Fig. 2. A $Pb_2$ pair, together with coordination shells of oxygen atoms. Thermal ellipsoids enclose 50% probability (Johnson, 1976).

addition of ionic radii (Shannon, 1976)]. Many of the Pb—O distances are short, indicating some degree of covalency. They are similar to those found in the β form of lead styphnate.

Fig. 3* shows the packing arrangement within a unit cell. The styphnate ions lie in approximately parallel planes linked by Pb atoms. The water of crystallization [O(3)] is coordinated to the metal and is also H-bonded to the anion [O(3)···O(2) is 2·718 (9) Å].

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* This figure has been deposited, see deposition footnote.

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# Structure of Tribromobis(pyridine)thallium(III), TlBr₃(C₅H₅N)₂

BY S. E. JEFFS, R. W. H. SMALL AND I. J. WORRALL

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**Abstract.** $M_r = 602\cdot3$, monoclinic, $P2_1$, $a = 8\cdot991$ (5), $b = 21\cdot59$ (2), $c = 8\cdot393$ (5) Å, $\beta = 117\cdot8$ (1)°, $V = 1441\cdot2$ Å$^3$, $Z = 4$, $D_x = 2\cdot77$, $D_m = 2\cdot68$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7106 Å, $\mu = 18\cdot9$ mm$^{-1}$, $F(000) = 1080$, room temperature. Final $R = 0\cdot073$ for 2184 unique observed reflections. The unit cell contains two crystallographically independent distorted trigonal-bipyramidal molecules which have similar geometrical parameters within the limits of experimental error. The two molecules differ in respect to the orientation of the pyridine ligands which occupy axial positions. A weak interaction between the two independent molecules accounts for the large distortions observed in the Br—Tl—Br equatorial bond angles (113·0–131·1°).

**Introduction.** Complexes of the Group III halides of stoichiometry $MX_3.2L$ are known for all the metallic

elements of the group and whilst many of these have trigonal-bipyramidal geometry around the metal, e.g. $AlCl_3.2$(dioxane) (Boardman, Small & Worrall, 1983), $AlCl_3.2NH(CH_3)_2$ (Lobovski, Korobov & Semenko, 1978), $InCl_3.2PPh_3$ (Veidis & Palenik, 1969), $TlBr_3.2Ph_3PO$ (Jeffs, Small & Worrall, 1984b), there are exceptions, e.g. $GaCl_3.2C_5H_5N$ (Sinclair, Small & Worrall, 1981) which is ionic, i.e. $[GaCl_2Py_4]^+.GaCl_4^-$. $TlX_3.2$(pyridine) complexes may also be exceptional since on the basis of spectroscopic data it has been proposed that these are either halogen-bridged dimers or polymers containing six-coordinate thallium (Walton, 1968). In this paper we report the crystal structure of $TlBr_3.2$(pyridine).

**Experimental.** Title compound prepared by adding stoichiometric amount of pyridine to an acetonitrile

solution of thallium(III) bromide; on removal of solvent needle-shaped crystals remained, and suitable crystals were transferred to Lindemann-glass tubes in a nitrogen-filled dry box; crystal dimensions $0.14 \times 0.04 \times 0.38$ mm. Crystal data obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). $D_m$ measured by flotation in methylene iodide/benzene solutions. Intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K$ radiation, $h$ $-11-9$, $k$ $-25-25$, $l$ $0-8$, $2\theta < 55°$. Absorption corrections (max. 0.23, min. 0.02) and scaling of data carried out by SHELX76 (Sheldrick, 1976). 4005 reflections measured, 2184 unique with $I > 3\sigma(I)$. Standards measured every 10 reflections: variation 1%. Same programs used for all other calculations. Tl-atom positions obtained from Patterson maps used to phase $(F_o-F_c)$ maps to give positions of remaining atoms (apart from H). Using 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 remaining non-H atoms carried out until convergence reached at $R = 0.073$. $(\Delta/\sigma)_{max} = 0.269$. Max. height in final difference Fourier map $4.09$ e Å$^{-3}$; this is associated mainly with Tl positions. No correction applied for secondary extinction. As the space group is without a centre of symmetry, the enantiomorphous structure was also refined but no significant changes were observed in either $R$ or structural parameters. Atomic scattering factors those of Cromer & Mann (1968) and Cromer & Liberman (1970).

**Discussion.** Final coordinates and isotropic thermal parameters are given in Table 1.* The crystal structure consists of two crystallographically independent discrete molecules of TlBr$_3$.2(pyridine) with similar dimensions (Table 2). The molecules have a distorted trigonal-bipyramidal structure with Br atoms occupying equatorial sites and pyridine ligands axial. Within the limits of error (0.05 Å) the Tl and Br of both molecules lie in the same plane which to within 1° is parallel to (100). The two TlBr$_3$ groups which show similar distortions from trigonal symmetry, with one large Br—Tl—Br angle (131°) and two small ones, are related by an approximate twofold axis such that Br(2) bisects the wider angle at Tl(2) and Br(4) bisects the wider angle at Tl(1). Since the direction [101] is indistinguishable from the perpendicular to (100) an explanation is provided of the marked pseudo-orthorhombic symmetry encountered during the early stages of the

*Lists of structure factors, anisotropic thermal parameters and angles between mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38896 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

investigation. The pseudo symmetry does not apply to the pyridine ligands; in both molecules the two pyridine rings are twisted slightly relative to each other, but to a first approximation the mean plane of these molecules in molecule (1) bisects the wider Br—Tl—Br angle while in the other molecule the mean plane of the pyridine rings is approximately perpendicular to the bisector of the wider Br—Tl—Br angle. The Tl—Br distances compare with those observed in other five-coordinate thallium(III) bromide complexes, e.g. TlBr$_3$.dioxane (Jeffs, Small & Worrall, 1984a) and in TlBr$_3$.4H$_2$O (Glaser,

Table 1. *Fractional atomic coordinates* ($\times 10^4$), *equivalent isotropic thermal parameters* ($\times 10^4$) *for Tl and Br and isotropic thermal parameters* ($\times 10^3$) *for C and N*

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

|        | $x$        | $y$       | $z$        | $U_{eq}/U(\text{Å}^2)$ |
|--------|-----------|-----------|-----------|------------|
| Tl(1)  | 7532 (3)  | 5000†     | 9979 (3)  | 418        |
| Tl(2)  | 7586 (3)  | 2539 (1)  | 3216 (3)  | 377        |
| Br(1)  | 7445 (10) | 5742 (5)  | 7589 (10) | 716        |
| Br(2)  | 7606 (9)  | 3874 (5)  | 9240 (14) | 935        |
| Br(3)  | 7564 (8)  | 5513 (4)  | 2690 (10) | 569        |
| Br(4)  | 7533 (10) | 3690 (4)  | 3904 (13) | 848        |
| Br(5)  | 7584 (9)  | 1790 (4)  | 5526 (9)  | 556        |
| Br(6)  | 7733 (8)  | 2004 (4)  | 618 (10)  | 573        |
| N(1)   | 4481 (32) | 4947 (19) | 8690 (47) | 53 (13)    |
| N(2)   | 556 (31)  | 5030 (18) | 1666 (44) | 42 (11)    |
| N(3)   | 4529 (31) | 2607 (20) | 1571 (46) | 37 (10)    |
| N(4)   | 693 (31)  | 2568 (20) | 4778 (45) | 40 (11)    |
| C(1)   | 3802 (32) | 4456 (19) | 9219 (47) | 46 (15)    |
| C(2)   | 3421 (32) | 5383 (19) | 7456 (47) | 48 (15)    |
| C(3)   | 2063 (32) | 4401 (19) | 8514 (47) | 76 (22)    |
| C(4)   | 1682 (32) | 5328 (19) | 6752 (47) | 54 (17)    |
| C(5)   | 1003 (32) | 4837 (19) | 7281 (47) | 63 (19)    |
| C(6)   | 1346 (31) | 4543 (18) | 2857 (44) | 37 (13)    |
| C(7)   | 1516 (31) | 5499 (18) | 1451 (44) | 50 (16)    |
| C(8)   | 3096 (31) | 4525 (18) | 3834 (44) | 97 (28)    |
| C(9)   | 3266 (31) | 5480 (18) | 2428 (44) | 60 (20)    |
| C(10)  | 4056 (31) | 4993 (18) | 3619 (44) | 98 (26)    |
| C(11)  | 3782 (31) | 2142 (20) | 285 (46)  | 87 (24)    |
| C(12)  | 3527 (31) | 3030 (20) | 1893 (46) | 109 (31)   |
| C(13)  | 1779 (31) | 2989 (20) | 928 (46)  | 53 (16)    |
| C(14)  | 2034 (31) | 2101 (20) | −679 (46) | 81 (23)    |
| C(15)  | 1033 (31) | 2524 (20) | −358 (46) | 42 (13)    |
| C(16)  | 1540 (31) | 2057 (20) | 4575 (46) | 66 (20)    |
| C(17)  | 1596 (31) | 3086 (20) | 5730 (45) | 73 (21)    |
| C(18)  | 3289 (31) | 2064 (20) | 5325 (45) | 112 (36)   |
| C(19)  | 3345 (31) | 3094 (20) | 6479 (45) | 55 (16)    |
| C(20)  | 4192 (31) | 2583 (20) | 6276 (45) | 57 (16)    |

† Constrained.

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

| Molecule (1) |            | Molecule (2) |            |
|--------------|-----------|--------------|-----------|
| Tl(1)—Br(1)  | 2.540 (9) | Tl(2)—Br(4)  | 2.557 (9) |
| Tl(1)—Br(2)  | 2.518 (10)| Tl(2)—Br(5)  | 2.524 (8) |
| Tl(1)—Br(3)  | 2.519 (9) | Tl(2)—Br(6)  | 2.525 (9) |
| Tl(1)—N(1)   | 2.44 (2)  | Tl(2)—N(3)   | 2.44 (2)  |
| Tl(1)—N(2)   | 2.41 (2)  | Tl(2)—N(4)   | 2.47 (2)  |
| Br(2)—Tl(1)—Br(1) | 114.2 (4) | Br(5)—Tl(2)—Br(6) | 112.9 (3) |
| Br(3)—Tl(1)—Br(2) | 131.1 (4) | Br(4)—Tl(2)—Br(6) | 130.8 (3) |
| Br(3)—Tl(1)—Br(1) | 114.7 (3) | Br(4)—Tl(2)—Br(5) | 116.2 (3) |
| N(1)—Tl(1)—Br(1)  | 93.8 (9)  | N(3)—Tl(2)—Br(4)  | 86 (1)    |
| N(1)—Tl(1)—Br(2)  | 90 (1)    | N(3)—Tl(2)—Br(5)  | 93.9 (9)  |
| N(1)—Tl(1)—Br(3)  | 87.6 (9)  | N(3)—Tl(2)—Br(6)  | 92.2 (9)  |
| N(2)—Tl(1)—Br(1)  | 93.3 (8)  | N(4)—Tl(2)—Br(4)  | 89 (1)    |
| N(2)—Tl(1)—Br(2)  | 91 (1)    | N(4)—Tl(2)—Br(5)  | 90.8 (9)  |
| N(2)—Tl(1)—Br(3)  | 85.6 (9)  | N(4)—Tl(2)—Br(6)  | 88.2 (9)  |
| N(1)—Tl(1)—N(2)   | 172 (1)   | N(3)—Tl(2)—N(4)   | 175 (1)   |

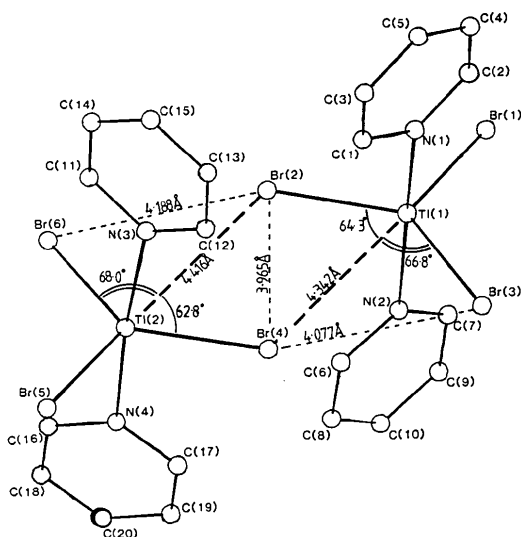C—C and C—N bond lengths were constrained at 1.395 Å using the in-house program AFIX.

Fig. 1. Structure of TlBr₃.2(pyridine) showing intermolecular distances and angles (e.s.d.'s ~0·01 Å, 0·4°).

five-coordinate monomers, *e.g.* TlBr₃.dioxane, and six-coordinate halogen-bridged dimers, *e.g.* TlCl₃.-(1,10-phenanthroline). Stronger bridging bonds would be expected in TlCl₃.2(pyridine) since the more electronegative Cl will enhance the Lewis acid strength of thallium and favour dimer formation. Thallium compounds involving strongly electron-withdrawing groups, but with shorter halogen-bridging distances have already been reported, *e.g.* in five-coordinate $[(p\text{-}HC_6F_4)_2TlX(OPPh_3)]_2$ (Henrick, McPartlin, Matthews, Deacon & Phillips, 1980) and in the four-coordinate halides $(p\text{-}HC_6F_4)_2TlX$ (Deacon, Phillips, Henrick & McPartlin, 1979) ($X$=Cl, Br).

1979) which are trigonal bipyramidal. The Tl—N distances [av. 2·44 (2) Å] compare with average values 2·364 (8) Å in TlCl₃.(1,10-phenanthroline) (Baxter & Gafner, 1972) and 2·43 (2) Å in TlCl₃.3(pyridine) (Jeffs, Small & Worrall, 1984c). The large distortions in the equatorial Br—Tl—Br angles (112·9–131·1°) and the planarity of all eight heavy atoms indicate a weak but significant interaction between Br and Tl atoms on pairs of adjacent molecules (Fig. 1).

It should be noted that the separation of the bridging Br atoms, 3·97 Å, is the van der Waals value; closer approach of the bridged Tl and Br in adjacent molecules would either shorten this distance or increase the distortion of the Br—Tl—Br angle. The compound may be regarded as being intermediate between

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# The Structure of Bis[2-amino-2-hydroxymethyl-1,3-propanediolato(1—)-O,N]copper(II)—Sodium Perchlorate Monohydrate, [Cu(C₄H₁₀NO₃)₂].NaClO₄.H₂O*

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**Abstract.** $M_r = 444·27$, monoclinic, $C2/c$, $a = 14·2872\ (6)$, $b = 10·9454\ (4)$, $c = 11·1921\ (5)$ Å, $\beta = 96·290\ (3)°$, $Z = 4$, $V = 1739·6\ (6)$ Å³, $D_x = 1·697\ (1)$, $D_m = 1·70\ (1)$ Mg m⁻³, $\lambda(\text{Mo }K\alpha) = 0·71073$ Å, $\mu(\text{Mo }K\alpha) = 1·54$ mm⁻¹, $F(000) = 916$, $T = 293$ K. $R = 0·044$ for 2826 reflections. The structure consists of uncharged $\text{Cu[NH}_2\text{C(CH}_2\text{O)-(CH}_2\text{OH})_2]_2$ complexes, Na⁺, ClO₄⁻ and water. The Cu

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* Metal Complexes with Mixed Ligands. 24.