



# Thallium(I) complexes with modified poly(pyrazolyl)borate ligands—metal-ligand coordination and crystal packing

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## Abstract

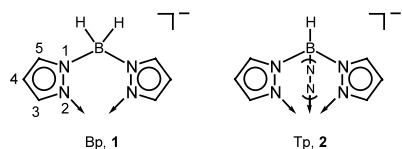
The structures of the thallium(I) complexes with hydrotris(pyrazolyl)borate (TpTl, **2-Tl**), and the modified Bp and Tp ligands dihydrobis(1,2,4-triazolyl)borate (**3-Tl**), hydrotris(imidazolyl)borate (**6-Tl**), dihydrobis(indazolyl)borate (**7-Tl**), and hydrotris(indazolyl)borate (**8-Tl**) are reported and discussed in terms of their (molecular) metal–ligand arrangement and their crystal packing. Compounds **2-Tl** and **7-Tl** feature molecular TpTl and Bp'Tl units with pronounced Tl $\cdots\pi_{\text{azolyl}}$  interactions between neighboring molecules. In **8-Tl** the molecular units are arranged in pairs through indazolyl  $\pi\cdots\pi$  stacking. Complexes **3-Tl** and **6-Tl** form extended 3D and 1D structures, respectively, through the bridging action of the poly(azolyl)borate ligand between three symmetry related thallium centers. Compounds **2-Tl**, **3-Tl**, and **8-Tl** crystallize in the chiral space groups  $P2_1$ ,  $P2_12_12_1$ , and  $C2$ , respectively. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Thallium(I) complexes; Scorpionate ligands; Crystal packing;  $\pi$ -Stacking; Cation– $\pi$  interaction

## 1. Introduction

Thallium(I) is formally a low-valence p-block metal with a closed sub-shell ( $s^2$ ). Yet its structural chemistry can feature unusual patterns of aggregation in the solid state [1–8] through what could be attractive metal–metal interactions [9–13]

Poly(pyrazolyl)borate ligands (scorpionates) are versatile ligands in physio-chemical, bio-inorganic and structurally oriented coordination chemistry [14–20]. The parent compounds are dihydrobis(pyrazolyl)borate (Bp, **1**) and hydrotris(pyrazolyl)borate (Tp, **2**).



-(N-N)- denotes the third pyrazolyl ring which is oriented to the rear

Thallium(I) derivatives of poly(pyrazolyl)borate ligands are important (i) as a means of isolation and characterization of new scorpionate ligands and (ii) as a mild (less reducing) and often more stable ligand transfer reagent in place of alkali metal salts of scorpionate ligands [21].

In recent years we, and others, have been interested in metal complexes with modified poly(pyrazolyl)borate ligands and in their supramolecular architecture. These modified scorpionate ligands are bis- and tris(1,2,4-triazolyl)borate (**3** and **4**) [22–27], bis(tetrazolyl)borate (**5**) [28–30], bis- and tris(imidazolyl)borate (**6**) [31–33] or bis- and tris(indazolyl)borate (**7** and **8**) [34,35]. Examples of modified poly(pyrazolyl)borate ligands studied by others are fluorinated tris(pyrazolyl)borate [36] and tris(mercaptoimidazolyl)borate [37–40].

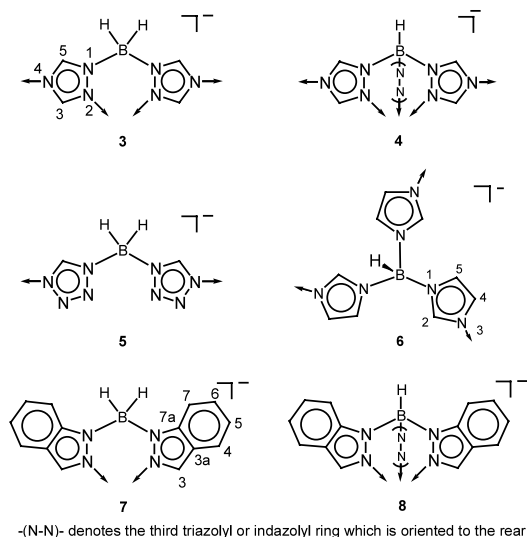
We report here the structures of the thallium(I) complexes with **2**, **3**, **6**, **7**, and **8**, with special consideration to their supramolecular assembly. Thallium(I) complexes are also used by others to investigate supramolecular metal–ligand structures [41]. The structural investigations of **2**, **6**, and **8** have already been communicated as short notes [42,43].

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## 2. Experimental

NMR spectra were collected on a Bruker ARX200 (200.1 MHz for  $^1\text{H}$ , 50.3 MHz for  $^{13}\text{C}$ ) or ARX400 (**8-Tl**) and calibrated against the solvent signal ( $\text{CDCl}_3$ ,  $^1\text{H}$  NMR 7.26 ppm,  $^{13}\text{C}$  NMR 77.0 ppm;  $d_6$ -DMSO  $^1\text{H}$  NMR 2.53 ppm,  $^{13}\text{C}$  NMR 39.5 ppm). Mass spectra were obtained on a Varian MAT 311A/AMD in solid-probe at an ionization energy of 70 eV. CHN analysis: Perkin–Elmer 2400 Series II CHNS/O-Analyzer and Analyzer E240 C. IR: Nicolet–Magna Spectrometer 750 or Bruker IFS 25 spectrometer, using KBr disks (only major peaks are listed).

The potassium salts of **2** [44], **3** [24], **6** [31], and **8** [34,43] were obtained as described in the literature. The synthesis of the potassium salt of **7** is given below.  $\text{CH}_3\text{OH}$  for the preparation of **7-Tl**, was dried with  $\text{CaO}$  by heating under reflux for 4 h under an inert gas, followed by distillation.

### 2.1. Syntheses

#### 2.1.1. Hydrotris(pyrazolyl)boratothallium(I) (**2-Tl**)

A solution of  $\text{TlNO}_3$  (530 mg, 1.99 mmol) in a mixture of 5 ml of methanol and 5 ml of water was overlaid with a solution of potassium hydrotris(pyrazolyl)borate (500 mg, 1.98 mmol) in 10 ml of methanol. Slow diffusion of the solutions together with evaporation of the solvent to half the initial volume led to crystal growth. The crystals were collected after 1 week (yield 450 mg, 54%). The melting point of 155 °C and the  $^1\text{H}$  NMR and mass spectrometric characterizations agree with literature values [45].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 104.11, 135.60, 139.14. IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3112w ( $\nu\text{CH}$ ), 2443m, 2400w, 2369w ( $\nu\text{BH}$ ),

1501m, 1422m, 1394m, 1382m, 1295s, 1210s, 1185m, 1114s, 1078m, 1048s, 1038s, 970s, 774m, 754s, 737m, 722s, 665 m, 627m, 619m.

$\text{C}_9\text{H}_{10}\text{BN}_6\text{Tl}$  (417.41): Calc. 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%. The absence of K in the crystals was confirmed by AAS.

#### 2.1.2. Dihydrobis(1,2,4-triazolyl)boratothallium(I) (**3-Tl**)

A solution of potassium dihydrobis(triazolyl)borate (0.19 g, 1.00 mmol) in methanol (5 ml) was added to a solution of 266 mg (1.00 mmol) of  $\text{TlNO}_3$  in a 1:1 mixture of  $\text{H}_2\text{O}$ – $\text{MeOH}$  (6 ml). The cloudy solution was filtered and left to stand, partially open to air, for 3 weeks. Filtering the clear solution, now half volume, yielded large, clear crystals within 2 days, in a reproducible process (crystal yield 41 mg, 12%). IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3114w ( $\nu\text{CH}$ ), 2405s, 2270w ( $\nu\text{BH}$ ), 1498s ( $\nu\text{CH}$ ), 1306w, 1264m, 1158vs, 1129s, 1016w, 966m, 874w, 669s.  $\text{C}_4\text{H}_6\text{BN}_6\text{Tl}$  (353.33): Calc. C, 13.60; H, 1.71; N 23.79. Found: C, 13.60; H, 1.85; N, 23.51%.

#### 2.1.3. Hydrotris(imidazolyl)boratothallium(I) (**6-Tl**)

A solution of  $\text{TlNO}_3$  (530 mg, 1.99 mmol) in methanol (5 ml) and water (5 ml) was overlaid with a solution of potassium hydrotris(imidazolyl)borate (500 mg, 1.98 mmol) in methanol (10 ml). Slow diffusion of the solutions together with evaporation of the solvent to half of the initial volume led to crystal growth. The colorless needle-shaped crystals were collected after 1 week (yield 520 mg, 63%). Melting point (m.p.) 268–270 °C.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  (ppm) = 6.80 (s, 2H, H-4 and H-5), 7.24 (s, 1H, H-2).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  (ppm) = 120.60 (C-4), 127.98 (C-5), 139.65 (C-2). IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2430m, 2412m ( $\nu\text{BH}$ ), 1477s, 1207s, 1119s, 1073s, 924s.  $\text{C}_9\text{H}_{10}\text{BN}_6\text{Tl}$  (417.41): Calc. C, 25.90; H, 2.41; N, 20.13. Found: C, 25.96; H, 2.40; N, 20.07%.

#### 2.1.4. Dihydrobis(indazolyl)boratopotassium(I) (**7-K**)

$\text{KBH}_4$  (2.41 g, 44.6 mmol) was added to indazole (20.75 g, 178.6 mmol) and the mixture heated for 2 h at 170 °C under nitrogen. The mixture melted, with evolution of hydrogen, and was cooled down after the theoretical amount (2.2 l by wet-test-meter) of hydrogen had evolved. The excess indazole was sublimed out (120 °C,  $5 \times 10^{-2}$  mbar). To ensure complete sublimation, the unsublimed residue was crushed and sublimation continued. At this stage, the product may be sufficiently pure in a yield usually above 95%. If the NMR of the unsublimed residue still indicates impurities of indazole, the impure product can be dissolved in a minimum amount of boiling toluene, filtered and cooled. Precipitation/crystallization of the product may have to be induced by overlaying with petroleum

ether (30/50). Recrystallization from toluene gives relatively pure products but results in a considerably decreased yield (30–45%). The potassium salt of **7** can also be purified by conversion to the thallium salt (see below).  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  (ppm) = 6.85 (dtd, 4H, H-5 and H-6), 7.15 (dt, 2H, H-4), 7.58 (dt, 2H, H-7), 7.85 (d, 2H, H-3) (see drawing **7** for the NMR labeling). IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2359m ( $\nu\text{BH}$ ), 1615s, 1495s, 1476m, 1459s, 1258s, 1201s, 978m, 944m, 912s, 864m, 697m, 658m, 647m, 595m, 474m, 427m. Calc. for  $\text{C}_{14}\text{H}_{12}\text{BN}_4\text{K}$  (286.19) C, 58.76; H, 4.23; N, 19.58. Found: C, 56.14; H, 4.25; N, 18.61%. The potassium salt of **7** is water sensitive. Dissolution in methanol and water yields indazole.

### 2.1.5. Dihydrobis(indazolyl)boratothallium(I) (**7-Tl**)

$\text{TlNO}_3$  (2.55 g, 9.57 mmol) was dissolved in dried methanol (200 ml) with heating and ultrasonication. The solution was added to **7-K** (2.74 g, 9.57 mmol) in methanol (50 ml). The product forms almost instantly upon mixing. The immediate product yield (2.51 g, 58%) can be enhanced by cooling of or slow solvent evaporation from the mother liquor. Crystals were grown by slow solvent evaporation of either the mother liquor or a methanol solution of **7-Tl**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.06 (td, 2H, H-6), 7.38 (td, 2H, H-5), 7.63 (dt, 2H, H-4), 8.04 (d, 2H, H-3), 8.10 (dd, 2H, H-7) (see drawing **7** for the NMR labeling). IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2360m ( $\nu\text{BH}$ ), 1614s, 1497s, 1459s, 1399m, 1337m, 1259m, 1211m, 1185m, 1132s, 1111s, 1008m, 986m, 912s, 837m, 820m, 757s, 746s, 691m, 656m, 638m, 596m, 433m. Calc. for  $\text{C}_{14}\text{H}_{12}\text{BN}_4\text{Tl}$  (451.47) C, 37.25; H, 2.68; N, 12.41. Found: C, 36.63; H, 2.55; N, 13.06%.

### 2.1.6. Hydrotris(indazolyl)boratothallium(I) (**8-Tl**)

$\text{TlNO}_3$  (0.53 g, 2.0 mmol) in  $\text{CH}_3\text{OH}$  (10 ml) reacts with the potassium salt of **8** (0.80 g, 2.0 mmol), forming a white precipitate. This precipitate was filtered off and crystallized from dioxane through overlaying with petroleum ether (30/50). The product formed as colorless crystals (yield 0.67 mg, 59%).  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  = 7.00 (ddd, 3H, H-5,  $J_{5,4}$  = 8.07 Hz,  $J_{5,6}$  = 6.77 Hz,  $J_{5,7}$  = 0.92 Hz), 7.26 (ddd, 3H, H-6,  $J_{6,7}$  = 8.58 Hz,  $J_{6,5}$  = 6.77 Hz,  $J_{6,4}$  = 1.10 Hz), 7.67 ('dt', 3H, H-4,  $J_{4,5}$  = 8.07 Hz,  $J_{4,6}$  = 1.10 Hz,  $J_{4,7}$  = 0.98 Hz), 7.89 ('dq', 3H, H-7,  $J_{7,6}$  = 8.58 Hz,  $J_{7,4}$  = 0.98 Hz,  $J_{7,3}$  = 0.93 Hz,  $J_{7,5}$  = 0.92 Hz), 8.15 (d, 3H, H-3,  $J_{3,7}$  = 0.93 Hz) (see drawing **7** for the NMR labeling). MS (230 °C): 568 (26%,  $[M]^+$ ). Calc. for  $\text{C}_{21}\text{H}_{16}\text{BN}_6\text{Tl}$  (567.59) C, 44.44; H, 2.84; N, 14.81; Tl, 36.00. Found: C, 43.67; H, 2.56; N, 14.51; Tl, 35.70%.

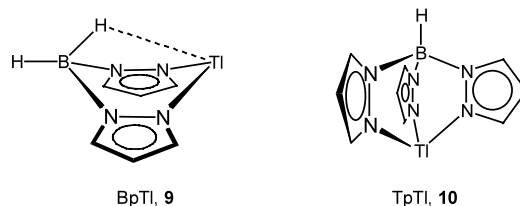
## 2.2. X-ray structure determinations

Data were collected using the  $\omega$ -scan method with

Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$ ) and a graphite monochromator on a Syntex  $P2_1$  four-circle diffractometer (**2-Tl**) or a Bruker AXS CCD diffractometer. All crystals were colorless. Structure solution was done using direct methods (SHELXS-97 [46]); refinement was done by full-matrix least squares on  $F^2$ , again using SHELXL-97 [46]. All non-hydrogen atoms were found and refined anisotropically. The hydrogen atoms on boron were found and refined in **3-Tl** and **6-Tl**, and calculated for **2-Tl**, **8-Tl** (AFIX 13) and **7-Tl** (AFIX 23) with  $U(\text{H}) = 0.08$ . The hydrogen atoms on carbons were placed at calculated positions with bond lengths free to refine (HFIX 44 for **6-Tl**) or with  $d_{\text{C-H}} = 0.94 \text{ \AA}$ , using appropriate riding models (HFIX 43) and isotropic temperature factors of  $U(\text{H}) = 0.08$  (**2-Tl**, **7-Tl**, **8-Tl**) or  $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$  (**3-Tl**) or  $U(\text{H}) = 1.5 U_{\text{eq}}(\text{C}, \text{N})$  (**6-Tl**). The growth of good quality crystals for **2-Tl** was difficult and hence its X-ray structure is not without problems (see Table 1 and Fig. 1). Crystal data are given in Table 1. Graphics were obtained with ORTEP3 for Windows [47] with displacement ellipsoids shown at the 50% probability level and H atoms shown as spheres of arbitrary radii.

## 3. Results and discussion

The basic metal-ligand motif of most BpTl [4] and TpTl complexes [21] is as depicted in compound **9** and **10**, respectively. The bonding of the bidentate Bp is supplemented by a weak agostic B–H $\cdots$ Tl interaction [48–50].



Otherwise there is little variation in the bis- and tris-chelating mode of the two scorpionate ligands towards thallium. A few structures show additional Tl $\cdots$ Tl contacts below 4.0 Å, namely BpTl [4], Bp<sup>bipy</sup>Tl (bipy = 6-2,2'-bipyridine) [51], Tp<sup>cyclopropyl</sup>Tl [52], and Tp<sup>p-tolyl</sup>Tl [53]. The abbreviation Bp<sup>XR</sup> and Tp<sup>XR</sup> follows the suggested nomenclature by Trofimenko [14,15] to indicate a substituent R in the X position on the pyrazolyl ring.

Exceptions to the common  $\text{C}_3$ -trigonal motif for TpTl complexes only occur when the hydrogen atom on boron is replaced by a more sterically demanding group. Known compounds are PhTp<sup>tBu</sup>Tl [54], FcTpTl (Fc = ferrocenyl) [55], and MeTp<sup>Me2</sup>Tl [56]. Probably due to steric effects, one of the pyrazolyl rings rotates

Table 1  
Crystal data for the thallium complexes of **2**, **3**, **6**, **7**, and **8**

Compound	2-Tl <sup>a</sup>	3-Tl	6-Tl	7-Tl	8-Tl
Formula	C <sub>9</sub> H <sub>10</sub> BN <sub>6</sub> Tl	C <sub>4</sub> H <sub>6</sub> BN <sub>6</sub> Tl	C <sub>9</sub> H <sub>10</sub> BN <sub>6</sub> Tl	C <sub>14</sub> H <sub>12</sub> BN <sub>4</sub> Tl	C <sub>21</sub> H <sub>16</sub> BN <sub>6</sub> Tl
<i>M</i> (g mol <sup>-1</sup> )	417.41	353.34	417.41	451.46	567.58
Crystal size (mm)	0.2 × 0.2 × 0.15	0.45 × 0.29 × 0.23	0.24 × 0.05 × 0.05	0.62 × 0.25 × 0.08	0.48 × 0.21 × 0.08
<i>T</i> (K)	298(2)	207(2)	298(2)	173(2)	173(2)
2θ Range (°)	2.4–55.0	5.7–56.5	5.2–50.0	3.7–55.0	4.0–55.0
<i>h</i> ; <i>k</i> ; <i>l</i> Range	0, 10; 0, 12; –22, 22	–9, 9; –22, 23; –7, 8	–10, 10; –10, 8; –18, 15	–12, 17; –6, 7; –22, 22	–34, 26; –9, 9; –14, 14
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2
<i>a</i> (Å)	7.928(6)	7.721(2)	8.706(2)	13.2472(6)	26.6043(4)
<i>b</i> (Å)	9.306(4)	17.793(4)	9.192(2)	5.8224(2)	7.1280(2)
<i>c</i> (Å)	17.16(2)	6.029(1)	15.261(4)	17.5104(8)	11.0435(4)
β (°)	92.06(8)	90.00	94.740(9)	94.681(3)	111.179(3)
<i>V</i> (Å <sup>3</sup> )	1265(2)	828.2(2)	1217.0(3)	1346.1(1)	1952.79(5)
<i>Z</i>	4	4	4	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.191	2.834	2.278	2.228	1.931
μ (cm <sup>-1</sup> )	127.5	194.5	132.6	119.9	82.9
<i>F</i> (000)	768	632	768	840	1080
Absorption correlation	none <sup>b</sup>	SADABS	SADABS	SADABS	SADABS [60]
Max; min transmission		1.000; 0.3015	1.0000; 0.408	1.000; 0.508	1.000; 0.321
Measured reflection	3330	7350	6084	9883	7635
Unique reflection ( <i>R</i> <sub>int</sub> )	3083 (0.0878)	1939 (0.0555)	2136 (0.0645)	3083 (0.0456)	4265 (0.0549)
Observed reflection [ <i>I</i> > 2σ( <i>I</i> )]	1637	1756	1618	2645	3583
Parameters refined	310	116	167	181	263
Max; min Δρ (eÅ <sup>-3</sup> ) <sup>c</sup>	1.042; –1.834 <sup>d</sup>	2.115; –1.660 <sup>d</sup>	0.969; –1.361 <sup>d</sup>	0.738; –1.152 <sup>d</sup>	1.918; –2.548 <sup>d</sup>
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0692; 0.1256	0.0287; 0.0600	0.0345; 0.0730	0.0259; 0.0535	0.0496; 0.1101
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> all reflection	0.1556; 0.1611	0.0304; 0.0602	0.0489; 0.0771	0.0358; 0.0558	0.0622; 0.1151
Extinction coefficient	0.00810(13)	0.0109(4)	not refined	not refined	not refined
GOF on <i>F</i> <sup>2</sup> <sup>e</sup>	1.081	0.963	0.923	1.026	1.006
Weighting scheme <i>w</i> <sup>f</sup> <i>a</i> ; <i>b</i>	0.0607; 0.000	0.023; 0.0000	0.0426; 0.0000	0.0165; 0.0000	0.0548; 0.0000
Absolute structure parameter (Fleck value)[61]	–0.02(4)	0.01(2)	–	–	0.14(2)

<sup>a</sup> Two independent molecules in the unit cell.

<sup>b</sup> An empirical absorption correction (DIFABS) for **2-Tl** was carried out but did not lead to a significant improvement and, therefore, was not included in the final refinement.

<sup>c</sup> Residual electron density, largest difference peak and hole.

<sup>d</sup> In the vicinity of the thallium atom.

<sup>e</sup> GOF, goodness of fit.

<sup>f</sup>  $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$  where  $P = (\max(F_o^2 \text{ or } 0) + 2 \cdot F_c^2)/3$ .

around the B–N bond and either coordinates with N1 to thallium, as in PhTp<sup>tBu</sup>Tl, or with N2 to a thallium atom of another molecule. The latter is the case in FcTpTl and MeTp<sup>Me2</sup>Tl, which exhibit polymeric structures due to the bridging nature of the ligand.

The molecular and crystal structures of the complexes reported here will be discussed in the following. Unremarkable distances and angles are not discussed in detail but are listed in the figure captions and are summarized in Table 2. Unless otherwise noted, the Tl–N distances fall in the normal range of 2.50–2.73 Å [1,21] found for Tl–N contacts in BpTl and TpTl structures.

A notable feature of most of the structures reported here is that they crystallize in chiral space groups. This is the case for **2-Tl** (*P*2<sub>1</sub>), **3-Tl** (*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) and **8-Tl** (*C*2). The structures of **2-Tl** and **3-Tl** were refined as pure

enantiomers. For **8-Tl** the crystal structure was refined as a twin with an enantiomer ratio of 86(2) to 14(2)%

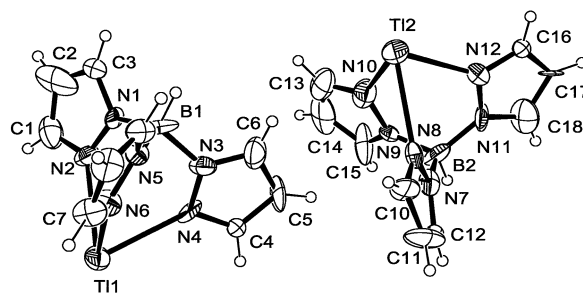


Fig. 1. The two independent molecular moieties in **2-Tl**. Selected distances (Å) and angles (°): Tl1–N2 2.665(6), Tl1–N4 2.575(7), Tl1–N6 2.730(7), Tl2–N8 2.651(7), Tl2–N10 2.547(7), Tl2–N12 2.590(8) Å, N–Tl–N 69.6(2)°–73.6°.



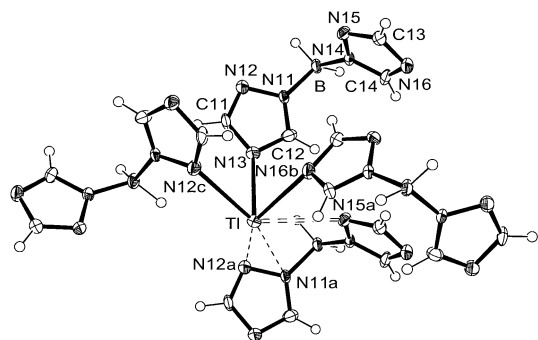


Fig. 3. Coordination environment around thallium in 3-Tl. Selected distances (Å) and angles (°): Tl–N12c 2.767(7), Tl–N13 2.674(7), Tl–N16b 2.803(7), Tl⋯N15a 3.132(7), Tl⋯N12a 3.360(7), Tl⋯N11a 3.762(7), N12c–Tl–N13 76.1(2), N12–Tl–N16b 77.4(2), N13–Tl–N16b 83.7(2). Symmetry relation  $a = x, y, z + 1$ ;  $b = -x + 1/2, -y, z + 1/2$ ;  $c = x + 1/2, -y + 1/2, -z + 2$ .

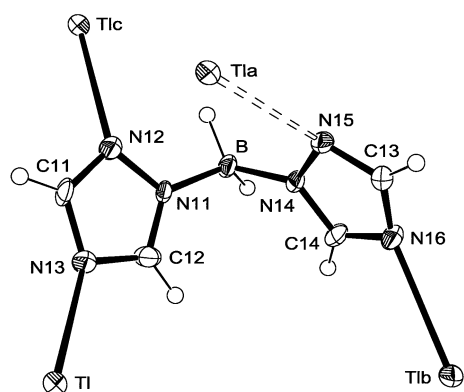


Fig. 4. Bridging action of the ligand in 3-Tl. For distances see the caption to Fig. 3. Symmetry relation  $a = x, y, z - 1$ ;  $b = -x + 1/2, -y, z - 1/2$ ;  $c = x - 1/2, -y + 1/2, -z + 2$ .

There are two different donor atoms in the 1,2,4-triazolyl ring, with both the endo-(2-N) and the exo-dentate (4-N) nitrogen atoms acting as donor atoms. Thus, each ligand bridges three thallium atoms (Fig. 4), leaving one of the endo-dentate nitrogen atoms (N15) with only a weak thallium coordination. Similar bridging actions of poly(triazolyl)borate ligands between transition-metal centers have been observed previously [22,23,25,26]. In 3-Tl, the bridging leads to an extended, three-dimensional (3D) structure (Fig. 5). Electrostatic interactions between thallium and triazolyl rings from neighboring molecules can also be seen (see Fig. 3).

Unlike **2**, the isomeric hydrotris(imidazolyl)borate ligand **6** cannot chelate a metal center but instead bridges metal ions. The formation of coordination polymers is then expected. In the structure of hydrotris(imidazolyl)boratothallium(I), **6-Tl**, each of the three imidazolyl rings coordinates to a different (albeit symmetry related) metal center, as shown in Fig. 6. Two adjacent ligands bridge two neighboring thallium ions. From this a one-dimensional (1D) ladder-like strand is

formed. A two- or even three-dimensional framework, as in **3-Tl**, may be another possibility for the metal-ligand assembly. The packing of adjacent strands in **6-Tl** is probably dictated by electrostatic interactions between the thallium ion and imidazolyl  $\pi$  manifolds as in **2-Tl**. These non-bonding Tl⋯C and Tl⋯N interactions appear less significant than in the structures of **1-Tl** and **7-Tl** (see Table 2). Tl⋯centroid contacts start at 3.69 Å and Tl⋯C/N distances are above 3.723/3.767 Å. At the same time, the packing of neighboring strands is such that there are no close Tl⋯Tl distances ( $> 4.69$  Å). The bridging action of **6** is again reminiscent of the bridge formation of the related poly(1,2,4-triazolyl)borate [22,23,25,26] and dihydrobis(tetrazolyl)borate ligand [28,30], which also possess nitrogen donors in a 1,3-position to the B–N bond.

In a first approximation the crystal structure of dihydrobis(indazolyl)boratothallium(I), **7-Tl** consists of monomeric units (Fig. 7). Yet these monomeric unit are arranged in centrosymmetric pairs, apparently through thallium– $\pi$  interactions, as indicated in Fig. 8. The indazolyl moiety from N21 to C27 which is engaged in the Tl– $\pi$  interaction has a longer Tl–N(22) bond [2.652(4) Å] than the other [Tl–N(12), 2.565(3) Å]. The Tl– $\pi$  contact may relieve the need for an agostic B–H⋯Tl interaction. The B⋯Tl and (B–)H⋯Tl distances are 3.52 and 3.16 Å, respectively, which is considerably greater than the B⋯Tl distance of 3.2–3.3 Å observed in most Bp<sup>RR</sup>Tl compounds [4]. Additional packing in the crystal structure of **7-Tl** is controlled by intermolecular C–H⋯ $\pi$  interactions [34,58], as may be seen in Fig. 9. Shortest C–H⋯C/N contacts are between C11–H of the five-membered ring to N11d (2.81 Å), N12d (2.72 Å) and C11d (2.80 Å) of a neighboring five-membered ring (symmetry relation  $d = 3/2 - x, -1/2 + y, 3/2 - z$ ). The dihedral angle between these two five-membered rings is 53.3°. C–H⋯C contacts between the six-membered rings of the indazolyl moiety are above 2.93 Å. The shortest Tl⋯Tl distances of 4.156 Å in **7-Tl** are not within the Tl⋯ $\pi$  pairs but are to a neighboring molecule with symmetry relation  $-x + 1, -y, -z + 1$ .

The molecular structure of hydrotris(indazolyl)boratothallium(I), **8-Tl**, is depicted in Fig. 10. At first sight, the molecule appears to show the typical  $C_{3v}$  symmetrical metal-ligand motif. However, there is a considerable Tl–N bond length variation; from 2.584(8) Å for Tl–N12 and 2.590(9) Å for Tl–N22 to 2.747(8) Å for Tl–N32. The cause of this variation becomes apparent from the molecular packing: in the crystal structure these molecules are arranged in pairs. These pairs are obviously held together by slipped face-to-face  $\pi$ -stacking [59] of two indenyl moieties as shown in Fig. 11. The  $\pi$ -stacking is such that the two thallium centers are pointing in the same direction. The molecular units of

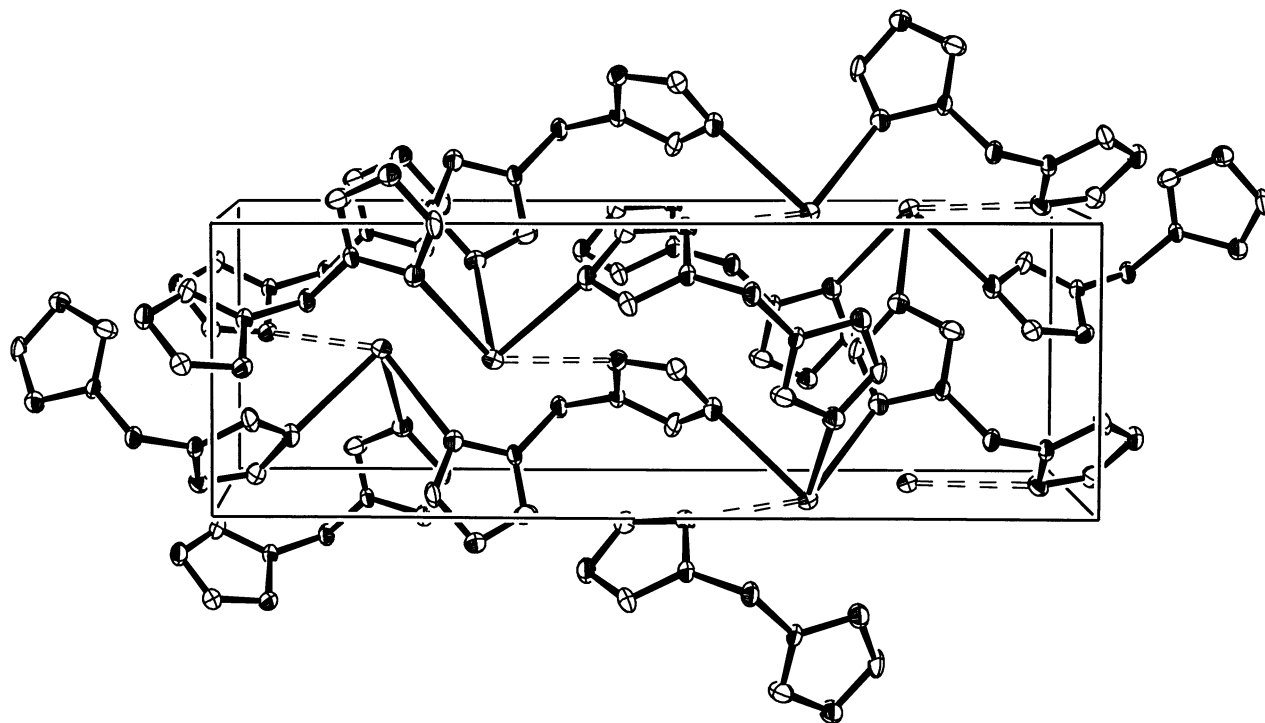


Fig. 5. Packing diagram of **3-Tl**, illustrating the extended 3D framework; view along *a*. Hydrogen atoms have been omitted for clarity. The weak Tl...N15 interactions are shown as dashed lines. Tl...Tl distances are 4.564 Å.

each pair are related through a  $C_2$ -symmetry operation, with no mirror plane or center of inversion. Hence each pair represents a chiral entity. As pointed out above, the single crystal did not show a 50:50 mixture of *R*- and *S*-pairs. Structure solution and refinement was only successful in the non-centrosymmetric space group  $C2$ . The crystal structure was refined as a (racemic) twin with an enantiomer ratio of 86(2) to 14(2)% for the selected crystal.

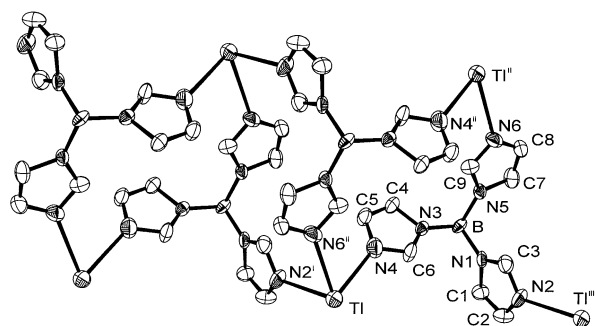


Fig. 6. Section of the one-dimensional polymeric structure of **6-Tl**. Hydrogen atoms have been omitted for clarity. The chains run along the crystallographic *a* direction. Selected distances (Å) and angles (°): Tl–N4 2.663(7), Tl–N2' 2.656(6), Tl–N6'' 2.633(7), N6''–Tl–N2' 80.8(2), N6''–Tl–N4 77.4(2), N2'–Tl–N4 86.3(2). Angles between the imidazolyl ring planes: ring N1·N2–N3·N4 89.8(5)°, ring N3·N4–N5·N6 72.4(5)°, ring N1·N2–N5·N6 79.4(5)°. Symmetry relations: ' =  $x - 1, y, z$ ; '' =  $1 - x, 1 - y, 1 - z$ ; ''' =  $x + 1, y, z$ .

Non-bonded Tl...C and Tl...N distances are again less significant than in the structures of **1-Tl** and **7-Tl** (see Table 2). Tl...centroid contacts start at 3.89 Å and Tl...C/N distances are above 3.968/3.672 Å, respectively. There are no close Tl...Tl distances ( $> 4.45$  Å). Further packing interactions are dictated by C–H... $\pi$  interactions between the indazolyl groups [34].

The Tl–N bond to the  $\pi$ -interacting indazolyl ring is longer than the other two Tl–N bonds. The solution NMR spectra of **8-Tl** shows that all three rings are equivalent due to loose or solvent-separated cation–anion contacts and to the absence of neighboring  $\pi$ -interactions, respectively.

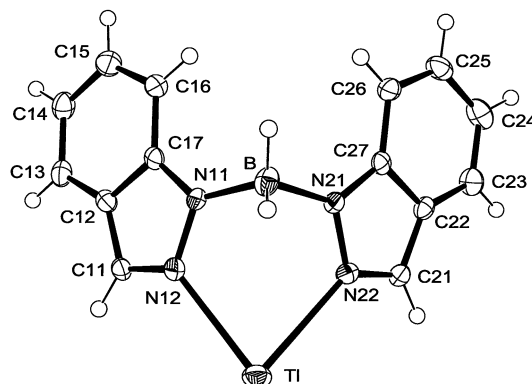


Fig. 7. Monomeric unit in **7-Tl**. Selected distances (Å) and angles (°): Tl–N12 2.565(3), Tl–N22 2.652(4), N21–Tl–N22 75.6(1).

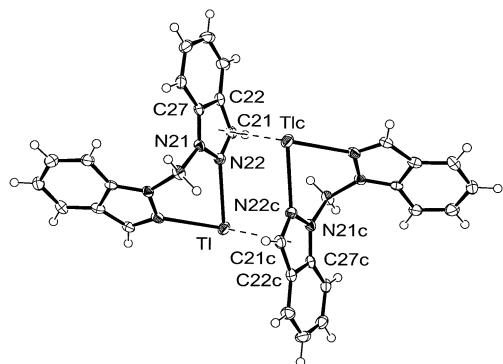


Fig. 8. Arrangement of centrosymmetric pairs in the structure of 7-Tl. Selected Tl- $\pi$  distances ( $\text{\AA}$ ): Tl...N21c 3.340(4), Tl...N22c 3.280(4), Tl...C21c 3.479(4), Tl...C22c 3.690(4), Tl...C27c 3.579(4), Tl...centroid (N21c-C27c) 3.267(4), Tl...Tlc 4.654(4). Symmetry relation  $c = -x + 1, -y + 1, -z + 1$ .

#### 4. Conclusions

Thallium complexes of modified poly(pyrazolyl)-borate ligands offer a great variability in their metal-ligand and crystal packing arrangement. Additional donor atoms in the azolyl ring or a 1,3- (cf. 1,2-) position of the nitrogen atoms in the ring gives rise to extended structures with bridging borate ligands. Electrostatic Tl... $\pi_{\text{azolyl}}$  interactions can be quite prominent in the crystal packing of the molecular

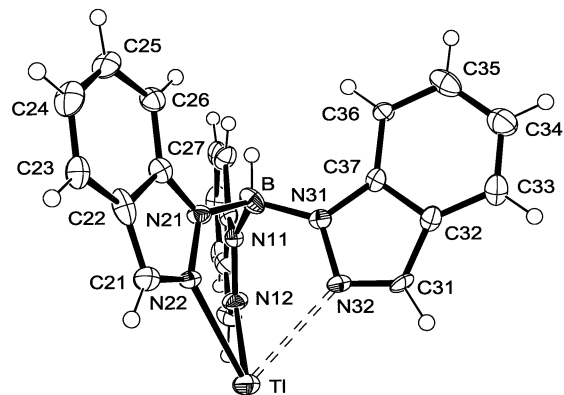


Fig. 10. Monomeric unit in 8-Tl. The indazolyl ring with N11 and N12 could not be fully labeled for obvious reasons, yet the numbering scheme follows that of the other two rings. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Tl-N12 2.590(9), Tl-N22 2.584(8), Tl-N32 2.747(8), N22-Tl-N12 74.6(3), N22-Tl-N32 70.2(3), N12-Tl-N32 68.4(3).

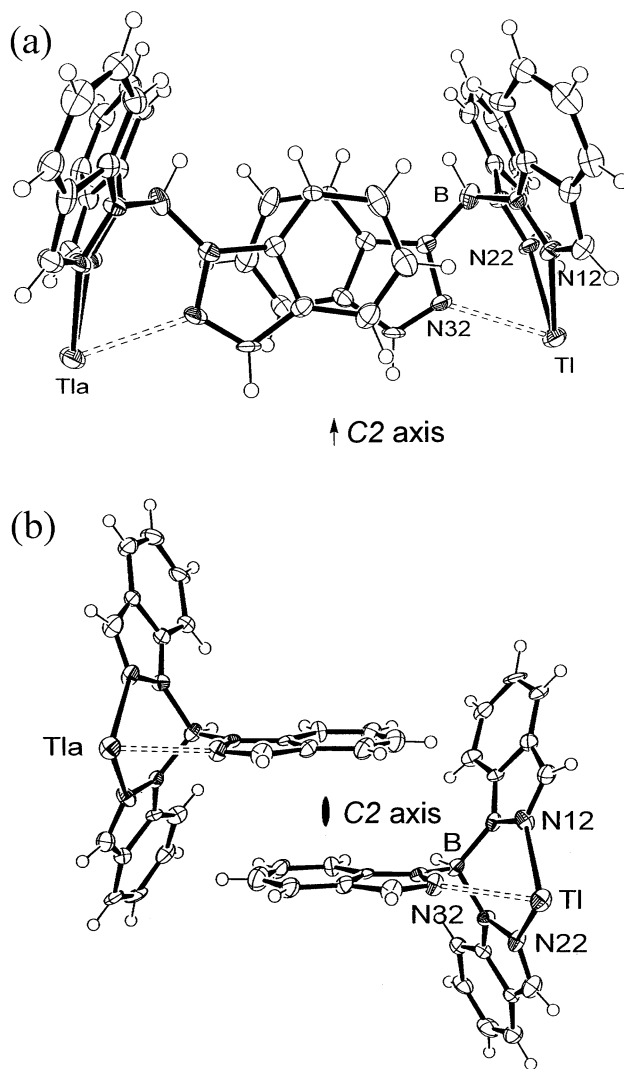


Fig. 11.  $\pi$ - $\pi$ -stacked pairs of molecular units of 8-Tl in the solid state, (a) top view, (b) front view. The  $\pi$ - $\pi$  separation is 3.58  $\text{\AA}$ . Symmetry relation  $a = 1 - x, y, 1 - z$ .

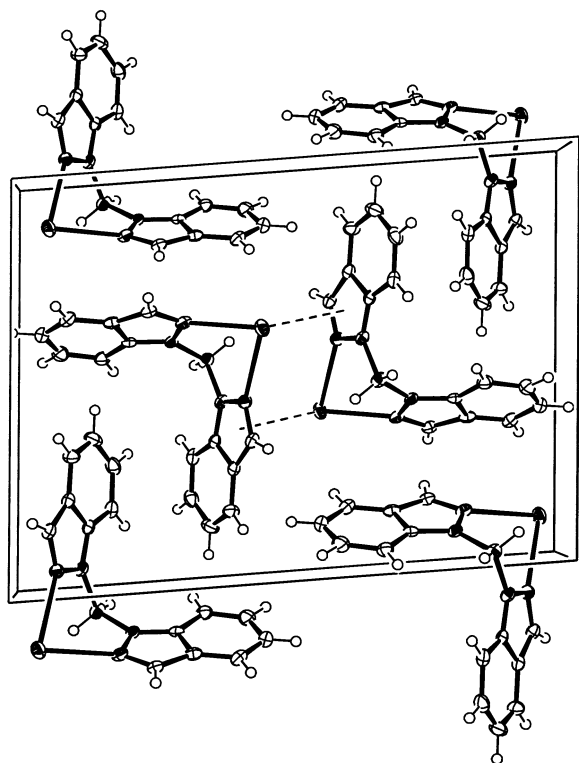


Fig. 9. Packing diagram for 7-Tl; view along *b*.



thallium-ligand chelate complexes. For azolyl rings with extended  $\pi$ -systems, such as indazolyl, an offset ( $\pi$ - $\pi$ )<sub>indazolyl</sub> stacking can also be significant. These solid-state packing effects are seen as the origin of the frequent crystallization of thallium(I) or in general metal(I) poly(azolyl)borate complexes in chiral space groups. The azolyl rings which are engaged in these type of  $\pi$  interactions show an increase in their Tl–N bond. There appears to be a reciprocal correlation between the strength of the  $\pi$  interactions and the Tl–N bonds.

## 5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-101006 (2-Tl), -168036 (3-Tl), -135180 (6-Tl), -168037 (7-Tl), -141090 (8-Tl). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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