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Hydridotris(3-t-butylpyrazolyl)boratothallium(I). A spectroscopic and structural study *

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Abstract

The crystal structure of hydridotris(3-t-butyl-1-pyrazolyl)boratothallium(I) is reported. The compound crystallizes in the orthorhombic space group *Pnma* (No. 62) with *a* 14.431(4), *b* 16.299(3), and *c* 10.562(2) Å. The Tl atom of each monomeric unit adopts a pyramidal geometry with respect to the three nitrogen atoms that constitute the "face" of the pyrazolylborate ligand. The average Tl–N distance of 2.584(9) Å possibly implies some ionic character.

Introduction

Thallium(I) complexes find considerable use as mild transfer reagents for organic and inorganic ligands and often yield products that are unobtainable by more conventional methods [1]. Particularly useful in this regard are the cyclopentadienyl- and substituted cyclopentadienyl-thallium reagents [1b,2]. The formal analogy between the cyclopentadienyl- and the hydridotris(1-pyrazolyl)-borate ((HB(pz)$_3$, pz = pyrazolyl or substituted)) ligands is well established in the realm of transition metal chemistry. However, pyrazolylborate ligands have been used very little in the context of main group chemistry. As part of our broader study of the hydridotris(1-pyrazolyl)borate complexes of the main group elements [3], we wish to report the structure of monomeric hydridotris(3-t-butyl-1-pyrazolyl)boratothallium(I).

Experimental

The title compound was prepared by the method of Trofimenko et al. [4]. X-ray quality crystals were grown from solutions of I in dimethoxyethane held at −20 °C.

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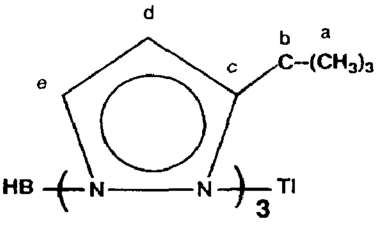
* This paper is dedicated to the memory of Professor J.J. Zuckerman in recognition of his many contributions to main-group and organometallic chemistry.

A transparent crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm was used for the determination of the unit cell dimensions and the collection of the intensity data.



^{1}H NMR for I (300.15 MHz, C_6D_6, 25 °C): δ 1.32, (d, ^5J(Tl–H) 13.2 Hz, 9 H, t-butyl), 6.0, (d, ^4J(Tl–H) 15.9 H, 1-H, pz-4-H), 7.6, (s, 1 H, pz-5-H). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 25 °C): δ 31.8, (d, ^4J(Tl–C) 170.59 Hz, C_a), 32.3 (s, C_b), 101.1 (d, ^3J(Tl–C) 13.51 Hz, C_d), 136.2 (s, C_e), 163.5 (d, ^2J(Tl–C) 50.87 Hz, C_c). The quaternary carbon resonance, C_b, appears inside the C_a doublet and its identity was confirmed by a spin echo experiment. Electron impact mass spectrum (70 eV): 585 (M^+, 40%), 463 (M^+ – t-butyl-pzH, 60%), 205 (Tl^+, 70%).

Crystal data. $C_{21}H_{34}BN_6Tl$, F. wt.: 585.7 a.m.u., a 14.431(4), b 16.299(3), c 10.562(2) Å, V 2484.3 Å^3, orthorhombic space group (*Pnma*, No. 62, from systematic absences and structure refinement), $Z = 4$, d_x 1.566 g cm^{-3}, (μ(Mo-K_α), λ 0.71073 Å), 65.8 cm^{-1}.

Intensity data, structure solution and refinement

1843 independent non-zero reflections were measured using Mo-K_α radiation and the ω–2θ scan mode on an Enraf–Nonius CAD4 diffractometer over the range

Table 1

Positional parameters and B values and their e.s.d.'s for the non-hydrogen atoms in I [a]

Atom	x	y	z	B (Å^2)
Tl	0.36153(3)	0.250	0.76723(4)	3.213(7)
N(11)	0.2199(4)	0.3466(1)	0.7589(7)	2.9(1)
N(12)	0.1524(5)	0.3276(4)	0.6713(6)	2.8(1)
N(21)	0.3269(7)	0.250	0.5269(9)	2.9(2)
N(22)	0.2345(7)	0.250	0.50	3.0(2)
C(13)	0.0852(6)	0.3852(5)	0.6714(9)	3.4(2)
C(14)	0.1091(6)	0.4446(5)	0.762(1)	4.0(2)
C(15)	0.1942(6)	0.4173(5)	0.8143(8)	3.2(2)
C(16)	0.2543(7)	0.4572(6)	0.9154(9)	4.0(2)
C(17)	0.1968(9)	0.5281(7)	0.979(1)	5.9(3)
C(18)	0.3425(8)	0.4924(7)	0.850(1)	6.0(3)
C(19)	0.2826(9)	0.3944(7)	1.017(1)	5.7(3)
C(23)	0.225(1)	0.250	0.369(1)	4.3(3)
C(24)	0.313(1)	0.250	0.315(1)	4.5(3)
C(25)	0.3735(9)	0.250	0.419(1)	3.5(3)
C(26)	0.4815(9)	0.250	0.413(1)	4.5(3)
C(27)	0.526(1)	0.250	0.542(2)	10.4(8)
C(28)	0.5093(9)	0.1722(8)	0.338(2)	8.6(4)
B	0.152(1)	0.250	0.598(1)	3.0(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)(a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3})$.

$3° \leq 2\theta \leq 55°$ at 25 °C. The structure was solved by Patterson syntheses, which located the Tl position. All other atoms were located from successive cycles of difference Fourier synthesis. The structure was refined by anisotropic full-matrix least squares. Hydrogen atoms were included in the structure factor calculations. The final R values were R 0.035 and R_w 0.043. The atomic parameters are given in Table 1.

Results and discussion

Cyclopentadienyl-substituted thallium(I) compounds display a fascinating variety of solid-state structures. Thus C_5H_5Tl [5], Me_5C_5Tl [6], and $Me_3SiC_5H_4Tl$ [7] possess polymeric zig-zag structures, $(Me_3Si)_2C_5H_3Tl$ is a hexameric, doughnut-shaped molecule [7], and $(PhCH_2)_5C_5Tl$ [8] can adopt either a polymeric or dimeric arrangement depending on the rate of crystallization. Interestingly, the cyclopenatdienide analogous ligand, 3-t-butyl-1-pyrazolylborate, affords yet another thallium(I) sold state structure, namely a monomer (Fig. 1). Each molecule of I contains a cyrstallographically imposed mirror plane involving the atoms, Tl,B,N(21), N(22), C(23), C(24), C(25), C(26) and C(27). The two independent Tl–N distances are the same within experimental error (Table 2) and the Tl atom adopts a pyramidal geometry with respect to N(11) and N(21). There is no evidence for dimerization, the closest Tl...Tl separation being 7.225 Å. Overall, the structure of I is similar to that of the anion $(3,1,2\text{-}TlC_2B_9H_{11})$ [9]; however, the Tl atom is more symmetrically located in the pyrazolylborato derivative. The average Tl–N distance (2.585(9) Å)

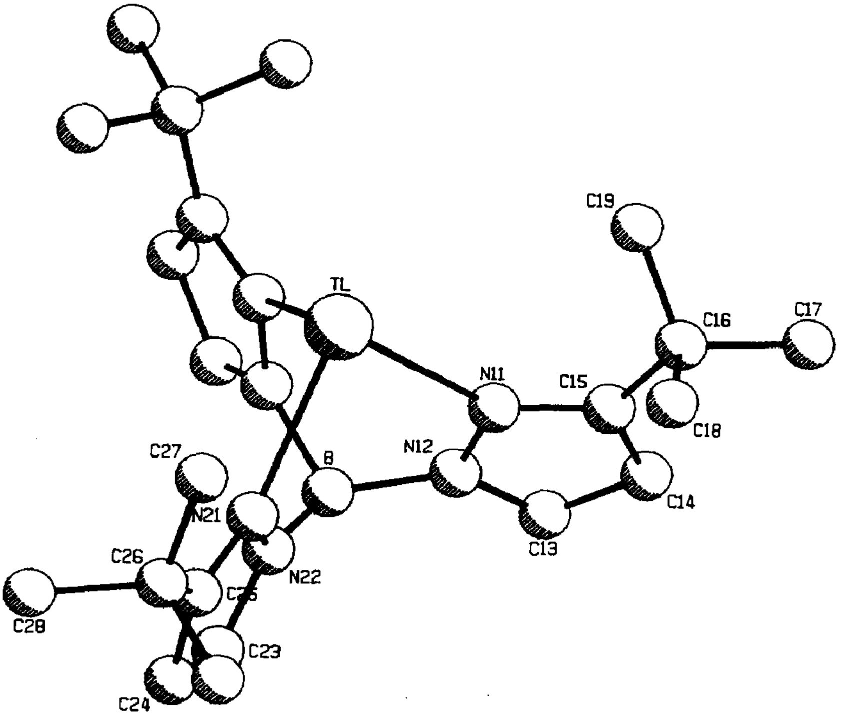


Fig. 1. View (ORTEP) of hydridotris(3-t-butylpyrazolyl)boratothallium showing the atom numbering scheme.

Table 2

Relevant bond distances (Å) and angles (°) for I

Tl–N(11)	2.582(6)
Tl–N(21)	2.587(9)
N(11)–N(12)	1.379(9)
N(21)–N(22)	1.365(14)
N(12)–B	1.535(10)
N(22)–B	1.52(2)
N(11)–Tl–N(21)	79.3(2)
N(11)–Tl–N(11)	75.2(2)
N(12)–Tl–N(22)	110.3(7)
N(12)–Tl–N(12)	111.0(8)

exceeds the sum of covalent radii (2.23 Å) possibly implying some ionic character. It should be noted though, that I is soluble in non-polar solvents such as benzene and toluene. Compound I is also sufficiently volatile to permit the observation of a parent peak in the mass spectrum (see Experimental). Additional evidence for the covalent character of I stems from the observation of ^{205}Tl coupling in the ^{1}H and ^{13}C NMR spectra. Thus the 4-pyrazolyl ring proton shows coupling to Tl(^4J(Tl–H) 15.9 Hz) as do the t-butyl groups (^5J(Tl–H) 13.2 Hz). Thallium coupling is also evident in the $^{13}C\{^1H\}$ resonances of the t-butyl-methyl carbons, C_a(^4J(Tl–C) 170.59 Hz), the 3-carbon, C_c(^2J(Tl–C 50.87 Hz), and the 4-carbon, C_d(^3J(Tl–C) 13.51 Hz). The relatively large Tl couplings to the t-butyl-methyl carbons and protons may imply through-space interactions. Finally we note that the chemical shift of the 3-carbon, C_c (163.5 ppm) appears to be the largest such value reported for a pyrazole carbon [10].

Acknowledgement

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