Table 2. *Principal distances* (Å) *and angles* (°) *in the tfa groups*

O(1)–C(1)	1·20 (2)	O(3)–C(3)	1·25 (2)	O(5)–C(5)	1·26 (2)	O(7)–C(7)	1·19 (3)
O(2)–C(1)	1·28 (2)	O(4)–C(3)	1·20 (2)	O(6)–C(5)	1·25 (3)	O(8)–C(7)	1·19 (3)
C(1)–C(2)	1·55 (2)	C(3)–C(4)	1·55 (2)	C(5)–C(6)	1·50 (2)	C(7)–C(8)	1·55 (2)
O(1)–C(1)–O(2)	131 (1)	O(3)–C(3)–O(4)	131 (1)	O(5)–C(5)–O(6)	131 (2)	O(7)–C(7)–O(8)	132 (2)
O(1)–C(1)–C(2)	120 (1)	O(3)–C(3)–C(4)	114 (1)	O(5)–C(5)–C(6)	114 (1)	O(7)–C(7)–C(8)	114 (1)
O(2)–C(1)–C(2)	109 (1)	O(4)–C(3)–C(4)	115 (1)	O(6)–C(5)–C(6)	115 (1)	O(8)–C(7)–C(8)	114 (2)

to TPP; O(5) of a third monodentate tfa and finally the O(7) and O(8) of a bidentate tfa group, giving a polyhedron described as an irregular pentagonal bipyramid (Fig. 2*a*). The distances of these O and U atoms to the best least-squares equatorial plane are: +0·006 (U), −0·10 [O(2)], +0·07 [O(3)], −0·05 [O(8)], −0·03 [O(7)], and +0·04 Å [O(5)]. The uranyl bonds are perpendicular to the equatorial plane.

The interatomic distances in the two 'protonated tfa' groups are close to those of trifluoroacetic acid (Nahringbauer, Lundgren & Andersen, 1979). The H atoms of these molecules were not located. The two C—O distances in the third unidentate tfa group are not differentiated and the distance C(5)—C(6) is a little shorter than normal. In contrast, in the bidentate tfa group, the distance C(7)—C(8) is normal but the C—O distances are rather short. The trifluoromethyl groups occupy many positions. The mean distance C—F is 1·33 Å and the F—C—F angles take values between 106 and 113° for all positions. In addition, slightly high thermal parameters are found for O(6), the non-bonded O of the third monodentate tfa, and C(73) of bidentate tfa. The principal distances and angles of the tfa groups are summarized in Table 2.

From Fig. 2(*b*) and values of the angles in the TPP molecule it can be seen that the TPP in this crystal has very similar distances and angles to those of free tetragonal and triclinic TPP within the limits imposed by the accuracy (Silvers & Tulinsky, 1967; Hamor, Hamor & Hoard, 1963). A closer examination of the distribution and deviations from planarity of TPP reveals that TPP has approximate molecular symmetry, as required in tetragonal TPP (some deviations are indicated in Table 3).

Table 3. *Deviations* (Å) *of atoms from the least-squares plane of the inner atoms in the TPP molecule*

N(1)	+0·08 (2)	N(3)	+0·09 (3)
C(12)	−0·22 (2)	C(22)	−0·23 (2)
C(13)	+0·04 (3)	C(23)	+0·06 (2)
C(14)	+0·30 (2)	C(24)	+0·29 (2)
N(2)	−0·04 (2)	N(4)	−0·11 (2)
C(17)	+0·22 (2)	C(27)	+0·26 (3)
C(18)	−0·07 (3)	C(28)	−0·06 (2)
C(19)	−0·32 (2)	C(9)	−0·32 (2)

The greatest difference between them is the tilt of the pyrrole and phenyl rings. The four pyrrole rings are planar [standard deviations for the distances to the best least-squares pyrrole planes: 0·003, 0·017, 0·006 and 0·003 Å for N(1), N(2), N(3) and N(4) pyrrole rings respectively] and are inclined 36, 24, 28 and 31° to the best plane through the four N atoms. Substituent aromatic rings are at 35, 35, 30 and 30° to this plane. The two inner-ring porphyrin H atoms are considered attached to the four central N atoms with an occupancy factor of one-half. This seems reasonable since the intramolecular differences in the pyrrole rings are small and also in view of the equivalent role of the N atoms in the crystal packing. This would imply rapid interconversion of N—H tautomers.

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Acta Cryst. (1983). C**39**, 1628–1630

The Structure of *catena*-Tribromo-μ-(1,4-dioxane-*O*,*O'*)-thallium(III), [$TlBr_3(C_4H_8O_2)$]

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(*Received* 22 *June* 1983; *accepted* 22 *August* 1983)

Abstract. $M_r = 532·1$, monoclinic, $C2/c$, $a = 11·56$ (1), $b = 6·966$ (5), $c = 15·50$ (2) Å, $\beta = 122·3$ (1)°, $V = 1054·8$ Å^3, $Z = 4$, $D_x = 3·35$, $D_m = 3·288$ Mg m^{-3}, $\mu = 25·9$ mm^{-1}, $F(000) = 936$, room temperature. The structure has been solved from 1110 diffractometer intensities with Mo $K\alpha$ radiation ($\lambda = 0·7106$ Å) and

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refined by full-matrix least squares to $R = 0{\cdot}051$. The crystal structure consists of distorted planar $TlBr_3$ units bridged by dioxane chairs to form chains parallel to the *c* axis. The molecule has twofold symmetry with Tl and one Br lying on the axis. The geometry around five-coordinate thallium is trigonal bipyramidal.

Introduction. The thallium(III) halides combine with a variety of ligands to form coordination compounds which have a range of stoichiometries 1–3 (Lee, 1971). Although there have been spectroscopic studies on some of these complexes (Walton, 1968) few definitive crystal structures have been determined. Recently the crystal structures of the following have been reported: $TlX_3.4H_2O$ (X = Cl, Br) (Glaser, 1979), $TlCl_3$.(1,10-phenanthroline) (Baxter & Gafner, 1972) and $TlCl_3$.2(4-pyridinecarbonitrile 1-oxide-*O*) (Gutiérrez-Puebla, Vegas & García-Blanco, 1980).

As part of a study into the stereochemistry of thallium we report the crystal structure of $TlBr_3$.dioxane in this paper. Dioxane is able to act as a monodentate ligand (Beamish, Small & Worrall, 1979) or bridging bidentate ligand towards Group III Lewis acids (Boardman, Small & Worrall, 1983) so that a number of geometries are possible.

Experimental. $TlBr_3$.dioxane was prepared by adding excess dry dioxane to thallium(III) bromide in acetonitrile at ambient temperature. Upon concentrating the solution by removing part of the dioxane on a vacuum line, needle crystals formed and these were transferred to Lindemann tubes in a nitrogen-filled dry-box.

Crystal data from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å), space group *Cc* or *C*2/*c* from systematic absences. Initially the former was used but showed no advantage over *C*2/*c* which was therefore adopted. D_m by flotation in methylene diiodide/benzene solutions, Stoe STADI-2 two-circle automatic diffractometer, graphite-monochromatized Mo K radiation, layers l= 0–16 measured, $2\theta < 55°$, crystal 0·045 × 0·059 × 0·610 mm, absorption corrections (maximum and minimum values 0·16, 0·05) and scaling of data carried out by *SHELX* (Sheldrick, 1976), 1236 reflections measured, 1110 unique reflections with $I > 3\sigma(I)$; standards measured every 10 reflections showed a variation of 1%. The same programs were used for all the other calculations. Thallium coordinates from Patterson maps, the positions of the remaining atoms (apart from H) from difference maps. Unit weights, full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for Tl and Br, and isotropic U values for the remaining non-H atoms gave $R = 0{\cdot}051$; $(\Delta/\sigma)_{\max} = 0{\cdot}212$, final $\Delta\rho$ excursions $< 1{\cdot}04$ e Å^{-3}; no correction for secondary extinction, atomic scattering factors from Cromer & Mann (1968) and Cromer & Liberman (1970).

Table 1. *Fractional atomic coordinates, equivalent isotropic thermal parameters for thallium and bromine and isotropic thermal parameters for oxygen and carbon* (×10^4)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}/U$ (Å^2)
Tl	0	652 (1)	2500	345 (13)
Br(1)	0	4238 (4)	2500	673 (25)
Br(2)	2253 (2)	−1060 (3)	3513 (1)	550 (17)
O(1)	200 (10)	452 (14)	947 (9)	333 (28)
C(1)	906 (17)	−1329 (29)	−8 (13)	530 (41)
C(2)	472 (18)	−1444 (27)	714 (14)	552 (43)

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

Tl–Br(1)	2·498 (3)	Tl–Br(2)	2·509 (2)
Tl–O(1)	2·543 (13)	C(2)–O(1)	1·45 (2)
C(1′)–O(1)	1·46 (2)	C(2)–C(1)	1·45 (2)
Br(2)–Tl–Br(2″)	123·2 (1)	C(1′)–O(1)–Tl	116·5 (7)
Br(1)–Tl–Br(2)	118·4 (1)	C(2)–O(1)–Tl	115 (1)
O(1)–Tl–Br(1)	93·1 (2)	O(1)–C(2)–C(1)	111 (1)
O(1)–Tl–Br(2)	88·7 (2)	C(2)–O(1)–C(1′)	109 (1)
O(1)–Tl–O(1″)	173·7 (4)	C(2)–C(1)–O(1′)	108 (1)

Table 3. *Torsion angles* (°)

C(2)–O(1)–Tl–Br(1)	170 (1)	C(2)–O(1)–Tl–Br(2)	52 (1)
C(2)–O(1)–Tl–Br(2″)	−72 (2)	C(1′)–O(1)–Tl–Br(1)	−60 (1)
C(1′)–O(1)–Tl–Br(2)	−1 (1)	C(1′)–O(1)–Tl–Br(2″)	58 (1)

Symmetry code: (′) $-x, -y, -z$; (″) $-x, y, \tfrac{1}{2}-z$.

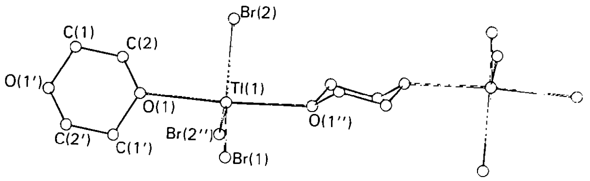

Fig. 1. The structure of $TlBr_3$.dioxane.

Discussion. Final coordinates and equivalent values ($U_{\rm eq}$) for Tl and Br, and isotropic thermal parameters for C and O are given in Table 1.* The crystal structure determination shows that $TlBr_3$.dioxane consists of distorted trigonal-planar $TlBr_3$ units bridged by dioxane chairs to form infinite chains parallel to the *c* axis. Trigonal bipyramidal geometry is observed around Tl (Fig. 1) with Br atoms in equatorial positions and O atoms located axially. The structure is similar to that of $AlCl_3$.2dioxane (Boardman, Small & Worrall, 1983).

There are only three reported crystal structures of complexes of the thallium(III) halides with trigonal bipyramidal geometry: $TlX_3.2H_2O$ (X=Cl,Br) (Glaser,

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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 38815 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1979) and $TlCl_3.2$(4-pyridinecarbonitrile 1-oxide-*O*) (Gutiérrez-Puebla, Vegas & Garcia-Blanco, 1980) although other complexes are known which contain five-coordinate thallium, *e.g.* $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ (Henrick, Matthews & McPartlin, 1980).

Bond distances and angles in $TlBr_3$.dioxane are given in Table 2. The Tl—Br distances are similar to those observed in $TlBr_3.2H_2O$ [Tl—Br=2·515 (3) Å, Glaser, 1979]. The Tl—O distance is similar to that found in the hydrate (2·59, 2·52 Å). It is greater than expected and significantly greater than in trichlorobis(4-pyridinecarbonitrile 1-oxide-*O*)thallium [2·36 (1), 2·40 (1) Å (Gutiérrez-Puebla *et al.*, 1980)] and tribromobis(triphenylphosphine oxide)thallium(III) [2·38 (2) Å (Jeffs, Small & Worrall, 1983)]. This may reflect the weak donor strength of the ligand dioxane. Distortions from trigonal bipyramidal geometry are to be expected for complexes with the axial positions occupied by low-symmetry ligands such as dioxane. These are indeed observed in the equatorial bond angles, Br(1)—Tl—Br(2), 118·4°, and Br(2)—Tl—Br(2''), 123·2°. The latter angle would be expected to be greater since torsion angles (Table 3) show that two carbon atoms C(2) are between Br(2) and Br(2'') (above and below the equatorial plane) whilst only one [C(1)] lies between Br(1), Br(2) and Br(1), Br(2''). These angular deviations are less than those observed in the analogous $AlCl_3$.2dioxane complex which contains an additional solvate dioxane molecule in the lattice. It has been proposed that interactions between dioxane solvate and bound dioxane are a contributing factor to these larger deviations (Boardman *et al.*, 1983).

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Acta Cryst. (1983). C**39**, 1630–1632

Structure of Tris(ethylenediamine)zinc(II) Chloride Dihydrate, $[Zn(C_2H_8N_2)_3]Cl_2.2H_2O$

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(*Received* 18 *March* 1983; *accepted* 28 *July* 1983)

Abstract. $M_r = 352·61$, monoclinic, $C2/c$, $a = 8·793$ (2), $b = 13·961$ (4), $c = 12·953$ (3) Å, $\beta = 93·37$ (2)°, $V = 1587$ Å^3, $Z = 4$, $D_x = 1·474$ g cm^{-3}, $\lambda = 0·71069$ Å, $\mu = 18·05$ cm^{-1}, $F(000) = 736$, room temperature. The final R value for 1136 unique reflections is 0·074. An approximately octahedral coordination around Zn is observed. The site symmetry for Zn is 2 (C_2) and not 32 (D_3) as concluded through Raman and IR spectral studies. One of the chloride ions appears to be disordered. The site symmetry 2 of the metal atom and the centrosymmetric space group favours the presence of a racemic mixture of $\Lambda\lambda\lambda\lambda$ and $\Delta\lambda\lambda\lambda$ configurations.

Introduction. Tris(ethylenediamine) complexes are of interest because of the sixfold octahedral coordination around the metal atom. Krishnan & Plane (1966) have reported from Raman and IR spectral studies that $Zn(en_3)Cl_2.2H_2O$ has D_3 symmetry. Paramagnetic complexes doped in a diamagnetic host lattice, having D_3 symmetry, are expected to exhibit the Jahn–Teller effect in an EPR experiment. Hence, we expected this complex to form an ideal host lattice for studying the Jahn–Teller effect.

The temperature-dependent EPR spectra of Cu^{2+} in this host lattice show the presence of dynamic distortions (Shakuntala, 1980). The EPR spectra of Mn^{2+} in the same complex show several sites at room temperature whereas the Cu^{2+} spectra show only one site. The

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0108-2701/83/121630-03$01.50