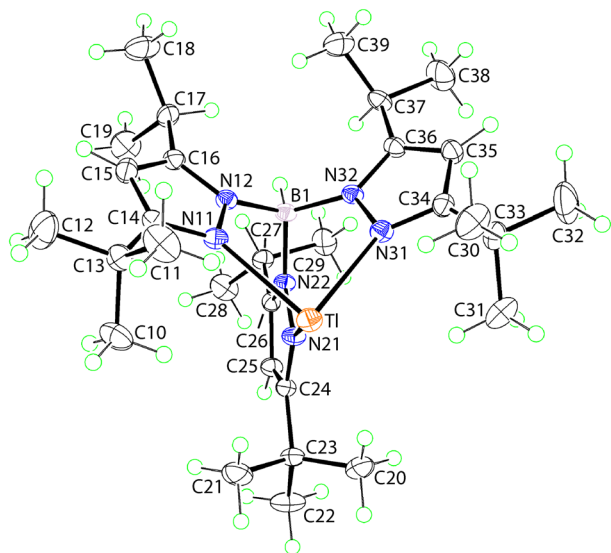


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# Crystal structure of {hydridotris[3-(*t*-butyl)-5-isopropylpyrazol-1-yl- $\kappa N^3$ ]borato}thallium(I), $C_{30}H_{52}BN_6Tl$



<https://doi.org/10.1515/ncrs-2020-0405>

Received July 26, 2020; accepted September 3, 2020;

published online October 2, 2020

## Abstract

$C_{30}H_{52}BN_6Tl$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 9.611(3)$  Å,  $b = 17.586(5)$  Å,  $c = 19.710(6)$  Å,  $\beta = 98.374(7)^\circ$ ,  $V = 3295.8(17)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.0152$ ,  $wR_{ref}(F^2) = 0.0381$ ,  $T = 182$  K.

CCDC no.: 2027109

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.27 × 0.09 × 0.04 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	4.93 mm <sup>-1</sup>
Diffractometer, scan mode:	Rigaku XtaLAB P200, $\omega$
$\theta_{max}$ , completeness:	27.5°, 99%
$N(hkl)_{measured}$ :	24,824, 7518, 0.023
$N(hkl)_{unique}$ , $R_{int}$ :	
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2 \sigma(I_{obs})$ , 6366
$N(param)_{refined}$ :	358
Programs:	NUMABS [1], CrystalClear [2], SIR2014 [3], SHELX [4], WinGX/ORTEP [5]

of the atoms including atomic coordinates and displacement parameters.

## Source of material

A solution of  $K\{HB(3-tBu-5-iPrpz)_3\}$  (326.0 mg, 0.596 mmol) in dichloromethane (15 mL) was added to a solution of TIOAc (192.8 mg, 0.732 mmol) in ethanol (35 mL). The mixture was stirred for 3 h and the solvent then evaporated under vacuum. The resulting solid was extracted with dichloromethane (35 mL). The filtrate was evaporated under vacuum, and a white powder was obtained. Colourless crystals were obtained by slow evaporation from a saturated dichloromethane/ethanol (5:1 v/v) solution at room temperature. Yield: 52% (219.3 mg, 0.308 mmol).

**Anal. Calcd.** for  $C_{30}H_{52}BN_6Tl$ . C, 50.61; H, 7.36; N, 11.80%. Found: C, 50.22; H, 7.20; N, 11.81%.

**IR** (JASCO FT/IR-6300 spectrophotometer, KBr; cm<sup>-1</sup>): 2963 (s)  $\nu(C-H)$ , 2867 (m)  $\nu(C-H)$ , 2562 (m)  $\nu(B-H)$ , 1529 (m)  $\nu(C=N)$ .

**<sup>1</sup>H NMR** (Bruker AVANCE III-500 NMR spectrometer, chemical shifts relative to CDCl<sub>3</sub> 298 K; ppm):  $\delta$  1.10 (doublet,  $J = 6.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>, 18H), 1.31 (singlet, C(CH<sub>3</sub>)<sub>3</sub>, 27H), 3.34 (septet,  $J = 6.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>, 3H), 5.85 (singlet, pyrazole-4, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR)  $\delta$ : 23.5 [CH(CH<sub>3</sub>)<sub>2</sub>], 26.4 [C(CH<sub>3</sub>)<sub>3</sub>], 32.3 [CH(CH<sub>3</sub>)<sub>2</sub>], 32.5 [C(CH<sub>3</sub>)<sub>3</sub>], 98.2 (pyrazole-4C), 155.5 (pyrazole-3C), 161.8 (pyrazol-5C).

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Tl	0.27659 (2)	0.26547 (2)	0.65845 (2)	0.02258 (3)
N11	0.40691 (14)	0.17760 (8)	0.74799 (7)	0.0198 (3)
N12	0.44197 (13)	0.20309 (8)	0.81438 (6)	0.0177 (3)
N21	0.14323 (14)	0.27354 (8)	0.76019 (7)	0.0190 (3)
N22	0.21860 (13)	0.27641 (8)	0.82514 (7)	0.0173 (3)
N31	0.40338 (14)	0.36588 (8)	0.73614 (7)	0.0206 (3)
N32	0.43995 (13)	0.34937 (8)	0.80487 (7)	0.0180 (3)
C10	0.27880 (18)	0.05073 (13)	0.65581 (10)	0.0362 (5)
H10A	0.233838	0.026046	0.691562	0.054*
H10B	0.264589	0.019618	0.614125	0.054*
H10C	0.237018	0.101064	0.645853	0.054*
C11	0.5081 (2)	0.09579 (13)	0.62434 (11)	0.0418 (5)
H11A	0.467972	0.146335	0.613574	0.063*
H11B	0.493100	0.063920	0.583136	0.063*
H11C	0.609217	0.100505	0.640259	0.063*
C12	0.4986 (3)	-0.02022 (12)	0.69604 (11)	0.0474 (6)
H12A	0.599037	-0.015812	0.713684	0.071*
H12B	0.486507	-0.050538	0.653872	0.071*
H12C	0.450089	-0.045118	0.730409	0.071*
C13	0.43649 (18)	0.05926 (10)	0.68063 (9)	0.0254 (4)
C14	0.45971 (16)	0.10721 (10)	0.74565 (8)	0.0201 (3)
C15	0.53087 (18)	0.08736 (10)	0.81035 (9)	0.0254 (4)
H15	0.578940	0.041068	0.822672	0.030*
C16	0.51701 (17)	0.14869 (10)	0.85260 (8)	0.0210 (3)
C17	0.56893 (18)	0.15472 (10)	0.92851 (8)	0.0256 (4)
H17	0.565998	0.209469	0.941947	0.031*
C18	0.7210 (2)	0.12717 (14)	0.94493 (10)	0.0428 (5)
H18A	0.724855	0.072454	0.935961	0.064*
H18B	0.756163	0.137083	0.993313	0.064*
H18C	0.779379	0.154308	0.916026	0.064*
C19	0.4740 (2)	0.11002 (13)	0.96988 (10)	0.0383 (5)
H19A	0.377053	0.128375	0.958750	0.057*
H19B	0.506290	0.117104	1.018959	0.057*
H19C	0.477621	0.055883	0.958464	0.057*
C20	-0.0981 (2)	0.33071 (12)	0.65806 (10)	0.0353 (5)
H20A	-0.109583	0.378232	0.682621	0.053*
H20B	-0.172439	0.326677	0.618516	0.053*
H20C	-0.006095	0.330400	0.642235	0.053*
C21	-0.0932 (2)	0.18890 (12)	0.66687 (10)	0.0380 (5)
H21A	-0.002023	0.188241	0.650187	0.057*
H21B	-0.168851	0.185700	0.627848	0.057*
H21C	-0.099316	0.145426	0.697408	0.057*
C22	-0.25254 (19)	0.26461 (13)	0.73012 (11)	0.0378 (5)
H22A	-0.261330	0.221005	0.760162	0.057*
H22B	-0.326075	0.261982	0.690141	0.057*
H22C	-0.262814	0.311846	0.755310	0.057*
C23	-0.10802 (17)	0.26307 (10)	0.70633 (9)	0.0224 (3)
C24	0.00743 (16)	0.26758 (9)	0.76787 (9)	0.0188 (3)
C25	-0.00631 (17)	0.26602 (10)	0.83722 (9)	0.0204 (3)
H25	-0.091209	0.261886	0.856328	0.024*
C26	0.12895 (17)	0.27172 (9)	0.87281 (8)	0.0175 (3)
C27	0.17461 (17)	0.27782 (9)	0.94914 (8)	0.0201 (3)
H27	0.268813	0.253030	0.960241	0.024*
C28	0.0731 (2)	0.23709 (12)	0.98929 (10)	0.0347 (4)
H28A	-0.018577	0.262524	0.981479	0.052*

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å & B–H = 1.00 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$  and  $1.2U_{\text{eq}}(\text{B})$ .

## Comment

Hydridotris(pyrazolyl)borate ligands,  $\{\text{HB}(3\text{-R-5-R}')_3\}^-$ , for R, R' = H, alkyl and aryl, are very effective, anionic tripod-type nitrogen-containing ligands and their coordination chemistry has provided many fascinating examples of unusual geometries and reactivities [6, 7]. The steric bulk of these ligands can be readily modified by the introduction of an appropriate alkyl and/or aryl substituent at the 3- and 5-positions of the pyrazolyl rings. For example, by using a less hindered ligand,  $[\text{HB}(3,5\text{-iPr})_2\text{pz}_3]^-$ , binuclear copper(II) complexes such as the  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxido}$  copper(II) complex,  $[\{\text{Cu}[\text{HB}(3,5\text{-iPr})_2\text{pz}_3]\}_2(\mu\text{-O}_2)]$ , and the  $\mu\text{-hydroxido}$  copper(II) complex,  $[\{\text{Cu}[\text{HB}(3,5\text{-iPr})_2\text{pz}_3]\}_2(\mu\text{-OH})_2]$ , were obtained [8]. On the other hand, in the case of the highly hindered ligand,  $[\text{HB}(3\text{-tBu-5-iPrpz})_3]^-$ , the mononuclear, side-on superoxido copper(II) complex,  $[\text{Cu}(\text{O}_2)\{\text{HB}(3\text{-tBu-5-iPrpz})_3\}]$  [9], and the mononuclear hydroxido copper(II) complex,  $[\text{Cu}(\text{OH})\{\text{HB}(3\text{-tBu-5-iPrpz})_3\}]$  [10], are selectively formed. Even more hindered adamantyl substituted ligands were prepared in order to ensure exclusive mononuclear complex formation [11, 12]. Attention has also been directed to evaluating the influence of systematic changes in the steric profiles in these ligands in thallium(I) complexes, especially with “super-hindered” ligands [13, 14]. In continuation of these studies, this report details the synthesis of a thallium(I) complex with a highly hindered ligand, i.e.  $[\text{Tl}\{\text{HB}(3\text{-tBu-5-iPrpz})_3\}]$  (I), along with spectroscopic characterization and X-ray crystal structure determination.

The molecular structure of (I) is illustrated in the figure (50% displacement ellipsoids) and shows the thallium(I) centre to be tri-coordinated by three nitrogen atoms of the  $\{\text{HB}(3\text{-tBu-5-iPrpz})_3\}^-$  anion. The Tl–N11 [2.5352(14) Å], Tl–N21 [2.5363(15) Å] and Tl–N31 [2.5307(15) Å] bond lengths are experimentally equivalent. The resulting N<sub>3</sub> donor set defines a trigonal-pyramidal geometry with the N11–Tl–N21 [74.88(5)°], N11–Tl–N31 [81.87(5)°] and N21–Tl–N31 [74.74(5)°] angles spanning a range of about 7°. The molecule approximates 3-fold symmetry when viewed down the spine and the Tl-bound lone-pair of electrons is projected to occupy a position along the extension of this axis.

Table 2: (continued)

Atom	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
H28B	0.110120	0.238380	1.038302	0.052*
H28C	0.062346	0.184138	0.973925	0.052*
C29	0.1903 (2)	0.36127 (11)	0.97006 (9)	0.0320 (4)
H29A	0.254690	0.386483	0.943009	0.048*
H29B	0.228022	0.364755	1.018904	0.048*
H29C	0.098146	0.386181	0.961709	0.048*
C30	0.5185 (2)	0.42674 (13)	0.60530 (10)	0.0405 (5)
H30A	0.619084	0.424830	0.623191	0.061*
H30B	0.505061	0.452141	0.560569	0.061*
H30C	0.481067	0.374894	0.600195	0.061*
C31	0.2842 (2)	0.47519 (13)	0.62709 (11)	0.0399 (5)
H31A	0.244773	0.423737	0.622958	0.060*
H31B	0.271678	0.499560	0.581891	0.060*
H31C	0.235778	0.505049	0.658516	0.060*
C32	0.4981 (3)	0.55250 (13)	0.66185 (12)	0.0539 (6)
H32A	0.450512	0.580503	0.694815	0.081*
H32B	0.480632	0.577775	0.617108	0.081*
H32C	0.599461	0.551326	0.677980	0.081*
C33	0.44121 (19)	0.47087 (11)	0.65504 (9)	0.0275 (4)
C34	0.46267 (17)	0.43287 (10)	0.72519 (9)	0.0215 (3)
C35	0.53899 (17)	0.45957 (10)	0.78619 (9)	0.0241 (4)
H35	0.591934	0.505300	0.792358	0.029*
C36	0.52228 (16)	0.40638 (10)	0.83568 (8)	0.0199 (3)
C37	0.58361 (17)	0.40756 (10)	0.91067 (8)	0.0234 (4)
H37	0.511888	0.386688	0.937675	0.028*
C38	0.6185 (2)	0.48894 (12)	0.93479 (10)	0.0405 (5)
H38A	0.691826	0.509530	0.910243	0.061*
H38B	0.652252	0.488870	0.984167	0.061*
H38C	0.533951	0.520542	0.925399	0.061*
C39	0.7148 (2)	0.35812 (12)	0.92414 (10)	0.0369 (5)
H39A	0.692826	0.306823	0.906305	0.055*
H39B	0.746882	0.355469	0.973614	0.055*
H39C	0.789105	0.380252	0.901190	0.055*
B1	0.38144 (19)	0.27889 (10)	0.83853 (9)	0.0180 (4)
H1	0.410793	0.282965	0.889201	0.022*

The same substitution pattern in the pyrazolyl ligand of (I) is found in a related structure but, containing only two pyrazolyl residues, i.e. [Tl{H<sub>2</sub>B(3-tBu-5-iPrpz)<sub>2</sub>}] [15]. Here, the thallium(I) centre is bi-coordinated by two pyrazolyl-N atoms with the Tl–N bond lengths [2.628(11) and 2.664(10) Å] being longer than those in (I), an observation explained in terms of the presence of an intramolecular Tl...HB interaction as well as two close, intermolecular Tl(lone-pair)...π(pyrazolyl) contacts; see ref. [16] for a discussion of related intermolecular Tl...π(arene) interactions. In another structure related to (I) where the t-butyl groups are replaced with adamantanyl substituents, i.e. [Tl{H<sub>2</sub>B(3-Ad-5-iPrpz)<sub>2</sub>}] [14], a disparity arises in the Tl–N bond lengths with one bond, i.e. 2.498(3) Å, being significantly shorter than the other two Tl–N bonds, i.e. 2.530(4) and 2.538(3) Å. The N–Tl–N angles span a

narrower range in the literature structure, i.e. 74.4(1) to 78.2(1)°, compared with (I). From the foregoing, it is apparent that no systematic variations in geometric parameters are evident that can be related to the presence of t-butyl or adamantanyl substituents in the 3-position of the pyrazolyl groups in these thallium(I) structures.

In the molecular packing, following the distance criteria assumed in PLATON [17], there are no directional interactions between complexes of (I). Thus, an analysis of the calculated Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots was conducted using Crystal Explorer 17 [18] and literature methods [19]. Reflecting the lack of directional interactions in the crystal, H...H contacts account for 88.4% of all contacts. The only other contributions to the calculated Hirshfeld surface are from H...C/C...H [5.9%], H...N/N...H [4.8%] and H...Tl/Tl...H [0.9%].

**Author contribution:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

**Research funding:** KF is grateful for support from the joint usage/research programme “Artificial Photosynthesis” based at Osaka City University. Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001–2019.

**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

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