

Three-coordinated Divalent Tellurium Complexes: The Crystal Structures of Tetraphenylarsonium Diiodophenyltellurate(II) and Tetraphenylarsonium Bromiodophenyltellurate(II)

SVERRE HAUGE and OLAV VIKANE*

Department of Chemistry, University of Bergen, Realfagbygget, N-5000 Bergen, Norway

Tetraphenylarsonium diiodophenyltellurate(II), $[(C_6H_5)_4As][C_6H_5TeI_2]$, I, and tetraphenylarsonium bromiodophenyltellurate(II), $[(C_6H_5)_4As][C_6H_5TeBrI]$, II, form isomorphous monoclinic crystals with space group $P2_1/n$, $Z=4$. The unit cell dimensions for I are: $a=9.9456(11)$, $b=23.1421(22)$, $c=13.5999(17)$ Å, $\beta=108.337(10)^\circ$, and for II: $a=9.8897(10)$, $b=23.1159(34)$, $c=13.4642(16)$ Å, $\beta=108.429(9)^\circ$.

The tellurium atom is three-coordinated, being bonded to a phenyl carbon atom and, in directions nearly normal to the Te-C bond, to two iodine atoms in I, and to one bromine atom and one iodine atom in II. The three-centre systems I-Te-I and I-Te-Br are nearly linear, and the Te-C bond nearly bisects the angle of the three-centre system. The bond lengths and angles involving tellurium are: Te-I=2.9634(13) Å, 2.9456(14) Å, Te-C=2.120(12) Å, I-Te-I=178.03(4)°, I-Te-C=89.0(3)°, 89.4(3)° in I, and Te-I=2.9033(18) Å, Te-Br=2.8676(22) Å, Te-C=2.119(14) Å, I-Te-Br=177.93(6)°, I-Te-C=88.5(4)°, Br-Te-C=89.7(4)° in II.

In a previous paper the crystal structures of tetramethylammonium phenyldithiocyanatotellurate(II) and tetramethylammonium phenyldiselenocyanatotellurate(II) were reported.¹ The present paper reports the crystal structures of tetraphenylarsonium diiodophenyltellurate(II) and tetraphenylarsonium bromiodophenyltellurate(II). These are so far the only structures of

anionic tellurium(II) complexes. In addition to the anionic complexes, divalent tellurium is known to form numerous complexes with ligands as thiourea or substituted thioureas, selenourea or substituted selenoureas, and halides or pseudohalides.¹⁻¹⁰ Tellurium(II) forms square planar or T-shaped complexes. The latter coordination is found when the phenyl group is one of the ligands. The bonding system in the complexes has been assumed to be based on $5p$ orbitals of tellurium.² In the square planar complexes the bonding consists of two linear $3c-4e$ bonding systems at right angle to each other. The T-shaped complexes have one linear $3c-4e$ system and the phenyl carbon is bonded at right angle to this by a $2c-2e$ bonding. The $3c-4e$ bonding system gives weak bonds, and a relative strong bond is followed by a weak bond in *trans* position. The present work is part of an investigation of the relative strength of the *trans* bond lengthening effect to ligands in tellurium(II) complexes.

EXPERIMENTAL

Synthesis and preliminary crystal data for the two present compounds have been reported elsewhere.¹¹

Intensity data were collected by use of an Enraf-Nonius CAD-4 computer controlled diffractometer with graphite-monochromatized $MoK\alpha$ radiation.

The crystals used were coated with epoxy glue. The intensity of two reference reflections of medium intensity, remeasured at intervals of

* Present address: Rogaland Regional College, N-4001 Stavanger, Norway.

Table 1. Crystal data and refinement characteristics.

	$[(C_6H_5)_4As][C_6H_5TeI_2]$	$[(C_6H_5)_4As][C_6H_5TeBrI]$
<i>a</i> (Å)	9.9456(11)	9.8897(10)
<i>b</i> (Å)	23.1421(22)	23.116(3)
<i>c</i> (Å)	13.5999(17)	13.4642(16)
β (°)	108.337(10)	108.429(9)
<i>V</i> (Å ³)	2971.2	2920.2
<i>M</i>	841.86	794.87
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
<i>Z</i>	4	4
$\lambda MoK\alpha$ (Å)	0.71073	0.71073
<i>D_x</i> (g cm ⁻³)	1.89	1.81
<i>D_{obs}</i> (g cm ⁻³)	1.88	1.82
μ (cm ⁻¹)	43.32	47.79
<i>T</i> (K)	293	293
<i>F</i> (000)	1584	1512
sin θ/λ range	0.578	0.578
Scan mode	ω -2 θ	ω -2 θ
No. of reflections	4928	4847
No. of reflections with $I > 3\sigma(I)$	2945	3161
Crystal dimensions (mm ³)	0.14 × 0.14 × 0.40	0.13 × 0.23 × 0.52
<i>R</i> (<i>F</i>)	0.046	0.062
<i>R_w</i> (<i>F</i>)	0.044	0.059
No. of parameters refined	157	157
Difference Fourier max. value (e Å ⁻³)	1.2	1.2

6000 s of exposure time, decreased by 15 % for I, and 17 % for II during the data collections. The intensity data were scaled in accordance with the variation in the intensities of the reference reflections.

The data were corrected for Lorentz and polarization, absorption and anomalous dispersion effects. The calculated structure factors were based on the scattering factors calculated from numerical Hartree-Fock wave function.¹²

The structures were solved by Patterson and Fourier methods and refined by the full-matrix least-squares method, minimizing the function $\sum w(F_o - KF_c)^2$ where *K* is a scale factor and $w = 1/\sigma^2(F_o)$. The refinement was performed with CRYLSQ of X-RAY 76.¹³ Hydrogen atoms were not included in the refinements, carbon atoms were included with isotropic thermal parameters and the rest of the atoms with anisotropic parameters. Crystal data and refinement characteristics are given in Table 1. Atomic coordinates are listed in Tables 2 and 3. A list of structure factors and thermal parameters is available from the authors on request.

RESULTS

Bond lengths and angles in tetraphenylarsonium diiodophenyltellurate(II), I, and tetraphenylarsonium bromiodophenyltellurate(II), II, based on the atomic coordinates in Tables 2 and 3, are listed in Tables 4 and 5.

Views of the structures of the anions, as seen normal to the plane through the coordination group, are shown in Fig. 1. A stereoscopic view of the content of the unit cell of the bromiodophenyltellurate(II) compound is shown in Fig. 2.

In each of the structures the tellurium atom is three-coordinated, being bonded to one phenyl carbon atom and, in directions nearly perpendicular to the Te-C bond, to two iodine atoms in I, and to one iodine and one bromine atom in II, so that each anion shows a T-shaped geometry.

The coordination around the tellurium atom is nearly planar in each structure. The largest deviation from a least-squares plane through Te,

Table 2. Atomic coordinates for tetraphenylarsonium diiodophenyltellurate(II), in fractions of monoclinic cell edges. Origin at a centre of symmetry. Standard deviations from least squares in parantheses.

	x	y	z
Te	0.19063(9)	0.09031(4)	0.21396(6)
I(1)	0.32344(10)	-0.01858(4)	0.17634(7)
I(2)	0.04904(10)	0.19697(4)	0.24705(7)
As	0.48546(12)	0.30500(5)	0.11500(8)
C(1)	0.0163(12)	0.0417(5)	0.2268(9)
C(2)	0.0214(13)	0.0227(5)	0.3285(9)
C(3)	-0.1016(15)	-0.0063(6)	0.3337(10)
C(4)	-0.2138(14)	-0.0144(6)	0.2535(10)
C(5)	-0.2209(15)	0.0013(6)	0.1534(10)
C(6)	-0.0962(14)	0.0308(5)	0.1401(9)
C(11)	0.4846(11)	0.2274(4)	0.0643(8)
C(12)	0.3574(12)	0.1961(5)	0.0377(8)
C(13)	0.3611(14)	0.1374(6)	0.0079(9)
C(14)	0.4850(15)	0.1135(6)	0.0028(10)
C(15)	0.6121(15)	0.1459(6)	0.0270(10)
C(16)	0.6108(13)	0.2043(5)	0.0626(9)
C(21)	0.6643(11)	0.3363(5)	0.1250(8)
C(22)	0.7754(12)	0.3300(5)	0.2161(8)
C(23)	0.9116(13)	0.3487(5)	0.2201(9)
C(24)	0.9359(13)	0.3733(5)	0.1335(9)
C(25)	0.8224(13)	0.3791(5)	0.0415(9)
C(26)	0.6825(13)	0.3623(5)	0.0353(8)
C(31)	0.3347(12)	0.3486(5)	0.0212(8)
C(32)	0.2714(13)	0.3925(5)	0.0618(9)
C(33)	0.1635(15)	0.4263(6)	-0.0144(11)
C(34)	0.1318(15)	0.4124(6)	-0.1170(11)
C(35)	0.1998(16)	0.3713(7)	-0.1555(11)
C(36)	0.3093(14)	0.3351(6)	-0.0857(10)
C(41)	0.4662(12)	0.3047(5)	0.2507(8)
C(42)	0.4862(14)	0.3568(6)	0.3022(10)
C(43)	0.4699(16)	0.3580(7)	0.4063(11)
C(44)	0.4428(15)	0.3063(7)	0.4446(10)
C(45)	0.4311(17)	0.2545(7)	0.3991(12)
C(46)	0.4433(14)	0.2513(6)	0.2909(10)

Table 3. Atomic coordinates for tetraphenylarsonium bromiodophenyltellurate(II), in fractions of monoclinic cell edges. Origin at a centre of symmetry. Standard deviations from least squares in parentheses.

	x	y	z
Te	0.19224(15)	0.08856(6)	0.21498(10)
I	0.32350(16)	0.01847(7)	0.17938(13)
Br	0.05268(17)	0.19239(8)	0.24681(14)
As	0.48855(17)	0.30359(8)	0.11396(14)
C(1)	0.0180(15)	0.0396(7)	0.2268(12)
C(2)	0.0232(16)	0.0204(8)	0.3302(13)
C(3)	-0.0901(17)	-0.0080(9)	0.3422(14)
C(4)	-0.2115(17)	-0.0150(9)	0.2541(15)
C(5)	-0.2206(17)	0.0001(9)	0.1496(15)
C(6)	-0.0940(16)	0.0314(8)	0.1373(14)
C(11)	0.4853(15)	0.2250(7)	0.0655(13)
C(12)	0.3604(15)	0.1954(7)	0.0368(13)
C(13)	0.3629(16)	0.1373(8)	0.0093(14)
C(14)	0.4923(17)	0.1122(9)	0.0023(15)
C(15)	0.6123(17)	0.1450(9)	0.0238(15)
C(16)	0.6098(16)	0.2030(8)	0.0552(14)
C(21)	0.6718(15)	0.3348(7)	0.1259(13)
C(22)	0.7804(16)	0.3266(7)	0.2196(14)
C(23)	0.9283(16)	0.3448(8)	0.2217(15)
C(24)	0.9468(16)	0.3727(8)	0.1359(15)
C(25)	0.8293(16)	0.3803(8)	0.0426(15)
C(26)	0.6871(15)	0.3645(7)	0.0337(14)
C(31)	0.3403(15)	0.3486(7)	0.0189(14)
C(32)	0.2764(16)	0.3924(8)	0.0586(15)
C(33)	0.1614(17)	0.4274(8)	-0.0184(15)
C(34)	0.1318(17)	0.4136(8)	-0.1193(15)
C(35)	0.2003(18)	0.3736(9)	-0.1563(16)
C(36)	0.3183(17)	0.3358(8)	-0.0904(15)
C(41)	0.4666(15)	0.3027(7)	0.2523(12)
C(42)	0.4843(16)	0.3567(8)	0.3004(14)
C(43)	0.4729(18)	0.3625(9)	0.4100(16)
C(44)	0.4429(18)	0.3034(9)	0.4458(16)
C(45)	0.4324(18)	0.2478(9)	0.3936(16)
C(46)	0.4408(16)	0.2458(8)	0.2838(15)

I(1), I(2), and C(1) is 0.021 Å in I, and the largest deviation from the corresponding least-squares plane through Te, Br, I, and C(1) is 0.017 Å in II.

The angles of the tellurium coordination in the two structures, are equal within errors. The three-centre systems I-Te-I and I-Te-Br have a deviation of 2.0° from linearity. The deviation is in such a way that the halogen atoms are approaching the carbon atom. The deviation is probably a result of lone electron pair repulsion on tellurium. Such deviation occurs in all the known structures of divalent three-coordinated

tellurium compounds. The angles are found in the range 171.9(5) to 177.22(3)°. Within errors, the Te-C bond bisects the angle of the three-centre system. Average value of the Hal-Te-C angles is 89.15°.

The I-Te-I bonding system in I is slightly asymmetric and the mean value of the two Te-I bond lengths, 2.955 Å, is about 0.26 Å longer than the sum of the single bond radii.¹⁴ In II the asymmetry of the I-Te-Br bonding system is more pronounced, the Te-Br and the Te-I bond is, respectively, about 0.36 Å and 0.20 Å

Table 4. Bond lengths (Å) and angles (°) in tetraphenylarsonium diiodophenyltellurate(II). Standard deviations in parentheses.

Te-I(1)	2.9634(13)	I(1)-Te-I(2)	178.03(4)
Te-I(2)	2.9456(14)	I(1)-Te-C(1)	89.0(3)
Te-C(1)	2.120(12)	I(2)-Te-C(1)	89.4(3)
C(1)-C(2)	1.438(18)	Te-C(1)-C(2)	117.4(8)
C(2)-C(3)	1.417(20)	Te-C(1)-C(6)	119.7(10)
C(3)-C(4)	1.305(17)	C(1)-C(2)-C(3)	115.0(10)
C(4)-C(5)	1.389(21)	C(2)-C(3)-C(4)	123.4(14)
C(5)-C(6)	1.475(21)	C(3)-C(4)-C(5)	123.3(15)
C(6)-C(1)	1.369(15)	C(4)-C(5)-C(6)	117.0(11)
		C(5)-C(6)-C(1)	118.1(12)
		C(6)-C(1)-C(2)	122.9(12)
As-C(11)	1.923(11)	C(11)-As-C(21)	106.4(5)
As-C(21)	1.887(11)	C(11)-As-C(31)	109.8(4)
As-C(31)	1.921(10)	C(11)-As-C(41)	110.6(5)
As-C(41)	1.915(12)	C(21)-As-C(31)	111.4(5)
		C(21)-As-C(41)	108.2(5)
		C(31)-As-C(41)	110.4(5)

longer than the sum of the single bond radii.¹⁴ Thus, on substituting iodine for bromine, it is seen that the length of the *trans*-positioned Te-I bond increases by about 0.06 Å. This clearly indicates the more pronounced *trans* bond-lengthening effect of iodine relative to bromine when bonded to divalent tellurium. Similar

trends in the *trans* bond-lengthening effect of bromine and iodine has previously been found when the ligand in *trans* position to halogen is ethylenethiourea or ethyleneselenourea.⁶⁻⁸ From the preparation of the present compounds as well as other tellurium(II) complexes, it is known that chlorine, bromine, and iodine displace each other in the order mentioned.^{2,3,11,15,16} On regarding tellurium(II) complexes as models for the transition states in nucleophilic displacements at divalent tellurium,¹⁷ it is seen that the nucleophilic reactivity relates to the ability of the nucleophile to engage the tellurium 5p orbital in bonding at the expense of the bond at 180°.

The Te-C bond lengths in I and II are equal within errors and they are not significantly different from the Te-C_{sp²} single covalent bond length, 2.107 Å.^{14,18}

Foss^{2,3} has stated that the coordination around the tellurium atom in phenyltellurium complexes may be regarded as based on a square-planar arrangement. Approach of the fourth ligand is not observed in the present structures. This is similar to the findings in structures of tetramethylammonium phenyldithiocyanatotellurate(II) and the corresponding selenocyanato compound.¹ The lack of ligand in *trans* position to the Te-C bond can be looked at as indication of the great *trans*-lengthening effect of the phenyl group.

The tellurium atom and the carbon atoms of the phenyltellurium group are nearly co-planar in

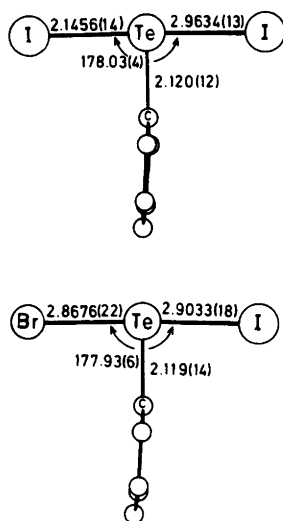


Fig. 1. The diiodophenyltellurate(II) ion, above, and the bromoiodophenyltellurate(II) ion, as seen normal to the plane through the coordination group.

Table 5. Bond lengths (Å) and angles (°) in tetraphenylarsonium bromiodophenyltellurate(II). Standard deviations in parentheses.

Te-I	2.9033(18)	I-Te-Br	177.93(6)
Te-Br	2.8676(22)	I-Te-C(1)	88.5(4)
Te-C(1)	2.119(14)	Br-Te-C(1)	89.7(4)
C(1)-C(2)	1.446(18)	Te-C(1)-C(2)	117.1(9)
C(2)-C(3)	1.351(26)	Te-C(1)-C(6)	117.5(10)
C(3)-C(4)	1.405(20)	C(1)-C(2)-C(3)	119.1(13)
C(4)-C(5)	1.425(27)	C(2)-C(3)-C(4)	118.3(15)
C(5)-C(6)	1.399(26)	C(3)-C(4)-C(5)	125.2(18)
C(6)-C(1)	1.368(19)	C(4)-C(5)-C(6)	115.6(18)
		C(5)-C(6)-C(1)	116.2(19)
		C(6)-C(1)-C(2)	125.2(19)
As-C(11)	1.927(16)	C(11)-As-C(21)	107.4(8)
As-C(21)	1.910(18)	C(11)-As-C(31)	110.9(7)
As-C(31)	1.919(16)	C(11)-As-C(41)	108.7(7)
As-C(41)	1.942(17)	C(21)-As-C(31)	110.8(8)
		C(21)-As-C(41)	108.3(7)
		C(31)-As-C(41)	110.6(8)

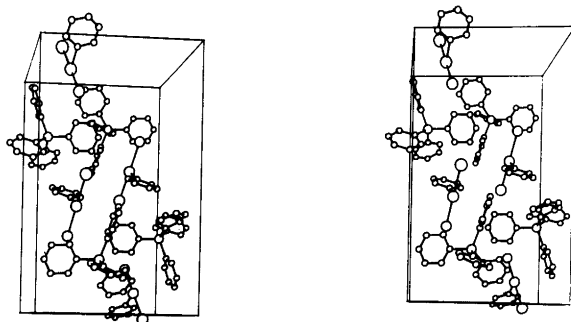


Fig. 2. A stereoscopic view of the content of the unit cell for tetraphenylarsonium bromiodophenyltellurate(II), as seen along the *a* crystal axis.

each structure, the largest deviation from a least-squares plane being 0.058 Å in I and 0.062 Å in II. The angle between this plane and the least-squares plane through the coordination group is 89.59° in I, and 89.47° in II.

In the tetraphenylarsonium ion the As atom is approximately tetrahedrally surrounded by the four phenyl groups, which are planar within the experimental error. The C-As-C bond angles vary from 106.4(5)° to 111.4(5)° in I, and from 107.4(8)° to 110.9(7)° in II. The average As-C bond length is 1.912 Å in I, and 1.925 Å in II. The C-C bond lengths and the C-C-C bond angles in the four phenyl groups are in the expected range in both structures.^{19,20}

REFERENCES

- Hauge, S. and Vikane, O. *Acta Chem. Scand. A* 29 (1975) 755.
- Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S., Eds., *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
- Foss, O. *Pure Appl. Chem.* 24 (1970) 31.
- Foss, O. and Marøy, K. *Acta Chem. Scand.* 20 (1966) 123.
- Foss, O. and Husebye, S. *Acta Chem. Scand.* 20 (1966) 132.
- Vikane, O. *Acta Chem. Scand. A* 29 (1975) 738.
- Vikane, O. *Acta Chem. Scand. A* 29 (1975) 763.

8. Vikane, O. *Acta Chem. Scand. A* 29 (1975) 787.
9. Hauge, S., Johanessen, Ø. and Vikane, O. *Acta Chem. Scand. A* 32 (1978) 901.
10. Foss, O. and Hauge, S. *Acta Chem. Scand. A* 19 (1965) 2395.
11. Klæboe, P., Nielsen, C. J., Suchi, R. and Vikane, O. *Acta Chem. Scand. A* 32 (1978) 565.
12. Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
13. Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446 of the Computer Science Center, University of Maryland, March 1976.
14. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca 1960.
15. Foss, O. and Hauge, S. *Acta Chem. Scand. A* 13 (1959) 2155.
16. Foss, O. and Fossen, S. *Acta Chem. Scand. A* 15 (1961) 1618.
17. Foss, O. *Acta Chem. Scand. A* 16 (1962) 779.
18. Bastiansen, O. and Tretteberg, M. *Tetrahedron* 17 (1962) 147.
19. Runsink, J., Swen-Walstra, S. and Michelsen, T. *Acta Crystallogr. B* 28 (1972) 1331.
20. Faithful, B. D. and Wallwork, S. C. *Acta Crystallogr. B* 28 (1972) 2301.

Received February 7, 1983.