Fig. 2. A projection of the structure viewed along c. Dashed lines denote hydrogen bonds. Only the water H atoms are represented for reasons of clarity.

Table 3. Geometry of the hydrogen bonds

D	H	A	$D \cdots A$ (Å)	$D-H$ (Å)	$H \cdots A$ (Å)	$D-H \cdots A$ (°)
O_w	$H_w(1)$	O(2)	2·820 (4)	0·89 (6)	1·94 (5)	172 (4)
O_w	$H_w(2)$	O(4^i)	2·893 (4)	0·95 (5)	1·95 (5)	171 (5)

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

planarity within ± 0.065 (2) Å and that adjacent to the resorcinol ring within ± 0.076 (2) Å.

A quinoid character of the resorcinol ring, as expected from the ^{1}H NMR spectra, is indicated by the short C(31)—O(4) bond length of 1·254 (4) Å and four longer and two shorter C—C bond lengths with averages of 1·449 (20) and 1·350 (13) Å respectively.

The N—N bond length of 1·343 (3) Å is a little longer than the analogous value of 1·323 (3) Å for the par complex, indicating a weakening of the azo double-bond character in the tar complex. On the other hand, the two neighbouring C—N bond lengths in the tar complex are a little shorter than in the par complex, so that their sum remains nearly the same for both complexes within the limits of the estimated standard deviations.

The intramolecular geometry in the tetraphenyl-phosphonium ion does not show any unusual features. The phenyl rings are planar within ± 0.009 (4) Å. The angle between the mean planes through C(4),C(1),P, C(13),C(16) and C(10),C(7),P,C(19),C(22) is 86·0 (1)°. All C—H bond lengths fall within the range 0·88 (5) to 1·11 (4) Å.

The three-dimensional network of the structure (Fig. 2) is stabilized by the hydrogen bonds formed between crystal water molecules and basal oxo and quinoid resorcinol O atoms from different neighbouring complex anions. The geometry of the hydrogen bonding is given in Table 3.

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Structure of Tribromobis(triphenylphosphine oxide)thallium(III), [TlBr₃{OP(C₆H₅)₃}₂]

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Abstract. $M_r = 1000.7$, monoclinic, $P2_1/c$, $a = 14.85$ (1), $b = 14.60$ (1), $c = 17.37$ (2) Å, $\beta = 107.7$ (1)°, $Z = 4$, $D_x = 1.85$, $D_m = 1.712$ Mg m^{-3}, $V = 3587.1$ Å^3, λ(Mo $K\alpha$) = 0.7106 Å, $\mu = 7.7$ mm^{-1}, $F(000) = 1912$, room temperature, $R = 0.0542$, 2670 intensities. The unit cell contains discrete TlBr₃.2OPPh₃ molecules which have distorted trigonal-bipyramidal geometry.

Introduction. Halogen bridging is a feature of several five- and six-coordinate thallium(III) halide complexes and a number of dimeric molecules have now been characterized, e.g. [TlCl$_3$.1,10-phenanthroline]$_2$ (Baxter & Gafner, 1972); [R_2TlXOPPh$_3$]$_2$, $R = p$-HC$_6$F$_4$, C$_6$F$_5$; $X =$ Cl, Br (Henrick, Matthews, McPartlin, Deacon & Phillips, 1980). Other complexes which do not contain bridging halogen are also known, e.g. TlBr$_3$.1,4-dioxane (Jeffs, Small & Worrall, 1983). We are presently investigating factors affecting the extent of halide bridging in such complexes and here report the crystal structure of TlBr$_3$.2OPPh$_3$.

Experimental. Title compound prepared by adding the stoichiometric amount of triphenylphosphine oxide to an acetonitrile solution of thallium(III) bromide; on removal of the solvent needle crystals remained, and suitable ones were transferred to Lindemann tubes in a nitrogen-filled dry-box. Crystal data obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å); D_m measured by flotation in methylene bromide/benzene solutions. Intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation; layers $k = 0$–13 measured; $2\theta < 55°$; crystal size $0.31 \times 0.10 \times 0.03$ mm. Absorption corrections (maximum and minimum values 0.64, 0.18) and scaling of data carried out by the $SHELX76$ suite of programs (Sheldrick, 1976). 3907 reflections measured; after elimination of those for which $I < 3\sigma$ (I) there remained 2670 unique reflections. Standards, for each layer, measured every 10 reflections: variation 1%. The same programs were used for all the other calculations. Tl-atom positions, obtained from Patterson maps, were used to phase (F_o–F_c) maps to give the positions of the remaining atoms (apart from H). Unit weights; full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for Tl, Br and P, and isotropic U values for the remaining non-H atoms; convergence at $R = 0.054$; the phenyl rings were constrained as rigid regular hexagons with C—C distances of 1.395 Å. $(\Delta/\sigma)_{max} < 10^{-3}$. Maximum height in final $\Delta\rho$ map 2.09 e Å^{-3}. No correction for secondary extinction. Atomic scattering factors from Cromer & Mann (1968) and Cromer & Liberman (1970).

Discussion. Final coordinates and U_{eq} values for Tl, Br and P, and isotropic thermal parameters for C and O are given in Table 1.* The structure consists of discrete molecules of TlBr$_3$.2OPPh$_3$ (Fig. 1); the coordination around Tl is distorted trigonal bipyramidal with Br

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39078 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
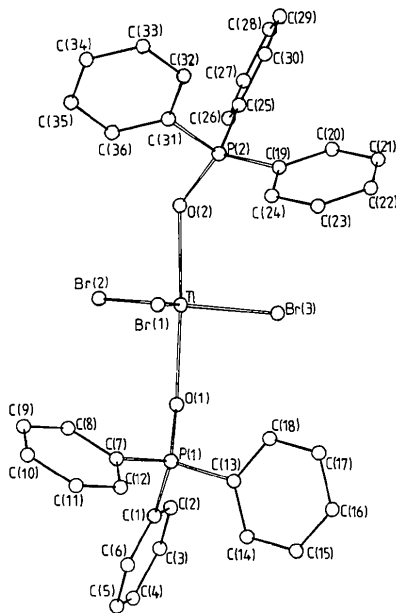
Table 1. *Fractional atomic coordinates, equivalent isotropic thermal parameters for thallium, bromine and phosphorus and isotropic thermal parameters for carbon and oxygen ($\times 10^4$)*

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

	x	y	z	U_{eq}/U (Å^2)
Tl	2172 (1)	352 (1)	1222 (1)	400
Br(1)	2318 (2)	349 (2)	−183 (1)	721
Br(2)	532 (2)	237 (2)	1327 (2)	813
Br(3)	3539 (3)	503 (3)	2480 (2)	1310
P(1)	2137 (4)	2901 (3)	774 (3)	411
P(2)	2962 (4)	−2106 (3)	1203 (3)	405
O(1)	2086 (10)	1980 (14)	1180 (9)	593 (53)
O(2)	2410 (12)	−1267 (13)	1304 (9)	682 (56)
C(1)	1621 (9)	3788 (8)	1193 (7)	428 (50)
C(2)	1604 (9)	3658 (8)	1984 (7)	382 (47)
C(3)	1224 (9)	4333 (8)	2363 (7)	527 (57)
C(4)	861 (9)	5137 (8)	1950 (7)	614 (62)
C(5)	878 (9)	5266 (8)	1159 (7)	603 (58)
C(6)	1258 (9)	4592 (8)	781 (7)	529 (53)
C(7)	1521 (9)	2853 (9)	−289 (6)	415 (49)
C(8)	683 (9)	2350 (9)	534 (6)	574 (59)
C(9)	158 (9)	2313 (9)	−1350 (6)	786 (74)
C(10)	471 (9)	2778 (9)	−1922 (6)	686 (68)
C(11)	1309 (9)	3282 (9)	−1667 (6)	729 (70)
C(12)	1834 (9)	3319 (9)	−861 (6)	566 (59)
C(13)	3319 (8)	3233 (10)	881 (8)	449 (52)
C(14)	3569 (8)	4154 (10)	878 (8)	744 (71)
C(15)	4501 (8)	4394 (10)	949 (8)	909 (86)
C(16)	5181 (8)	3714 (10)	1024 (8)	750 (72)
C(17)	4931 (8)	2793 (10)	1028 (8)	850 (80)
C(18)	4000 (8)	2553 (10)	956 (8)	711 (70)
C(19)	4147 (7)	−1877 (9)	1192 (8)	331 (44)
C(20)	4928 (7)	−2167 (9)	1820 (8)	685 (68)
C(21)	5840 (7)	−1992 (9)	1789 (8)	902 (84)
C(22)	5970 (7)	−1527 (9)	1129 (8)	683 (66)
C(23)	5188 (7)	−1238 (9)	500 (8)	677 (66)
C(24)	4276 (7)	−1413 (9)	532 (8)	607 (61)
C(25)	3031 (9)	−2900 (8)	2008 (7)	420 (50)
C(26)	2578 (9)	−2689 (8)	2582 (7)	503 (54)
C(27)	2616 (9)	−3301 (8)	3207 (7)	639 (64)
C(28)	3106 (9)	−4126 (8)	3259 (7)	632 (62)
C(29)	3558 (9)	−4337 (8)	2686 (7)	669 (67)
C(30)	3521 (9)	−3724 (8)	2060 (7)	520 (55)
C(31)	2375 (9)	−2685 (9)	269 (7)	470 (52)
C(32)	2815 (9)	−3381 (9)	−718 (7)	470 (52)
C(33)	2306 (9)	−3871 (9)	−718 (7)	729 (70)
C(34)	1357 (9)	−3664 (9)	−1099 (7)	918 (86)
C(35)	917 (9)	−2969 (9)	−796 (7)	855 (80)
C(36)	1426 (9)	−2479 (9)	−112 (7)	645 (65)

Table 2. *Bond distances (Å) and angles (°)*

Tl–Br(1)	2.515 (2)	Tl–Br(2)	2.503 (2)
Tl–Br(3)	2.497 (3)	Tl–O(1)	2.38 (2)
Tl–O(2)	2.39 (2)	P(1)–O(1)	1.53 (2)
P(2)–O(2)	1.51 (2)	P(1)–C(1)	1.77 (1)
P(1)–C(7)	1.80 (1)	P(1)–C(13)	1.77 (1)
P(2)–C(19)	1.80 (1)	P(2)–C(31)	1.80 (1)

Br(1)–Tl–Br(2)	116.4 (1)	O(2)–Tl–Br(1)	90.0 (4)
Br(1)–Tl–Br(3)	124.2 (1)	O(2)–Tl–Br(2)	93.4 (4)
Br(3)–Tl–Br(2)	119.4 (1)	O(2)–Tl–Br(3)	88.2 (4)
O(1)–Tl–Br(1)	89.5 (3)	O(2)–Tl–O(1)	174.8 (5)
O(1)–Tl–Br(2)	91.5 (4)	Tl–O(1)–P(1)	152 (1)
O(1)–Tl–Br(3)	87.7 (4)	Tl–O(2)–P(2)	150 (1)

The C—C bond distances were constrained at 1.395 Å using $AFIX$ (local program).

Table 3. *Torsion angles (°)*

P(1)–O(1)–Tl–Br(1)	−6 (1)	P(1)–O(1)–Tl–Br(2)	−123 (1)
P(1)–O(1)–Tl–Br(3)	118 (1)	P(2)–O(2)–Tl–Br(1)	49 (1)
P(2)–O(2)–Tl–Br(2)	166 (1)	P(2)–O(2)–Tl–Br(3)	−75 (1)
P(1)–O(1)–O(2)–P(2)	40 (2)		

Fig. 1. The structure of TlBr$_3$.2OPPh$_3$.

atoms occupying equatorial positions and O atoms axial. Within the limits of error (0·05 Å) the Tl and Br atoms are coplanar. Bond distances and angles are given in Table 2; the Tl—Br distances are not significantly different [av. 2·505 (2) Å] and compare with those observed in other five-coordinate thallium(III) bromide complexes, e.g. av. 2·505 (2) Å in TlBr$_3$.dioxane (Jeffs, Small & Worrall, 1983), av. 2·536 (9) Å in TlBr$_3$.2pyridine (Jeffs, Small & Worrall, 1984). The Tl—O distances 2·38 (2) and 2·39 (2) Å are similar to those observed in trichlorobis(4-pyridine-carbonitrile 1-oxide-O)thallium, 2·36 (1), 2·40 (1) Å

(Gutiérrez-Puebla, Vegas & García-Blanco, 1980) and in [(p-HC$_6$H$_4$)$_2$TlCl(OPPh$_3$)]$_2$, 2·391 (9) Å (Henrick et al., 1980) but shorter than in TlBr$_3$.dioxane, 2·54 (1) Å. This difference may reflect the ligand strengths.

The relatively large U_{ij} of Br atoms may indicate disorder.

Angular distortions are observed both in the equatorial plane (116·4–124·2°) and along the axial direction of the trigonal bipyramid [O(1)–Tl–O(2) 174·8°]. Torsion angles (Table 3) show that P(1) and P(2) lie in a plane between Br(1) and Br(3) and this may explain the large angle. The P—O—Tl angles, 150, 152°, are smaller than in [(p-HC$_6$F$_4$)$_2$TlCl(OPPh$_3$)]$_2$, 168° (Henrick et al., 1980). However, large variations in M—O—P bond angles are well known, and it has been concluded that they are easily deformed and may be considerably affected by crystal-packing effects (Henrick et al., 1980).

Centrosymmetrically related molecules are well separated, the closest distance involving Tl; Tl—Br(2′) = 5·06 Å is too large to suggest a bridging role for the Br.

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Structure of s-fac-[Bis(3-aminopropyl)amine](diethylenetriamine)cobalt(III) Dithionate Perchlorate Monohydrate, [Co(C$_4$H$_{13}$N$_3$)(C$_6$H$_{17}$N$_3$)]$^{3+}$.S$_2$O$_6^{2-}$.ClO$_4^-$.H$_2$O, and Comparison with the Geometry Calculated by Molecular Mechanics

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Abstract. $M_r = 570·9$, orthorhombic, $Pc2_1b$, $a = 9·592$ (3), $b = 13·454$ (3), $c = 16·748$ (9) Å, $Z = 4$, $U = 2161·3$ Å^3, $D_m = 1·77$ (2), $D_x = 1·754$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 1·115$ mm^{-1}, $F(000) =$ 1192, $T = 295$ K, $R = 0·037$ on 1058 observed [$I > 2·5\sigma(I)$] reflections. The two tridentate ligands coordinate to Co giving an s-fac topology. The two six-membered chelate rings adopt chair and flattened-