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Structure of Tribromotris(pyridine)thallium(III), [TlBr₃(C₅H₅N)₃]

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Abstract. $M_r = 681\cdot4$, orthorhombic, $P2_12_12_1$, $a = 13\cdot39$ (1), $b = 15\cdot60$ (2), $c = 8\cdot840$ (5) Å, $V = 1846\cdot5$ Å³, $Z = 4$, $D_x = 2\cdot450$, $D_m = 2\cdot56$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot7106$ Å, $\mu = 1\cdot48$ mm⁻¹, $F(000) = 1248$, room temperature. Final $R = 0\cdot050$ for 2064 unique observed reflections. The crystal structure consists of neutral molecules of TlBr₃(C₅H₅N)₃; the configuration around the Tl is a distorted octahedron with *mer* geometry. The *trans* bonds show deviations from linearity within a range of 7–10°; intermolecular effects involving the pyridines are considered to be important in attributing the deviations of the N from regular octahedral sites.

Introduction. The Group III halides InBr₃, InCl₃ and TlCl₃ react with excess pyridine to form complexes of stoichiometry $MX_3.4C_5H_5N$ (Small & Worrall, 1982; Jeffs, Small & Worrall, 1984c) which contain $MX_3.3C_5H_5N$ molecules with *mer* geometry and an additional pyridine solvate molecule. Under similar conditions TlBr₃ forms only the 3:1 complex. For MX_3 octahedral complexes there are two possible isomers and we have determined the crystal structure of the title compound to see if the other isomer (*fac*) might occur in the absence of the extra solvate molecule.

Experimental. Title compound prepared by adding excess dry pyridine to a solution of Tlᴵᴵᴵ bromide in acetonitrile. Suitable crystals obtained by recrystallizing from pyridine were transferred to Lindemann tubes in a nitrogen-filled dry box. Crystal data obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å); D_m measured by flotation in benzene/methylene dibromide solutions. Intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation; layers $l = 0$–9 measured; $2\theta < 50°$; crystal size $0\cdot19 \times 0\cdot18 \times 0\cdot40$ mm. Absorption corrections (max., min. values $0\cdot06$, $0\cdot02$) and scaling of data carried out with *SHELX*76 (Sheldrick, 1976). 2461 reflections measured; elimination of those with $I < 3\sigma(I)$ gave 2064 unique reflections. Standards measured every ten 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). Full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for Tl and Br, isotropic U values for remaining non-H atoms, convergence at $R = 0\cdot050$; $wR = 0\cdot056$, $w = 0\cdot2962/[\sigma^2(F_o) + 0\cdot017182F_o^2]$. The enantiomorph was also refined and increased R slightly. $(\Delta/\sigma)_{max}$ $0\cdot215$; max. in final difference Fourier map $1\cdot97$ e Å⁻³ (associated mainly with Tl). No correction applied for secondary extinction. Atomic scattering factors those of Cromer & Mann (1968) and Cromer & Liberman (1970).

Discussion. Final coordinates and equivalent isotropic thermal parameters (U_{eq}) for Tl and Br, and isotropic thermal parameters for C and N are given in Table 1.* The crystal structure contains 'octahedral' neutral molecules TlBr₃.3C₅H₅N with *mer* (*trans*) geometry (Fig. 1) and is similar to that of TlCl₃.3C₅H₅N found in TlCl₃.4C₅H₅N (Jeffs *et al.*, 1984c) but lacks the twofold rotation axis present in that structure. Selected bond distances and angles are listed in Table 2. It is seen that

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* Lists of structure factors, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39628 (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* (×10⁴), *equivalent isotropic thermal parameters for* Tl *and* Br *and isotropic thermal parameters for* C *and* N (×10⁴)

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

	x	y	z	$U_{eq}/U(\text{Å}^2)$
Tl	897 (1)	1553 (1)	1689 (1)	301 (3)
Br(1)	1435 (1)	30 (1)	744 (3)	466 (8)
Br(2)	102 (1)	3047 (1)	2335 (2)	429 (8)
Br(3)	2734 (1)	1930 (1)	2658 (2)	439 (8)
N(1)	395 (9)	1005 (8)	4142 (17)	327 (26)
N(2)	1188 (11)	2132 (9)	−882 (21)	437 (33)
N(3)	−831 (10)	1033 (8)	1065 (18)	378 (28)
C(1)	932 (14)	356 (11)	4741 (22)	448 (37)
C(2)	753 (18)	51 (15)	6161 (33)	620 (55)
C(3)	−29 (15)	452 (13)	7009 (25)	497 (44)
C(4)	−558 (15)	1142 (13)	6355 (24)	487 (43)
C(5)	−353 (12)	1371 (9)	4928 (22)	353 (32)
C(6)	635 (13)	2731 (11)	−1527 (23)	413 (36)
C(7)	776 (17)	3037 (14)	−2888 (28)	592 (52)
C(8)	1563 (16)	2736 (14)	−3741 (28)	540 (48)
C(9)	2194 (15)	2083 (12)	−3057 (25)	474 (42)
C(10)	1931 (14)	1794 (11)	−1630 (25)	466 (39)
C(11)	−1481 (12)	1488 (10)	273 (21)	371 (33)
C(12)	−2415 (13)	1182 (12)	−170 (24)	436 (38)
C(13)	−2642 (15)	356 (13)	139 (26)	515 (4)
C(14)	−1948 (15)	−136 (12)	1031 (28)	483 (42)
C(15)	−1037 (12)	250 (10)	1422 (21)	391 (35)

Table 2. *Important bond distances* (Å) *and angles* (°) *for* TlBr₃.3C₅H₅N

Tl–Br(1)	2·618 (2)	Tl–Br(2)	2·626 (2)
Tl–Br(3)	2·670 (2)	Tl–N(1)	2·425 (14)
Tl–N(2)	2·477 (18)	Tl–N(3)	2·514 (14)
Mean C–N	1·32 (2)	Mean C–C	1·39 (1)

Br(1)–Tl–Br(2)	170·5 (1)	N(2)–Tl–Br(3)	94·0 (4)
Br(1)–Tl–Br(3)	92·8 (1)	N(3)–Tl–Br(1)	83·7 (3)
Br(2)–Tl–Br(3)	96·2 (1)	N(3)–Tl–Br(2)	87·8 (3)
N(1)–Tl–Br(1)	92·4 (3)	N(3)–Tl–Br(3)	171·7 (3)
N(1)–Tl–Br(2)	90·3 (3)	N(2)–Tl–N(1)	173·0 (4)
N(1)–Tl–Br(3)	92·6 (3)	N(1)–Tl–N(3)	80·1 (5)
N(2)–Tl–Br(1)	89·7 (4)	N(2)–Tl–N(3)	93·5 (5)
N(2)–Tl–Br(2)	86·5 (4)		
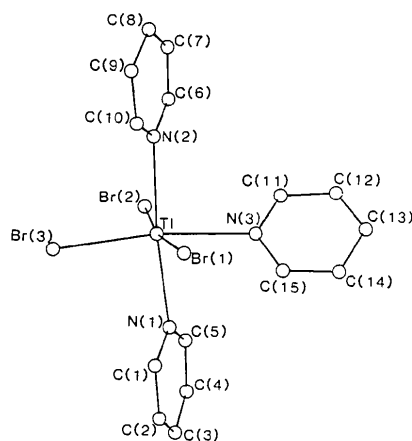
Fig. 1. Molecular structure of TlBr₃.3C₅H₅N.

there is a considerable distortion in the *trans* bond angles, 170·5 (1)–173·0 (4)°; these values are considerably less than those observed in the analogous *mer* pyridine complexes of InBr₃ [175 (1)–178 (1)°; Small & Worrall, 1982], InCl₃ [175·1 (2)–180°] and TlCl₃ [174·2 (1)–180°; Jeffs *et al.*, 1984c]. The close intermolecular contacts shown in Fig. 2 can be used to account for the displacement of N atoms from regular octahedral sites but there is no explanation in terms of intermolecular effects of the displacement of Br atoms from regular octahedral sites. In the title compound, however, the planes of the *trans* pyridine ligands are parallel [plane angle 4 (3)°] and these planes are at 30° to the Tl–Br(1) and Tl–Br(2) directions and 60 (3)° to the Tl–N(3) and Tl–Br(3) directions. In the analogous molecules the planes of the *trans* pyridines are at 90° and these lie at 45° to the *M*–*X* and *M*–N directions. These comparisons are not ideal, however, since the latter have an additional solvate molecule within the unit cell and its packing may affect the bond angles.

The Tl–Br(3) bond distance *trans* to N(3) is considerably longer [2·670 (2) Å] than the other Tl–Br distances [2·618 (2), 2·626 (2) Å]. This effect is not general, since in InBr₃.3C₅H₅N the reverse is observed. As expected the Tl–Br distances are larger than those observed in simple compounds which contain five-coordinate Tl, *e.g.* TlBr₃.dioxane 2·498 (3)–2·509 (2) Å (Jeffs, Small & Worrall, 1983); TlBr₃.2OPPh₃ 2·497 (3)–2·515 (2) Å (Jeffs, Small & Worrall, 1984b). The Tl–Br distance in TlBr₃.2pyridine [2·518–2·557 (9) Å (Jeffs, Small & Worrall, 1984a)] lies
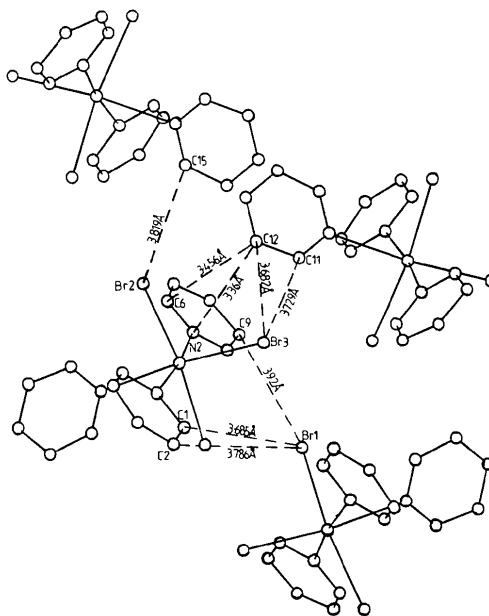

Fig. 2. Close intermolecular contacts within the unit cell (e.s.d.'s: C−Br 0·015, C−N 0·025 and C−C 0·030 Å).

between five- and six-coordinate values and this may be attributed to weak dimer association. The Tl—N distances in the title compound [2·42 (1)–2·51 (1) Å] are similar to those in TlCl₃.3pyridine [2·38 (1)–2·48 (1) Å] suggesting similar bond strengths in the two environments.

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Structure of Ammonium Tris(oxalato)gallate(III) Trihydrate, (I) (NH₄)₃[Ga(C₂O₄)₃].3H₂O, and Ammonium Tris(oxalato)aluminate(III) Trihydrate, (II) (NH₄)₃[Al(C₂O₄)₃].3H₂O

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Abstract. (I), $M_r = 441\cdot94$, triclinic, $P\bar{1}$, $a = 7\cdot901$ (1), $b = 10\cdot674$ (2), $c = 10\cdot710$ (2) Å, $\alpha = 83\cdot14$ (1), $\beta = 70\cdot18$ (1), $\gamma = 69\cdot88$ (1)°, $V = 798\cdot0$ Å³, $Z = 2$, $D_x = 1\cdot839$, $D_m = 1\cdot823$ Mg m⁻³ (by flotation), λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 1\cdot798$ mm⁻¹, $F(000) = 452$, $T = 293$ (1) K, final $R = 0\cdot047$ for 3326 observed reflections; isomorphous to (II), $M_r = 399\cdot20$, triclinic, $P\bar{1}$, $a = 7\cdot888$ (4), $b = 10\cdot667$ (4), $c = 10\cdot643$ (2) Å, $\alpha = 83\cdot33$ (2), $\beta = 70\cdot44$ (2), $\gamma = 69\cdot10$ (4)°, $V = 788\cdot3$ Å³, $Z = 2$, $D_x = 1\cdot682$, $D_m = 1\cdot664$ Mg m⁻³ (by flotation), λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 0\cdot206$ mm⁻¹, $F(000) = 416$, $T = 293$ (1) K, final $R = 0\cdot047$ for 3210 observed reflections. The Ga and the Al atoms are six-coordinated by O atoms from the bidentate oxalate groups in the form of a distorted octahedron. The average Ga—O bond distance is $1\cdot97$ (1) Å and Al—O $1\cdot90$ (1) Å. The coordination octahedra are linked together by hydrogen bonds.

Introduction. The structure determinations of the title compounds were undertaken as part of studies of M^{III} oxalate complexes (van Niekerk & Schoening, 1952a,b; Bulc, Golič & Šiftar, 1982, 1983).

Experimental. (I) prepared from freshly precipitated gallium hydroxide, aqueous solution of oxalic acid and ammonium oxalate (1:1·5:1·5); crystallization effected by addition of absolute ethanol. (II) prepared from aqueous solution of aluminium oxalate and ammonium oxalate (1:3). Crystal size 0·20 × 0·25 × 0·28 (I), 0·30 × 0·30 × 0·20 mm (II), Enraf–Nonius CAD-4 diffractometer, cell dimensions determined by least-squares refinement from θ values of 54 (I), 64 (II) reflections, range $9 < \theta < 16$ (I), $10 < \theta < 15°$ (II), graphite-monochromatized Mo $K\alpha_1$ radiation, $\lambda = 0\cdot70926$ Å, no absorption correction applied; three-dimensional diffractometer data collected with Mo $K\alpha$ radiation, ω–2θ scan, 2θ scan width (°) $= 0\cdot8 + 0\cdot3 \times \tan\theta$, aperture (mm) $= 2\cdot4 + 0\cdot9 \tan\theta$, max. scan time 40 s, $2\theta_{max}$ 60°, full sphere measured, $(\sin\theta/\lambda)_{max}$ 0·7 Å⁻¹, standard reflections 053, 04$\bar{3}$, 15$\bar{1}$ (I), 063, 06$\bar{1}$, 035 (II); 9434 (I), 9325 (II) measured, 4639 (I), 4567 (II) unique reflections, $R_{int}[\sum(I-|\bar{I}|)/\sum I] = 4\cdot5\%$ (I), 2·7% (II), 1313 (I), 1357 (II) unobserved reflections $[I < 3\cdot5|4|\sigma(I)]$, Patterson and Fourier methods, difference Fourier synthesis to reveal H atoms; full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms, H atoms not refined, yielded final $R = 0\cdot047$ (I), 0·047 (II), $R_w = 0\cdot067$ (I), 0·054 (II); empirical weighting function $w = W_F \times W_S$, where $W_F(|F_o| < 7\cdot0) = |F_o|/7\cdot0$, $W_F(|F_o| > 13\cdot0) = 13\cdot0/|F_o|$, $W_F(7\cdot0 < |F_o| < 13\cdot0) = 1\cdot0$ and $W_S(\sin\theta < 0\cdot45) = (\sin\theta/0\cdot45)^{1\cdot5}$, $W_S(\sin\theta > 0\cdot50) = 0\cdot50/\sin\theta$, $W_S(0\cdot45 < \sin\theta < 0\cdot50) = 1\cdot0$ (I) and $W_F(|F_o| < 2\cdot0) = (|F_o|/2\cdot0)^{1\cdot5}$, $W_F(|F_o| > 6\cdot0) = 6\cdot0/|F_o|$, $W_F(2\cdot0 < |F_o| < 6\cdot0) = 1\cdot0$ and $W_S(\sin\theta < 0\cdot44) = (\sin\theta/0\cdot44)^{2\cdot5}$, $W_S(\sin\theta > 0\cdot95) = 0\cdot95/\sin\theta$, $W_S(0\cdot44 < \sin\theta < 0\cdot95) = 1\cdot0$ (II) applied in order to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin\theta/\lambda)$ and $|F_o|$, $(\Delta/\sigma)_{max}$ in final refinement cycle 1·74 (I), 1·13