaisons hydrogène, forment des couches imbriquées, non liées entre elles, parallèles au plan *bc*. Les molécules d'eau connectent par liaisons hydrogène les groupements organiques et inorganiques.

(I)
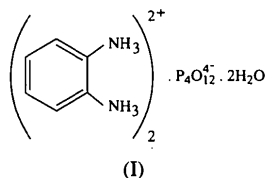
L'anion $P_4O_{12}^{4-}$ est non acide, ses quatre phosphores forment un carré pratiquement non déformé. Les valeurs des angles P—P—P [89,44 (2) et 90,47 (2)°] sont du même ordre que celles correspondant à $(HOCH_2CH_2NH_3)_4P_4O_{12}$ (Averbuch-Pouchot, Durif & Guitel, 1988a). Les principales caractéristiques géométriques des cycles P_4O_{12} sont en bon accord avec celles des cycles dans les différents cyclo-tétraphosphates cités dans ce travail.

Dans ce composé se manifeste une liaison hydrogène mettant en jeu un des oxygènes liants avec la molécule d'eau [OW···OL21 2,996 (3) Å]. La participation d'un oxygène liant à une liaison hydrogène n'a pas été observée pour les autres cyclo-tétraphosphates connus (Averbuch-Pouchot & Durif, 1993; Averbuch-Pouchot, Durif & Guitel, 1988a,b, 1989; Bdiri & Jouini, 1989a,b). Chaque cycle P_4O_{12} est engagé par l'intermédiaire de tous ses oxygènes, sauf OL12, dans des liaisons hydrogène avec quatre groupements organiques et quatre molécules d'eau. L'examen des liaisons hydrogène montre que l'ensemble des distances N(O)···O varient entre 2,682 (3) et 2,996 (3) Å. En se basant sur le critère habituel des distances (Blessing, 1986; Brown, 1976), on peut mettre en évidence deux liaisons fortes [N2···OE22 2,682 (3), N1···OE21 2,723 (3) Å]. Les six autres étant faibles.
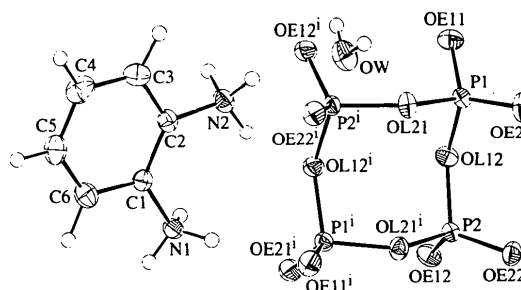

Fig. 1. Représentation *ORTEPII* (Johnson, 1990) du composé (I). Les ellipsoïdes thermiques correspondent à 50% de probabilité; les atomes d'hydrogène sont représentés par des cercles de diamètres arbitraires.

Partie expérimentale

L'acide cyclo-tétraphosphorique est préparé par passage d'une solution concentrée de cyclo-tétraphosphate de sodium $Na_4P_4O_{12}$ à travers une colonne de résine échangeuse d'ions de type Amberlite IR 120. Il est rapidement neutralisé par une solution d'o-phénylènediamine. Le mélange est ensuite filtré et abandonné à la température ambiante jusqu'à l'apparition de cristaux en forme de prismes stables à l'air.

Données cristallines

$2C_6H_{10}N_2^{2+}.P_4O_{12}^{4-}.2H_2O$	Mo $K\alpha$ radiation
$M_r = 572,23$	$\lambda = 0,71069$ Å
Monoclinique	Paramètres de la maille à
$C2/c$	l'aide de 23 réflexions