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

Emma Craven 1, Esra Mutlu, Daniel Lundberg 2, Savaş Temizdemir, Sebastian Dechert, Horst Brombacher, Christoph Janiak *

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany

Received 2 August 2001; accepted 27 November 2001

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···azolyl interactions between neighboring molecules. In 8-Tl the molecular units are arranged in pairs through indazolyl···azolyl 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 P21, P212121, and C2, respectively.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Thallium(I) complexes; Scorpionate ligands; Crystal packing; π-Stacking; Cation−π interaction

1. Introduction

Thallium(I) is formally a low-valence p-block metal with a closed sub-shell (s²). 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 - denotes the third pyrazolyl ring which is oriented to the rear

* Corresponding author. Tel.: +49-761-203-6127; fax: +49-761-203-6147.
E-mail address: janiak@uni-freiburg.de (C. Janiak).

1 Exchange student from the University of Western Australia, Perth, Australia.
2 Erasmus fellow from Uppsala University, Uppsala, Sweden.

Thallium(I) derivatives of poly(pyrazolyl)borato 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(mercaptopimidazolyl)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].
2. Experimental

NMR spectra were collected on a Bruker ARX200 (200.1 MHz for $^1$H, 50.3 MHz for $^{13}$C) or ARX400 ($^8$-Tl) and calibrated against the solvent signal (CDCl$_3$, $^1$H NMR 7.26 ppm, $^{13}$C NMR 77.0 ppm; $d_6$-DMSO $^1$H NMR 2.53 ppm, $^{13}$C NMR 39.5 ppm). Mass spectra were obtained on a Varian MAT 311A CHNS/O-Analyzer C. IR: Nicolet–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. CH$_3$OH for the preparation of 7-Tl was dried with 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 TlNO$_3$ (530 mg, 1.99 mmol) in a mixture of 5 ml of methanol and 5 ml of water was overlayered 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 $^1$H NMR and mass spectrometric characterizations agree with literature values [45]. $^{13}$C NMR (CDCl$_3$): δ (ppm) = 104.11, 135.60, 139.14. IR: $\tilde{\nu}$ (cm$^{-1}$) = 3112w (vCH), 2443m, 2400w, 2369w (vBH), 1501m, 1422m, 1394m, 1382m, 1295s, 1210s, 1185m, 1114s, 1078m, 1048s, 1038s, 970s, 774m, 754s, 737m, 722s, 665 m, 627m, 619m.

$\text{C}_{9}H_{10}BN_{6}Tl$ (417.41): Calc. C, 13.60; H, 1.85; N, 23.51%. Found: C, 13.60; H, 1.85; N, 23.51%.

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 TlNO$_3$ in a 1:1 mixture of H$_2$O–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: $\tilde{\nu}$ (cm$^{-1}$) = 3114w (vCH), 2405s, 2270w (vBH), 1498s (vCH), 1306w, 1264m, 1158s, 1129s, 1016w, 966m, 874w, 669s. 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 TlNO$_3$ (530 mg, 1.99 mmol) in methanol (5 ml) and water (5 ml) was overlayered 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 155 °C, yield 41 mg, 12%. IR: $\tilde{\nu}$ (cm$^{-1}$) = 3114w (vCH), 2405s, 2270w (vBH), 1498s (vCH), 1306w, 1264m, 1158s, 1129s, 1016w, 966m, 874w, 669s. Calc. C, 25.90; H, 2.41; N, 20.13. Found: C, 25.96; H, 2.40; N, 20.07%.

2.1.4. Dihydrobis(imidazolyl)boratothallium(I) (7-K)

$\text{KBH}_4$ (2.41 g, 44.6 mmol) was added to indazole (40.75 g, 178.6 mmol) and the mixture heated for 2 h at 170 °C under nitrogen. The mixture melted, with evaporation 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 at 120 °C, 5 × 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 overlayering with petroleum

$\text{C}_{9}H_{10}BN_{6}Tl$ (417.41): Calc. C, 13.60; H, 1.85; N, 23.51%.

$\text{C}_{9}H_{10}BN_{6}Tl$ (417.41): Calc. C, 13.60; H, 1.85; N, 23.51%.

$\text{C}_{9}H_{10}BN_{6}Tl$ (417.41): Calc. C, 13.60; H, 1.85; N, 23.51%.
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). $^1$H NMR ($d_e$-DMSO): $\delta$ (ppm) = 6.85 (ddt, 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: $\tilde{\nu}$ (cm$^{-1}$) = 2359m ($\nu$BH), 1615s, 1495s, 1476m, 1459s, 1258s, 1201s, 978m, 944m, 912s, 864m, 697m, 658m, 647m, 595m, 474m, 427m. Calc. for C$_{14}$H$_{12}$BN$_4$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)

TINO$_3$ (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 filtered off and washed with ethanol (2.50 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. $^1$H NMR (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: $\tilde{\nu}$ (cm$^{-1}$) = 2360m ($\nu$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 C$_{14}$H$_9$BN$_5$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)

TINO$_3$ (0.53 g, 2.0 mmol) in CH$_3$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 overlayering with petroleum ether (30/50). The product formed as colorless crystals (yield 0.67 mg, 59%). $^1$H NMR ($d_e$-DMSO): $\delta$ = 7.00 (ddd, 3H, H-5, J$_{5,6}$ = 8.07 Hz, J$_{5,4}$ = 6.77 Hz, J$_{5,7}$ = 0.92 Hz), 7.26 (ddd, 3H, H-6, J$_{6,3}$ = 8.58 Hz, J$_{6,5}$ = 6.77 Hz, J$_{6,4}$ = 1.10 Hz), 7.67 (tdt, 3H, H-4, J$_{4,5}$ = 6.07 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$_{3,7}$ = 9.3 Hz) (see drawing 7 for the NMR labeling). MS (230 °C): 568 (26%, [M$^+$. Calc. for C$_{21}$H$_{16}$BN$_6$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 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 $U$(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 $d_{C-H} = 0.94$ Å, using appropriate riding models (HFIX 43) and isotropic temperature factors of $U$(H) = 0.08 (2-Tl, 7-Tl, 8-Tl) or $U$(H) = 1.2 $U$eq(C, N) (3-Tl) or $U$(H) = 1.5 $U$eq(C, 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···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···Tl contacts below 4.0 Å, namely BpTl [4], Bp$^{bipy}$Tl (bipy = 6-2,2'-bipyridine) [51], Tp$^{scloprop}$Tl [52], and Tp$^{toly}$Tl [53]. The abbreviation Bp$_{NR}$ and Tp$_{NR}$ 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 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$^\text{Bu}$Tl [54], FcTpTl (Fc = ferrocenyl) [55], and MeTp$^{sec}$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

<table>
<thead>
<tr>
<th>Compound</th>
<th>2-Tl a</th>
<th>3-Tl</th>
<th>6-Tl</th>
<th>7-Tl</th>
<th>8-Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₄H₁₂BN₄Tl</td>
<td>C₁₄H₁₀BN₄Tl</td>
<td>C₁₄H₁₀BN₄Tl</td>
<td>C₁₄H₁₀BN₄Tl</td>
<td>C₁₃H₁₆BN₄Tl</td>
</tr>
<tr>
<td>M (g mol⁻¹)</td>
<td>417.41</td>
<td>353.34</td>
<td>417.41</td>
<td>451.46</td>
<td>567.58</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.2×0.2×0.15</td>
<td>0.45×0.29×0.23</td>
<td>0.24×0.05×0.05</td>
<td>0.62×0.25×0.08</td>
<td>0.48×0.21×0.08</td>
</tr>
<tr>
<td>T (K)</td>
<td>298(2)</td>
<td>207(2)</td>
<td>298(2)</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>2θ Range (°)</td>
<td>2.4–55.0</td>
<td>5.7–56.5</td>
<td>5.2–50.0</td>
<td>3.7–55.0</td>
<td>4.0–55.0</td>
</tr>
<tr>
<td>h; k; l Range</td>
<td>0, 10; 0, 12; –9, 9; –22, 23; –10, 10; –10, 8; –12, 17; –6, 7; –34, 26; –9, 9; –18, 15</td>
<td>–22, 22</td>
<td>–22, 22</td>
<td>–14, 14</td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>C2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.928(6)</td>
<td>7.721(2)</td>
<td>8.706(2)</td>
<td>13.2472(6)</td>
<td>1952.79(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.93(4)</td>
<td>17.93(4)</td>
<td>9.19(2)</td>
<td>5.8224(2)</td>
<td>7.1280(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.16(2)</td>
<td>6.02(1)</td>
<td>15.26(1)</td>
<td>17.5(1)</td>
<td>11.0435(4)</td>
</tr>
<tr>
<td>β (°)</td>
<td>92.06(8)</td>
<td>94.740(9)</td>
<td>111.179(3)</td>
<td>111.179(3)</td>
<td>111.179(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1265(2)</td>
<td>828.2(2)</td>
<td>1217.0(3)</td>
<td>1346.1(1)</td>
<td>1952.79(5)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dcalc (g cm⁻³)</td>
<td>2.191</td>
<td>2.834</td>
<td>2.278</td>
<td>2.228</td>
<td>1.931</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
<td>127.5</td>
<td>194.5</td>
<td>132.6</td>
<td>119.9</td>
<td>82.9</td>
</tr>
<tr>
<td>F(000)</td>
<td>768</td>
<td>632</td>
<td>768</td>
<td>840</td>
<td>1080</td>
</tr>
<tr>
<td>Absorption correlation</td>
<td>none b</td>
<td>SADABS</td>
<td>SADABS</td>
<td>SADABS</td>
<td>SADABS [60]</td>
</tr>
<tr>
<td>Max; min transmission</td>
<td>1.000; 0.3015</td>
<td>1.000; 0.408</td>
<td>1.000; 0.508</td>
<td>1.000; 0.321</td>
<td>1.000; 0.321</td>
</tr>
<tr>
<td>Measured reflection</td>
<td>3330</td>
<td>7350</td>
<td>9883</td>
<td>7635</td>
<td>7635</td>
</tr>
<tr>
<td>Unique reflection (Rint)</td>
<td>3083(0.0878)</td>
<td>1939(0.0555)</td>
<td>2136(0.0645)</td>
<td>3083(0.0456)</td>
<td>4265(0.0549)</td>
</tr>
<tr>
<td>Observed reflection [I&gt;2σ(I)]</td>
<td>1637</td>
<td>1756</td>
<td>1618</td>
<td>2645</td>
<td>3583</td>
</tr>
<tr>
<td>Parameters refined</td>
<td>310</td>
<td>116</td>
<td>167</td>
<td>181</td>
<td>263</td>
</tr>
<tr>
<td>Max; min Δρ (eÅ⁻³)</td>
<td>1.042; –1.834</td>
<td>-1.660</td>
<td>0.969; –1.361</td>
<td>0.738; –1.152</td>
<td>1.918; –2.548</td>
</tr>
<tr>
<td>R₁; wR₁ [I&gt;2σ(I)]</td>
<td>0.0692; 0.1256</td>
<td>0.0287; 0.0600</td>
<td>0.0345; 0.0730</td>
<td>0.0259; 0.0535</td>
<td>0.0496; 0.1101</td>
</tr>
<tr>
<td>R₂; all reflection</td>
<td>0.1556; 0.1611</td>
<td>0.0304; 0.0602</td>
<td>0.0489; 0.0771</td>
<td>0.0358; 0.0558</td>
<td>0.0622; 0.1115</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00810(13)</td>
<td>0.0109(4)</td>
<td>not refined</td>
<td>not refined</td>
<td>not refined</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.081</td>
<td>0.963</td>
<td>0.923</td>
<td>1.026</td>
<td>1.006</td>
</tr>
<tr>
<td>Weighting scheme w = 1/[(σ²(F₀²)+αP²+bP)] where P = (max(F₀² or 0)+2F²)/3.</td>
<td>0.0607; 0.000</td>
<td>0.023; 0.0000</td>
<td>0.0426; 0.0000</td>
<td>0.0165; 0.0000</td>
<td>0.0548; 0.0000</td>
</tr>
<tr>
<td>Absolute structure parameter (Flack value)</td>
<td>–0.02(4)</td>
<td>0.01(2)</td>
<td>–</td>
<td>–</td>
<td>0.14(2)</td>
</tr>
</tbody>
</table>

a Two independent molecules in the unit cell.

b 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.

c Residual electron density, largest difference peak and hole.

d In the vicinity of the thallium atom.

e GOF, goodness of fit.

around the B–N bond and either coordinates with N1 to thallium, as in PhTp⁺³Tl, or with N2 to a thallium atom of another molecule. The latter is the case in FcTl and MeTlMe₂Tl, 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 (P2₁), 3-Tl (P2₁/n), and 8-Tl (C2). 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°.
for the selected crystal. The crystallization of these poly(azolyl)borate thallium structures in non-centrosymmetric space groups cannot be dismissed as accidental but instead may be a more general phenomena in poly(azolyl)borate complexes with univalent metals. Unresolved chiral materials usually crystallize as a racemate and the frequency of spontaneous resolution is unusual here. A non-centrosymmetric space group (Pna2₁) is also found for hydrotris(1,2,4-triazolyl)boratosilver(I) [25]. In addition, the same chiral space group (P2₁2₁2₁) was determined for both dihydrobis(1,2,4-triazolyl)boratopotassium [57] and the thallium analog 3-Tl. The chirality is due to the solid-state packing in these structures. The ligands (or metal centers) by themselves are achiral. In 2-Tl the chirality may be traced to the formation of 2₁-helical strands. In 3-Tl it is due to the pyramidal or pseudo-tetrahedral coordination (taking into account the space of the presumed lone-pair) of the thallium centers by three (four) different ligands which creates the asymmetric centers. The structure of 8-Tl features pairs of molecules where the two halves are related through a C₂ symmetry operation. Each pair represents a chiral entity. The molecular structure of the prototypical hydrotris(pyrazolyl)thallium, 2-Tl shows the usual pyramidal geometry of the thallium atom (Fig. 1). The packing of 2-Tl reveals kinked, chain-type arrangements of the metal-ligand moieties (Fig. 2), with two different chain types present in the unit cell for the two crystallographically different Tl centers. The packing is most likely dictated by electrostatic interactions between the thallium and pyrazolyl π-manifolds from neighboring molecules. These non-bonded Tl–C and Tl–N distances are in the range of 3.683–3.781 Å (ring N1b–C3b) and 3.668–4.162 Å (ring C7b–C9b) for T11, and 3.557–3.884 Å (ring N7b–N12b) and 3.638–4.036 Å (ring N11b–C18b) for T12. These, along with the Tl–C/N contacts in the other structures, are included in Table 2. It can be seen that the distances in 2-Tl are among the shortest (see also the Tl···centroid distances) and hence, are more significant. Resulting Tl···Tl contacts of 4.80 and 5.12 Å are too long for any metal–metal interaction. There is a Tl···N bond length variation from 2.575(7) to 2.665(6) and 2.730(7) Å. For T12···N the variation is from 2.547(7) to 2.651(7) Å. The longer Tl···N bonds are to those pyrazolyl rings which are engaged in Tl···π interactions. There is a reciprocal correlation between the length of the Tl···N contacts and the Tl···N bonds. The building blocks of the extended 3D-structure of dihydrobis(1,2,4-triazolyl)boratothallium, 3-Tl, are illustrated in Figs. 3 and 4. The essentially threefold nitrogen coordination in a pyramidal geometry around thallium is constructed from three different, albeit symmetry related ligands. A fourth nitrogen interaction is present at a considerably greater distance of 3.132 Å.

For Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>2-Tl</th>
<th>3-Tl</th>
<th>6-Tl</th>
<th>7-Tl</th>
<th>8-Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl–N range</td>
<td>2.547(7)–2.730(7)</td>
<td>2.674(7)–2.803(7)</td>
<td>2.633(7)–2.663(7)</td>
<td>2.565(3)–2.652(4)</td>
<td>2.584(8)–2.747(8)</td>
</tr>
<tr>
<td>B–H</td>
<td>calculated</td>
<td>1.05(9), 1.14(9)</td>
<td>1.04(9)</td>
<td>calculated</td>
<td>calculated</td>
</tr>
<tr>
<td>N–Tl–N range</td>
<td>69.6(2)–73.6(2)</td>
<td>76.1(2)–83.7(2)</td>
<td>77.4(2)–86.3(2)</td>
<td>75.6(1)</td>
<td>68.4(3)–74.6(3)</td>
</tr>
</tbody>
</table>

Shortest Tl···π contacts


*Two independent molecules in the unit cell.

Fig. 2. Section of the strands formed in 2-Tl. The left strand contains the Tl1, the right strand the Tl2-molecular units. The strands run along b. Pyrazolyl π contacts to thallium between neighboring molecules are indicated. Shortest Tl···C/N distances (Å): T11···N2b 3.685, T11···C1b 3.683, T11···centroid (N1b–C3b) 3.555, T12···N6b 3.668, T12···C7b 3.817, T12···centroid (N5b–C8b) 3.748, T12···N7b 3.557, T12···C12b 3.654, T12···centroid (N7b–C12b) 3.500, T12···N11b 3.638, T12···C11b 3.760, T12···centroid (N11b–C11b) 3.665. Symmetry relation for T11: b = x+1, y+1/2, z; for T12: b = −x+1, y+1/2, −z+1, b’ = −x+1, y−1/2, −z+1.
tion-metal centers have been observed previously actions of poly(triazolyl)borate ligands between transi-
ing one of the endo-dentate nitrogen atoms (N15) with each ligand bridges three thallium atoms (Fig. 4), leav-
ting 

There are two different donor atoms in the 1,2,4-tria-
zolyl ring, with both the endo-(2-N) and the exo-den-
tate (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-lig-

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–π interactions, as indicated in Fig. 8. The indazolyl moiety from N21 to C27 which is engaged in the Tl–π interaction has a longer Tl–N(22) bond [2.652(4) Å] than the other [Tl–N12, 2.565(3) 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.

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 π-stack-
ing [59] of two indenyl moieties as shown in Fig. 11. The π-stacking is such that the two thallium centers are pointing in the same direction. The molecular units of

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 $a = x, y, z − 1$; $b = −x + 1/2, −y, z − 1/2$; $c = x − 1/2, −y + 1/2, −z + 2$. 

...
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.

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

The Ti–N bond to the π-interacting indazolyl ring is longer than the other two Ti–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 π-interactions, respectively.
Fig. 8. Arrangement of centrosymmetric pairs in the structure of 7-Tl. Selected Tl-π distances (Å): Tl···N21c 3.340(4), Tl···N22c 3.280(4), Tl···C21c 3.479(4), Tl···C22c 3.690(4), Tl···centroid (N21c,C27c) 3.267(4), Tl···Tlc 4.654(4). Symmetry relation $e = -x + 1, -y + 1, -z + 1$.

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···π azolyl interactions can be quite prominent in the crystal packing of the molecular

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

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 (Å) and angles (°): 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. π···π-stacked pairs of molecular units of 8-Tl in the solid state, (a) top view, (b) front view. The π···π separation is 3.58 Å. Symmetry relation $a = 1 - x, y, 1 - z$.
thallium-ligand chelate complexes. For azolyl rings with extended \(\pi\)-systems, such as indazolyl, an offset \((\pi - \pi)_{\text{indazolyl}}\) 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 TI–N bond. There appears to be a reciprocal correlation between the strength of the \(\pi\) interactions and the TI–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).

Acknowledgements

This work is supported by the Deutsche Forschungsgemeinschaft (Grant Ja466/11-1) and the Fonds der Chemischen Industrie.

References

[46] (b) L.J. Farrugia, ORTEP3 for windows, version 1.0.1f, University of Glasgow, 1997.
[60] G. Sheldrick, Program SADABS: Area-Detector Absorption Correction, University of Göttingen, Germany, 1996.