

lithium(II)] (Schubert, Neugebauer & von Rague Schleyer, 1982) in which the biphenyl unit is perfectly planar suggests that the H atoms *ortho* to the phenylene link are sterically not very demanding. Further, comparison of the non-bonding interactions between the I<sup>-</sup> ligands and the respective phenyl and methyl carbons (mean distance 3.835 Å) indicates the distances are very similar to the non-bonding contacts which cushion the I<sup>-</sup> ligands in Ni(diars)<sub>2</sub>I<sub>2</sub> (Stephenson, 1964). In both complexes it is the non-bonding contacts which determine how close the I<sup>-</sup> ligands can approach the central Ni atom. In Ni(diars)<sub>2</sub>I<sub>2</sub> the I<sup>-</sup> ligands cannot approach very closely and so interaction between the Ni and As ligands must be strong in order for the Ni to achieve electrical neutrality. Conversely, in Ni(dmab)<sub>2</sub>I<sub>2</sub> where the I<sup>-</sup> ligands approach more closely the Ni-As interaction must be reduced and this is reflected in the long Ni-As bond lengths. The variation in bond lengths in the two structures is a direct result of the operation of the electroneutrality principle.

The authors wish to thank Dr Ward T. Robinson, University of Canterbury, for use of diffractometer

facilities and Dr Robert G. Cunninghame for helpful discussions.

#### References

- ALLEN, D. W., ASHFORD, D. F., HOGARTH, D. & MANN, F. G. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1597-1600.  
 ALLEN, D. W., KENNEDY, D. A. & NOWELL, I. W. (1980). *Inorg. Chim. Acta*, **40**, 171-177.  
 CUNNINGHAME, R. G. & HANTON, L. R. (1986). In preparation.  
 HAMM, D. J., BORDNER, J. & SCHREINER, A. F. (1973). *Inorg. Chim. Acta*, **7**, 637-641.  
 HAWKINSON, S. W. & FLEISCHER, E. B. (1969). *Inorg. Chem.* **8**, 2402-2410.  
*International Tables for X-ray Crystallography* (1969). Vol. I. Birmingham: Kynoch Press.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 JOHNSTON, D. L. & HORROCKS, W. DE W. JR (1971). *Inorg. Chem.* **10**, 687-691.  
 LALANCETTE, R. A., MACCHIA, D. J. & FUREY, W. F. (1976). *Inorg. Chem.* **15**, 548-551.  
 SCHUBERT, U., NEUGEBAUER, W. & VON RAGUE SCHLEYER, P. (1982). *J. Chem. Soc. Chem. Commun.* pp. 1184-1185.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 STEPHENSON, N. C. (1964). *Acta Cryst.* **17**, 592-596.

*Acta Cryst.* (1986). **C42**, 1289-1291

## Structure of Dibromiodobis(triphenylphosphine oxide)thallium(III)

BY A. CASTINEIRAS AND W. HILLER

*Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Federal Republic of Germany*

AND M. R. BERMEJO AND M. GAYOSO

*Departamento de Química Inorgánica, Facultad de Química, Universidad de Santiago, Santiago de Compostela, Spain*

(Received 18 September 1985; accepted 22 April 1986)

**Abstract.** [TlBr<sub>2</sub>I{OP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sub>2</sub>, *M*<sub>r</sub> = 1047.68, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 14.954 (3), *b* = 14.605 (4), *c* = 17.489 (2) Å, β = 107.84 (4)°, *V* = 3635.9 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.91 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 76.2 cm<sup>-1</sup>, *F*(000) = 1984, *T* = 293 K, *R* = 0.049 for 3158 significant reflections. The coordination around the Tl atom is distorted trigonal bipyramidal with the halide atoms in equatorial sites and the triphenylphosphine oxide (tppo) ligands in axial positions. The metal atom is only 0.019 (1) Å out of the plane of the halide atoms. The crystal structure is isotypic with that of [TlBr<sub>3</sub>(tppo)<sub>2</sub>].

**Introduction.** Thallium(III) halides react with triphenylphosphine oxide to form [TLX<sub>3</sub>(tppo)<sub>2</sub>] complexes (*X* = halide, tppo = triphenylphosphine oxide), in which the Tl atom exhibits a distorted trigonal-bipyramidal coordination sphere. In order to gain more insight into the relation between spectroscopic and structural properties of the TLX<sub>3</sub> compounds, we prepared the mixed halocompounds [TlBrClI(tppo)<sub>2</sub>] (Castineiras, Hiller, Strähle, Bermejo & Gayoso, 1986) and [TlBrI<sub>2</sub>(tppo)<sub>2</sub>] (Castineiras, Hiller, Strähle, Bermejo & Gayoso, 1985). Here we report the crystal structure of [TlBr<sub>2</sub>I(tppo)<sub>2</sub>].

**Experimental.** Compound prepared by reaction of TlI with Br<sub>2</sub> in presence of triphenylphosphine oxide. A yellow–orange, plate-like crystal having approximate dimensions 0.5 × 0.2 × 0.15 mm was mounted on a glass fiber; Enraf–Nonius CAD-4 diffractometer, Mo K $\alpha$  radiation, graphite monochromator; cell dimensions obtained from least-squares refinement using setting angles of 25 reflections in range 8 <  $\theta$  < 23°. Data collected with  $\omega/\theta$  scan, 7023 reflections measured (3 <  $\theta$  < 23°, -16 <  $h$  < 16, -16 <  $k$  < 16, 0 <  $l$  < 19), orientation (every 200 reflections) and intensity control (every 2 h of X-ray exposure) by means of three standard reflections, no detectable decomposition; Lorentz and polarization corrections. Conditions limiting possible reflections  $h0l$ :  $l = 2n$  and  $0k0$ :  $k = 2n$ , space group  $P2_1/c$ . Tl, I and Br positions from inspection of Patterson map, all other non-H atoms by subsequent difference Fourier synthesis. Isotropic refinement of all non-H atoms converged at  $R = 0.146$  (for all 5018 unique reflections). An empirical absorption correction was undertaken using *DIFABS* (Walker & Stuart, 1983) whereupon  $R$  dropped to 0.097 ( $R_{\text{int}} = 0.024$  based on  $F$ ). H atoms in idealized positions with  $d(\text{C–H}) = 0.95 \text{ \AA}$  and only included in structure-factor calculations, other atoms with anisotropic thermal parameters; secondary-extinction correction with a final coefficient of  $2.975 \times 10^{-9}$ , refined in least squares (Zachariasen, 1963). Refinement based on  $F$  by full-matrix least-squares techniques using 3158 reflections with intensities  $I > 3\sigma(I)$ ,  $R = 0.049$ ,  $wR = 0.054$ ,  $w = 1/\sigma^2(F_o)$ , 398 parameters,  $S = 5.88$ , max.  $(\Delta/\sigma) < 0.01$ . Final difference Fourier map qualitatively featureless,  $\Delta\rho < |1.82| \text{ e \AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on a VAX 11/750 computer (Zentrum für Datenverarbeitung der Universität Tübingen) with *VAXSDP* (B. A. Frenz & Associates, 1985).

**Discussion.** Atomic positional parameters and equivalent isotropic thermal parameters are listed in Table 1, selected bond distances and angles in Table 2.\* Fig. 1 shows the atomic numbering and Fig. 2 a stereoscopic view of the structure.

The crystal structure is isotypic with that of [TlBr<sub>3</sub>(tppo)<sub>2</sub>] (Jeffs, Small & Worrall, 1984) and consists of discrete molecules of [TlBr<sub>2</sub>I(tppo)<sub>2</sub>] with a distorted trigonal-bipyramidal coordination sphere of Tl, with Br and I in equatorial and the O atoms of the

tppo ligands in axial sites. The metal atom is not significantly removed [0.019 (1) Å] from the plane of the halide atoms. The largest angular distortion from trigonal-bipyramidal symmetry is reflected in the I–Tl–Br(2) angle of 116.66 (2)° and in the O(1)–Tl–O(2) angle of 175.3 (2)°. The Tl–Br distances

Table 1. *Atom coordinates and equivalent isotropic temperature factors* ( $\text{\AA}^2 \times 10^3$ )

	$U_{\text{eq}} = \frac{1}{3}$ (trace of orthogonalized U tensor).			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Tl	0.21680 (4)	0.46420 (5)	0.12003 (3)	5.2 (4)
I	0.04324 (8)	0.4750 (1)	0.12813 (8)	10.2 (1)
Br(1)	0.3601 (1)	0.4517 (2)	0.2486 (1)	9.1 (1)
Br(2)	0.2352 (1)	0.4629 (2)	-0.01960 (9)	8.1 (1)
P(1)	0.2152 (3)	0.2089 (3)	0.0757 (2)	5.1 (2)
P(2)	0.2931 (3)	0.7115 (3)	0.1172 (2)	5.3 (2)
O(1)	0.2115 (7)	0.2980 (7)	0.1171 (6)	6.4 (6)
O(2)	0.2362 (7)	0.6311 (8)	0.1250 (6)	7.6 (7)
C(11)	0.154 (1)	0.213 (1)	-0.0302 (8)	6 (1)
C(12)	0.069 (1)	0.259 (1)	-0.0543 (9)	6 (1)
C(13)	0.019 (1)	0.262 (1)	-0.136 (1)	8 (1)
C(14)	0.050 (1)	0.220 (1)	-0.1905 (9)	9 (1)
C(15)	0.135 (1)	0.177 (1)	-0.1676 (9)	9 (1)
C(16)	0.188 (1)	0.173 (1)	-0.0866 (9)	8 (1)
C(21)	0.1623 (9)	0.120 (1)	0.1172 (7)	3 (1)
C(22)	0.126 (1)	0.042 (1)	0.0762 (8)	7 (1)
C(23)	0.088 (1)	-0.025 (1)	0.1124 (9)	6 (1)
C(24)	0.089 (1)	-0.014 (1)	0.190 (1)	8 (1)
C(25)	0.123 (1)	0.064 (1)	0.2313 (9)	7 (1)
C(26)	0.1613 (9)	0.129 (1)	0.1955 (8)	5 (1)
C(31)	0.3330 (9)	0.176 (1)	0.0857 (8)	6 (1)
C(32)	0.359 (1)	0.083 (1)	0.084 (1)	9 (1)
C(33)	0.451 (1)	0.062 (2)	0.089 (1)	11 (2)
C(34)	0.518 (1)	0.129 (2)	0.099 (1)	11 (2)
C(35)	0.492 (1)	0.217 (2)	0.102 (1)	10 (2)
C(36)	0.401 (1)	0.241 (1)	0.094 (1)	7 (1)
C(41)	0.3013 (9)	0.789 (1)	0.1979 (8)	8 (1)
C(42)	0.258 (1)	0.771 (1)	0.2560 (8)	6 (1)
C(43)	0.263 (1)	0.833 (1)	0.3184 (8)	8 (2)
C(44)	0.312 (1)	0.910 (1)	0.3223 (9)	7 (1)
C(45)	0.354 (1)	0.931 (1)	0.2657 (9)	8 (1)
C(46)	0.348 (1)	0.874 (1)	0.2048 (8)	7 (1)
C(51)	0.236 (1)	0.772 (1)	0.0246 (8)	6 (1)
C(52)	0.279 (1)	0.842 (1)	-0.0059 (9)	7 (1)
C(53)	0.232 (1)	0.888 (1)	-0.074 (1)	9 (1)
C(54)	0.138 (1)	0.867 (2)	-0.108 (1)	11 (2)
C(55)	0.093 (1)	0.801 (2)	-0.081 (1)	11 (3)
C(56)	0.142 (1)	0.751 (1)	-0.0130 (9)	8 (2)
C(61)	0.411 (1)	0.688 (1)	0.1179 (8)	5 (1)
C(62)	0.427 (1)	0.646 (1)	0.0522 (9)	7 (1)
C(63)	0.518 (1)	0.629 (1)	0.0533 (9)	9 (1)
C(64)	0.593 (1)	0.653 (1)	0.115 (1)	8 (1)
C(65)	0.579 (1)	0.695 (2)	0.179 (1)	10 (2)
C(66)	0.489 (1)	0.712 (1)	0.1808 (9)	9 (2)

Table 2. *Selected bond lengths* ( $\text{\AA}$ ) *and bond angles* ( $^\circ$ )

Tl–I	2.647 (1)	P(1)–C(21)	1.785 (6)
Tl–Br(1)	2.594 (1)	P(1)–C(31)	1.788 (7)
Tl–Br(2)	2.540 (1)	P(2)–O(2)	1.478 (5)
Tl–O(1)	2.426 (4)	P(2)–C(41)	1.786 (6)
Tl–O(2)	2.457 (5)	P(2)–C(51)	1.805 (7)
P(1)–O(1)	1.500 (4)	P(2)–C(61)	1.798 (6)
P(1)–C(11)	1.800 (6)		
I–Tl–Br(1)	121.39 (3)	O(1)–P(1)–C(11)	112.7 (3)
I–Tl–Br(2)	116.66 (2)	O(1)–P(1)–C(21)	110.5 (3)
I–Tl–O(1)	91.9 (1)	O(1)–P(1)–C(31)	111.9 (3)
I–Tl–O(2)	92.7 (1)	C(11)–P(1)–C(21)	106.9 (3)
Br(1)–Tl–Br(2)	121.93 (3)	C(11)–P(1)–C(31)	106.7 (3)
Br(1)–Tl–O(1)	87.8 (1)	C(21)–P(1)–C(31)	107.9 (3)
Br(1)–Tl–O(2)	89.0 (1)	O(2)–P(2)–C(41)	109.3 (3)
Br(2)–Tl–O(1)	89.1 (1)	O(2)–P(2)–C(51)	110.0 (3)
Br(2)–Tl–O(2)	89.7 (1)	O(2)–P(2)–C(61)	116.3 (3)
O(1)–Tl–O(2)	175.3 (2)	C(41)–P(2)–C(51)	107.5 (3)
Tl–O(1)–P(1)	150.8 (3)	C(41)–P(2)–C(61)	106.7 (3)
Tl–O(2)–P(2)	148.1 (3)	C(51)–P(2)–C(61)	106.7 (3)

\* Lists of anisotropic thermal parameters, positional parameters of the H atoms, bond distances and angles, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43000 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[2.594 (1), 2.540 (1) Å] are longer than those in [TlBr<sub>3</sub>(tppo)<sub>2</sub>] [2.515 (2), 2.503 (2), 2.497 (3) Å] but similar to that observed in [TlBrI<sub>2</sub>(tppo)<sub>2</sub>] [2.580 (1) Å]. This variation in bond distances is also observed for the Tl—I bond, with the bond length of 2.647 (1) Å shorter than those in [TlI<sub>3</sub>(3-CH<sub>3</sub>-C<sub>5</sub>H<sub>4</sub>NO)<sub>2</sub>] [2.700 (1) Å] (Bermejo, Castineiras, Gayoso, Hiller, Englert & Strähle, 1984) or in [TlBrI<sub>2</sub>(tppo)<sub>2</sub>] [2.685 (1), 2.667 (1) Å]. The Tl—O distances in the title compound [2.426 (4), 2.457 (5) Å] are longer than those in [TlBr<sub>3</sub>(tppo)<sub>2</sub>] [2.38 (2), 2.39 (2) Å]. These effects are attributed to distinct halide atoms in equatorial positions.

The geometry of the tppo ligand is very similar to that of the free ligand (Bandoli, Bortolazzo, Clemente, Croato & Panattoni, 1970).

We thank the Ministerio de Educación y Ciencia (Spain) for financial support (AC) and Dr Kanelopoulos for helpful discussion.

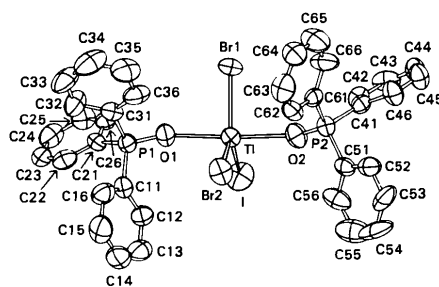


Fig. 1. View of the molecule with the labelling scheme used. Thermal ellipsoids at 80% probability level.

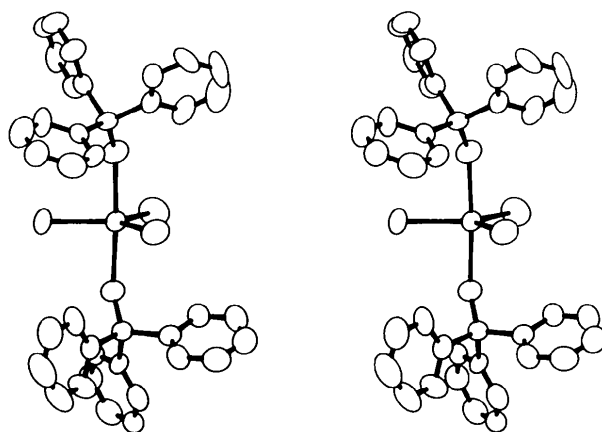


Fig. 2. Stereoscopic view of the molecule.

#### References

- B. A. FRENZ & ASSOCIATES INC. (1985). VAXSDP *Structure Determination Package*, version 2.2. College Station, Texas, and Enraf-Nonius, Delft.
- BANDOLI, G., BORTOLAZZO, G., CLEMENTE, D. A., CROATO, U. & PANATTONI, G. (1970). *J. Chem. Soc. A*, pp. 2778–2780.
- BERMEJO, M. R., CASTINEIRAS, A., GAYOSO, M., HILLER, W., ENGLERT, U. & STRÄHLE, J. (1984). *Z. Naturforsch. Teil B*, **39**, 1159–1161.
- CASTINEIRAS, A., HILLER, W., STRÄHLE, J., BERMEJO, M. R. & GAYOSO, M. (1985). *An. Quim.* In the press.
- CASTINEIRAS, A., HILLER, W., STRÄHLE, J., BERMEJO, M. R. & GAYOSO, M. (1986). *Inorg. Chem.* In the press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JEFFS, S. E., SMALL, R. W. H. & WORRALL, I. J. (1984). *Acta Cryst.* **C40**, 381–383.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

*Acta Cryst.* (1986). **C42**, 1291–1294

## Structure of an Antitumor Platinum(II) Compound *cis*-[PtCl<sub>2</sub>(Cyclobutylamine)(NH<sub>3</sub>)]

BY F. D. ROCHON AND ROBERT MELANSON

*Département de Chimie, Université du Québec à Montréal, CP 8888, succ. A, Montréal, Canada H3C 3P8*

(Received 16 September 1985; accepted 29 April 1986)

**Abstract.** *cis*-Ammine-dichloro(cyclobutylamine)-platinum(II), C<sub>4</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>Pt, *M<sub>r</sub>* = 354.15, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.730 (3), *b* = 9.944 (3), *c* = 10.082 (4) Å, β = 105.01 (2)°, *V* = 845.4 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.782, *D<sub>m</sub>* = 2.77 (2) Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 17.976 mm<sup>-1</sup>, *F*(000) = 648, *T* = 295 K, *R* = 0.057 for 1806 unique observed reflections. The coordination around the Pt atom is *cis* square planar, Pt—Cl 2.308 (4) and 2.312 (4) Å, Pt—N 2.053 (14)

and 2.067 (13) Å. Hydrogen bonding involving the NH<sub>3</sub> ligand plays an important role in stabilizing the crystal.

**Introduction.** Platinum amine complexes of the types *cis*-[PtCl<sub>2</sub>(*L*)<sub>2</sub>] and *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)(*L*)], with *L* = cyclic amine, have shown a better therapeutic index and a greater antitumor activity against several animal tumors than cisplatin, *cis*-Pt[Cl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] or non-cyclic