

Kurze Mitteilung

The Structure of Hydrotris(pyrazolyl)boratothallium(I)

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Dedicated to Professor Georg Brauer on the Occasion of his 90th Birthday

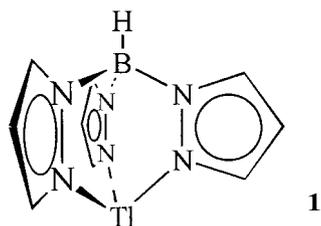
Abstract. The title compound crystallizes in the monoclinic space group $P2_1$ with $a = 7.928(6)$, $b = 9.306(4)$, $c = 17.16(2)$ Å, $\beta = 92.06(8)^\circ$, $V = 1265(2)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.191$ g cm⁻³. From two independent molecular units, metal-ligand strands are formed based on electrostatic interactions

between the thallium centers and pyrazolyl π manifolds from neighboring molecules.

Keywords: Thallium(I) compound; Hydrotris(pyrazolyl)-borate ligand; Crystal structure

The hydrotris(pyrazolyl)borate ligand (also abbreviated as Tp) is a uninegative, six-electron donor ligand. It is the prototype of a large variety of C-substituted, sterically demanding tris(pyrazolyl)borate ligands. These pyrazolylborate ligands are especially popular in bio-inorganic chemistry as the transition-metal complexes derived therefrom can be models for metallo-enzymes and -proteins [1–3].

For the major part, the interest in Tp-thallium(I) chemistry derives from one or more of the following points: (i) as a means of isolation and characterization of a (new) hydrotris(pyrazolyl)borate ligand; (ii) as a mild (less reducing) and often more stable ligand transfer reagent in place of alkali metal salts of hydrotris(pyrazolyl)borate ligands; (iii) and occasionally from the structural diversity of thallium(I) compounds in combination with ligand-Tl bonding and bond-theoretical aspects of the in/active lone-pair of electrons [1, 4–6]. We report here on the structure of the prototypical hydrotris(pyrazolyl)boratothallium(I) complex (**1**).



The basic metal-ligand motif of all TpTl structures is as depicted in **1**, there is little variation in the tris-chelating coord-

dination mode of the Tp ligand towards thallium. The structures exhibit pyramidal geometry for the thallium atom with respect to the three nitrogen atoms of the pyrazolylborate ligand and are of local C_3 symmetry if one disregards the rotameric dispositions of the pyrazolyl substituents [6]. The structure of the parent compound **1** reveals kinked chain-type arrangements of the metal-ligand moieties (Figure 1 and 2), with two different chain types present in the unit cell for the two crystallographically different Tl centers. Resulting Tl...Tl' contacts of 4.80 and 5.12 Å are, however, too long for any metal-metal interaction and the packing is most likely dictated by electrostatic interactions between the thallium and pyrazolyl π manifolds from neighboring molecules. The structure of **1** is somewhat unusual in the sense that all, but two, other TpTl-structures are clearly built up from molecular units. The two exceptions are HB(3-cyclopropyl-pz)₃Tl [5] and HB{3-(4-MeC₆H₄)-pz}₃Tl (pz = pyrazolyl) [7]. The former complex forms a stable tetramer with a perfect tetrahedron of Tl atoms and each thallium atom in an octa-

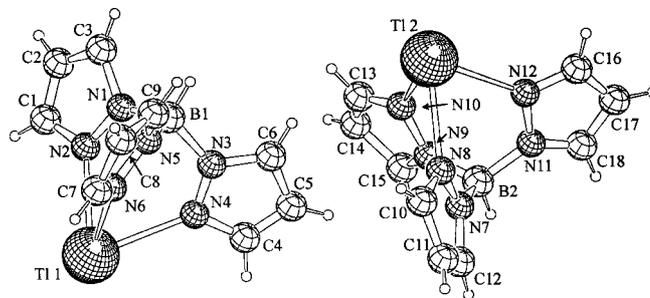


Fig. 1 The two independent molecular moieties of **1**. Selected distances [Å] and angles:

Tl1–N2 2.665(6), Tl1–N4 2.575(7), Tl1–N6 2.730(7), Tl2–N8 2.651(7), Tl2–N10 2.547(7), Tl2–N12 2.590(8) Å, N–Tl–N 69.6(2)–73.6°.

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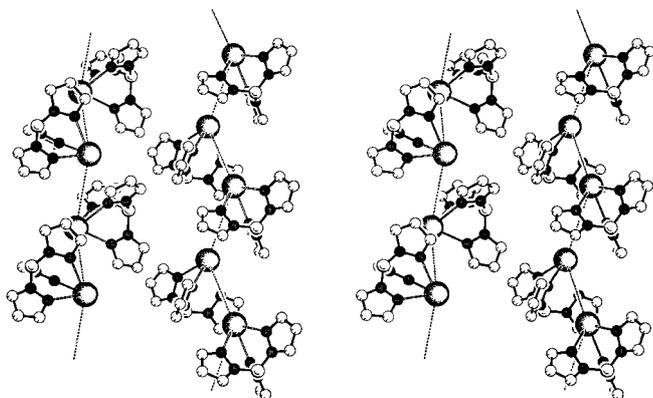


Fig. 2 Stereoscopic packing diagram for **1** showing the formation of strands for the two different molecular units; the dashed lines connecting the thallium centers are not meant to imply a chemical bond but are intended as a visual aid for the chain arrangement. The left strand contains the TlI-, the right strand the TlII-molecular units. Note the pyrazolyl π contact to thallium between neighboring molecules. These non-bonded Tl \cdots C and Tl \cdots N distances are in the range of 3.683 to 3.781 Å for TlI and 3.638 to 4.036 Å for TlII.

hedral environment. The Tl \cdots Tl contacts are 3.647 Å. The latter compound crystallizes as two independent molecules in the unit cell and the tolyl substituents on the pyrazolyl rings are interwoven such that a Tl \cdots Tl contact of 3.86 Å arises. The last two Tl \cdots Tl contacts are similar to the Tl \cdots Tl distances observed in the solid-state structures of C₅(CH₂Ph)₅Tl [8] and Tl[-1,3-^tBu₂]H₂C₅-C₅H₂[-1',3'-^tBu₂]Tl [9] which in the absence of bridging is suggestive of some metal-metal interaction. Theoretical studies on the possibility of such weak thallium-thallium interactions have been carried out [10]. The Tl-N distances observed in **1** fall in the normal range of 2.50–2.73 Å [6] found for Tl-N contacts in TpTl structures.

Experimental

Synthesis of Hydrotris(pyrazolyl)boratothallium(I) 1: 530 mg (1.99 mmol) of TlNO₃ were dissolved in a mixture of 5 ml of methanol and 5 ml of water. This solution was overlaid with a solution of 500 mg (1.98 mmol) of potassium hydrotris(pyrazolyl)borate [11] in 10 ml of methanol. Slow diffusion of both solutions together with evaporation of the solvent to half of the initial volume leads to crystal growth. The crystals were collected after one week (yield 450 mg, 54%). The melting point of 155 °C and the ¹H NMR and mass spectrometric characterization agree with literature values [12]. ¹³C-NMR (CDCl₃): δ /ppm = 104.11, 135.60, 139.14. IR (KBr): $\tilde{\nu}$ /cm⁻¹ = 3133 w, 3112 w (ν CH), 2581 w, 2443 m, 2400 w, 2369 w (ν BH), 1501 m, 1422 m, 1416 w, 1394 m, 1382 m, 1326 w, 1295 s, 1210 s, 1194 w, 1185 m, 1125 sh, 1114 s, 1088 w, 1078 m, 1063 sh, 1057 sh, 1048 s, 1038 s, 970 s, 921 w, 893 w, 879 w, 872 w, 838 w, 800 w, 783 sh, 774 m, 754 s, 737 m, 726 sh, 722 s, 671 sh, 665 m, 627 m, 619 m.

C₉H₁₀BN₆Tl (417.41): calculated C 25.90, H 2.41, N 20.13, Tl 48.96; found C 26.09, H 1.93, N 20.68, Tl 48.52%. No potassium was found in the crystals by AAS.

Crystal structure determination of 1: Crystal data: Molecular formula C₁₈H₂₀B₂N₁₂Tl₂ (two independent molecules in

the unit cell), formula weight 834.82 g mol⁻¹, $a = 7.928(6)$, $b = 9.306(4)$, $c = 17.16(2)$ Å, $\beta = 92.06(8)^\circ$, $V = 1265(2)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.191$ g cm⁻³, monoclinic, space group P2₁. **Data collection:** Syntex P2₁ four-circle diffractometer, Mo-K α radiation ($\lambda = 0.71069$ Å), graphite monochromator, crystal size 0.2 × 0.2 × 0.15 mm³, 298(2) K, ω -scan, $2.4^\circ \leq 2\theta \leq 55.0^\circ$, $0 \leq h \leq 10$, $0 \leq k \leq 12$, $-22 \leq l \leq 22$, 3330 reflections measured, 3083 independent, $\mu(\text{Mo-K}\alpha) 12.75$ mm⁻¹. **Structural Analysis and Refinement:** Structure solution was performed by direct methods (SHELXS-86 [13]). Refinement: Full-matrix least squares on F^2 (SHELXL-93 [13]); all non-hydrogen atomic positions found and refined anisotropically, the hydrogen positions were placed at calculated positions with $d_{\text{C-H}} = 0.95$ and an isotropic temperature factor of $B_{\text{eq}} = 0.08$. 310 refined parameters, final $RI = 0.0692$, $wR2 = 0.1256$ for 1638 reflections with $I > 2\sigma I$, goodness-of-fit on $F^2 = 1.081$, absolute structure parameter $-0.02(4)$, largest difference peak and hole 1.042/−1.834 e Å⁻³ in the vicinity of the thallium atom. An empirical absorption correction (DIFABS) did not lead to a significant improvement and, therefore, was not included in the final refinement. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. 101006).

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