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The Structure of Bromobis(2,3,5,6-tetrafluorophenyl)thallium(III)

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Although numerous bis(pentafluorophenyl)thallium(III) compounds have been prepared and their structures proposed [1–6], only two crystal structures have been reported [7, 8]. In each case, major features of the structure were not predictable from molecular weight and spectroscopic data, *e.g.* $(C_6F_5)_2TlOH$ is a five coordinate polymer in the solid state but dimeric in solution [7], and $(C_6F_5)_2Tldpa$ (dpa = 2,2′-dipyridylamide) surprisingly contains a four-membered chelate ring [8]. Accordingly, it is likely that some reported structural proposals [1–6] are incorrect, making further crystallographic studies highly desirable. Examination of $(C_6F_5)_2TlBr$, the parent bis(pentafluorophenyl)thallium(III) compound [1], has been frustrated by inability to obtain suitable crystals. However, the thallium–bromine infrared vibrational absorptions [9] are similar to those of the recently prepared [10] bromobis(2,3,5,6-tetrafluorophenyl)thallium(III), and the crystal structure of this compound has now been determined.

Crystal data

Crystals obtained from benzene: $BrC_{12}F_8H_2Tl$, M = 582.416, monoclinic, space group $C2/c$, a = 20.354(5), b = 13.306(4), c = 22.735(6) Å, β = 113.20(3)°, V = 5659.5 Å^3, Z = 16, D_c = 2.73 g cm^{-3}, graphite crystal monochromated Mo-K_α radiation (μ = 138.1 cm^{-1}). Blocked full-matrix refinement using 3011 absorbtion corrected data with $I/\sigma(I) > 3.0$ has given an R of 0.036 (Tl, Br and F anisotropic).

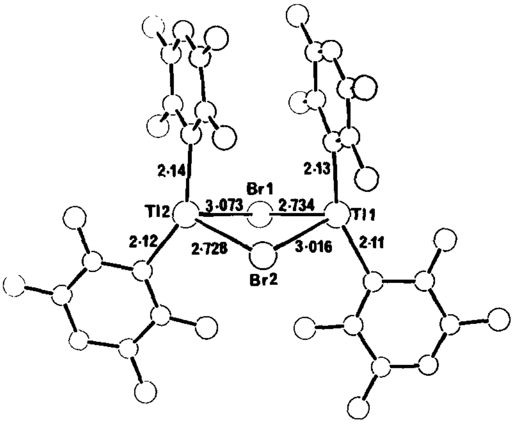

Fig. 1. The two crystallographically independent $(p\text{-}C_6HF_4)_2$-TlBr units. The e.s.d.'s in the bond lengths average Tl–Br 0.002 and Tl–C 0.01 Å. The principal angles are C–Tl(1)–C 149.9(5), C–Tl(2)–C 144.2(4), Br(1)–Tl(1)–Br(2) 83.7(1), Br(1)–Tl(2)–Br(2) 82.7(1), Tl(1)–Br(1)–Tl(2) 91.4(1) and Tl(1)–Br(2)–Tl(2) 92.8(1)°. The dihedral angle between the planes Tl(1), Br(1), Br(2) and Tl(2), Br(1), Br(2) is 148.4°.

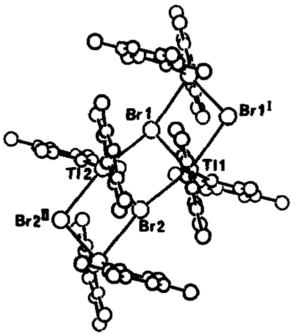

Fig. 2. Part of the polymeric chain structure of $(C_6HF_4)_2$-TlBr. The superscripts refer to atoms at the following equivalent position: I 0.5 – x, –0.5 – y, –z; II –x, –y, –z.

Two crystallographically independent $(p\text{-}HC_6F_4)_2$-TlBr molecules form an unsymmetrical bromine-bridged dimer unit (Fig. 1, which gives principal bond distances and angles). The Tl–Br contacts between the dimeric units, Tl(1)....Br(1^I) 3.214(1) and Tl(2)....Br(2^{II}), 3.172(1) Å, also represent significant bonding interactions (sum of Van der Waals radii of Tl [11] and Br, 3.9 Å), and give rise to the polymeric chain structure shown in Fig. 2. Each thallium is five coordinate with distorted trigonal bipyramidal stereochemistry, the three closest atoms [*e.g.* two carbons and Br(1) for Tl(1)] occupying equatorial positions. This arrangement has previously been observed in $(C_6F_5)_2TlOH$ [7] and $(C_6F_5)_2Tldpa$ [8]. The C–Tl–C angles of $(p\text{-}HC_6F_4)_2TlBr$ (Fig. 1) are somewhat larger than those of $(C_6F_5)_2TlOH$ (138.5° [7]) and $(C_6F_5)_2Tldpa$ (122.5 and 126.5° [8]).

Since the thallium–bromine vibrational frequencies of $(C_6F_5)_2TlBr$ (151 and 74 cm^{-1} [9]) are similar to those (148 and 74 cm^{-1}) of $(p\text{-}HC_6F_4)_2TlBr$, the former is probably also polymeric with five coordinate thallium. The same conclusion applies to $(C_6F_5)_2TlCl$, as X-ray powder data indicate that $(C_6F_5)_2TlBr$ and

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$(C_6F_5)_2TlCl$ are isomorphous. The earlier proposal of a dimeric structure for these compounds was based on dimeric behaviour in benzene [1]; $(p\text{-}HC_6F_4)_2$-TlBr is also dimeric in this solvent [Found: mol. wt., 1046 (1.42%, w/w); $(p\text{-}HC_6F_4)_2TlBr$ calcd.: mol. wt., 582]. Rupture of the weakest bonds of $(p\text{-}HC_6F_4)_2$-TlBr (Fig. 2) on dissolution would give a dimer (Fig. 1). Observation that the coordination number in solid $(p\text{-}HC_6F_4)_2TlBr$ and $(C_6F_5)_2TlX$ (X = Cl or Br) is higher than that suggested by molecular weight measurements raises the possibility that the complexes $(C_6F_5)_2LTlX$ (L = Ph_3PO, 2,2′-bipyridyl *etc.*) do not have the proposed monomeric structures [1, 2] with four or five coordinate thallium. Weak halogen bridging giving structures of higher coordination number may occur in the solid state. Indeed, careful reinvestigation of the molecular weights of representative complexes in benzene [12] provides evidence for association.

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