

The Structure of Hydrotris(imidazolyl)boratothallium(I) – the First Structurally Authenticated Tris(imidazolyl)borate Metal Complex

Christoph Janiak*, Savaş Temizdemir, and Caroline Röhr

Freiburg, Institut für Anorganische und Analytische Chemie der Universität

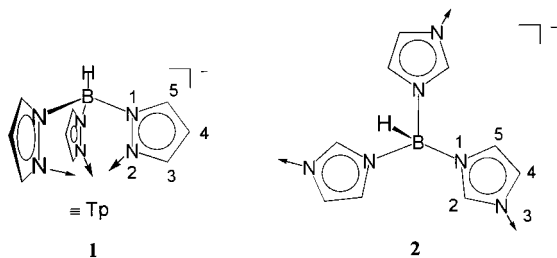
Received September 8th, 1999.

Dedicated to Professor Heinrich Vahrenkamp on the Occasion of his 60th Birthday

Abstract. The title compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.706(1)$, $b = 9.192(1)$, $c = 15.261(2)$ Å, $\beta = 94.740(3)^\circ$, $V = 1217.0(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.278$ g cm⁻³. The tris(imidazolyl)borate ligand bridges between three thallium atoms. The structure consists of one-dimensional twisted ladder-like strands.

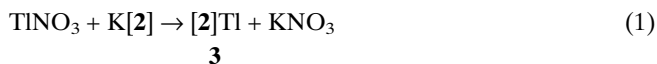
Keywords: Thallium(I) compound; Scorpionate ligand; Hydrotris(pyrazolyl)borate ligand; Crystal structure

Poly(pyrazolyl)borate ligands (scorpionates) are highly popular and versatile ligands in inorganic coordination chemistry. The mostly tris-chelating hydrotris(pyrazolyl)borate (Tp) system **1** is the prototype. Recent interest in transition-metal complexes with these ligands is driven by their model-character for metallo-enzymes and proteins [1–3]. Only few other scorpionates with azolyl groups other than pyrazolyl have been investigated, examples are poly(1,2,4-triazolyl)borates and -(tetrazolyl)borates [4]. Poly(imidazolyl)borates, such as **2**, have been described but their metal complexes have, to the best of our knowledge, never been structurally authenticated [5, 6]. Unlike **1**, the isomeric hydrotris(imidazolyl)borate ligand **2** cannot chelate a metal center but has to bridge between metal ions. The formation of coordination polymers has to be expected. We note an interest in tripodal poly(imidazolyl)-type ligands to model the histidine imidazole coordination in metalloproteins [7].



* Prof. Dr. C. Janiak
Institut für Anorganische und Analytische Chemie
Universität Freiburg
Albertstr. 21
D-79104 Freiburg, Germany
email: janiak@uni-freiburg.de

The hydrotris(imidazolyl)boratothallium compound (**3**) is obtained through the reaction of thallium(I) nitrate with the potassium salt of **2** according to eq. 1.



Thallium derivatives of poly(pyrazolyl)borato ligands have played an important role in the development of this ligand system because they can be used as ligand transfer agents [8, 9]. In addition there is an interest in thallium(I) structures because of their diversity and theoretical aspects of the in/active lone pair of electrons [10, 11]. Thallium complexes with **1** and other [Tp^{RR'}] ligands [12] show a C_{3v}-symmetrical trihapto, η³-metal coordination [8, 9, 13, 14]. Exceptions from this common trigonal motif do only occur when the hydrogen atom on boron atom is replaced by a more sterically demanding organyl group. With the ligands [PhTp^{tBu}] [9], [FcTp] (Fc = Ferrocenyl) [15], and [MeTp^{MeMe}] [14] the borato group becomes bidentate apparently due to steric demands of the organyl group which does not allow for the simultaneous trihapto coordination of all three pyrazolyl rings [14]. The third pyrazolyl ring then exhibits either only a weak interaction to the chelated metal center or bridges to a neighboring thallium ion to give a polymeric structure. In the structure of hydrotris(imidazolyl)boratothallium(I) (**3**), the position of the nitrogen donor atoms in the imidazolyl rings prevents a chelate formation of this borato ligand. Hence, each of three imidazolyl rings has to coordinate to a different (albeit symmetry related) metal atom as shown in Figure 1. In **3** two adjacent ligands bridge between two neighboring thallium ions. From this a one-dimensional ladder-like strand is formed. A two- or even three-dimensional framework may have been another possibility for the metal-ligand assembly. The packing of adjacent strands in **3** is most

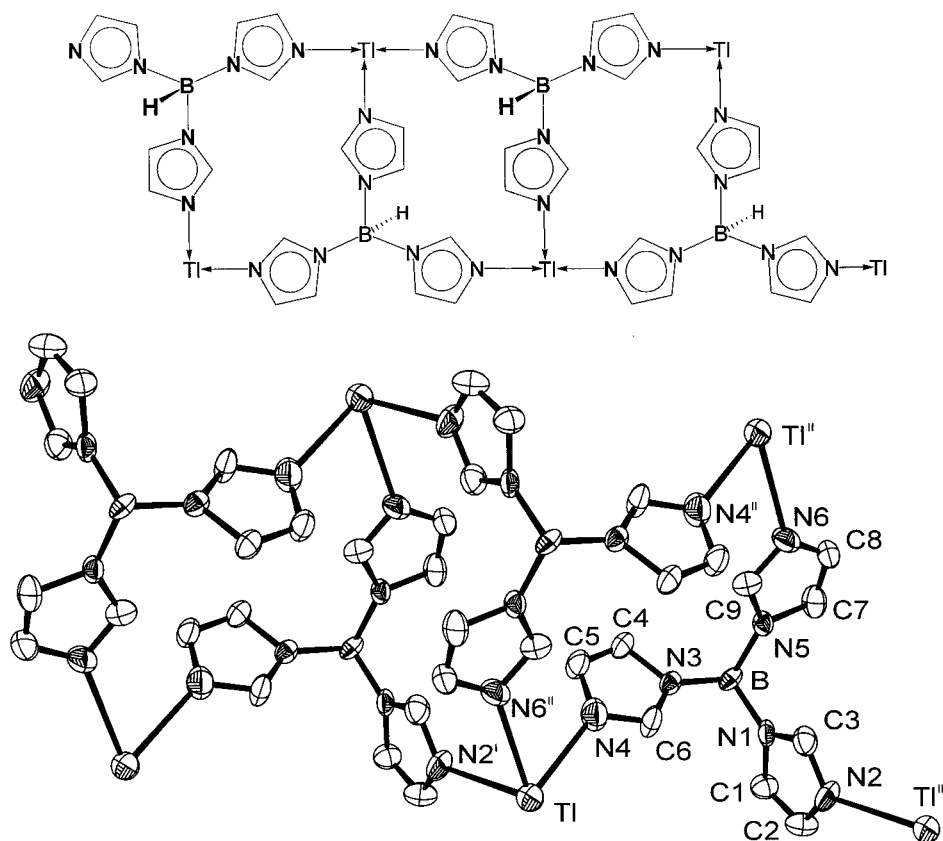


Fig. 1 Section of the one-dimensional polymeric structure of **3** as a schematic drawing (above) and as an ORTEP plot (below). Hydrogen atoms have been omitted in b for clarity. The chains run along the crystallographic *a* direction. Selected distances/Å and angles: Tl–N4 2.663(7), Tl–N2' 2.656(6), 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 equivalent positions: ' = *x* – 1, *y*, *z*; '' = 1 – *x*, 1 – *y*, 1 – *z*; ''' = *x* + 1, *y*, *z*.

likely dictated by electrostatic interactions between the thallium ion and imidazolyl π manifolds. These non-bonded Tl \cdots C and Tl \cdots N distances are in the range of 3.69 to 4.00 Å. Related pyrazolyl π contacts to thallium ions were found between neighboring molecules in [Tp]Tl [13]. At the same time, the packing of neighboring strands is such that there are no close Tl \cdots Tl contacts. The bridging action of **2** in the structure of **3** is reminiscent of the bridge formation of the related poly(1,2,4-triazolyl)borate and the dihydrobis(tetrazolyl)borate ligand, which also possess nitrogen donors in a 1,3-position to the B–N bond [4, 16]. The Tl–N distances observed in **3** fall in the normal range of 2.50–2.73 Å found for Tl–N contacts in tris(pyrazolyl)boratothallium structures [8]. The structure of **3** is the first one for a tris(imidazolyl)boratometal complex [6]. As such it does not support the chelate formation of **2** which was suggested in the literature [5].

Experimental

The experiments were carried out under argon. – CHN analysis: Perkin-Elmer 2400 Series II CHNS/O-Analyzer. – IR: Nicolet-Magna Spectrometer 750 as KBr disks (only major peaks are listed). – NMR: Bruker ARX 200 (200.1 MHz for ^1H , 50.3 MHz for ^{13}C) with calibration against the solvent signal (CDCl_3 ^1H -NMR 7.26 ppm, ^{13}C -NMR 77.0 ppm).

Synthesis of Hydrotris(imidazolyl)boratopotassium: KBH_4 (2.31 g, 42.6 mmol) and imidazole (13.87 g, 204 mmol) were combined in a flame-dried Schlenk-flask which was equipped with a gas meter. The mixture was heated to 100 °C. With the melting of the imidazole a brisk hydrogen evolution started. Whenever the gas evolution subsided, the temperature was raised further to eventually 190 °C. After about 24 h, the reaction has finished and 2.8 l of H_2 were evolved which corresponded to 90% of the estimated hydrogen (ideal gas law). The excess imidazole was sublimed off under vacuum at 1.5 mbar to leave 9.57 g (89%) of the off-white product. – ^1H -NMR (D_2O): δ/ppm = 6.64 (s, 1H, H-4), 6.76 (s, 1H, H-5), 7.23 (s, 1H, H-2); see **2** for the numbering scheme of the imidazolyl ring; the B–H signal is not observed possibly due to its broad resonance because of quadrupolar coupling and relaxation effects from the boron atom [17]. – ^{13}C -NMR (D_2O): δ/ppm = 121.79 (C-4), 127.85 (C-5), 141.03 (C-2). – IR: ν/cm^{-1} = 2435 m, 2416 m (vBH), 1494 s, 1476 s, 1302 s, 1205 s, 1124 s, 1095 s, 1080 s, 919 s, 786 s, 740 s, 723 s, 672 s, 667 s. – $\text{C}_9\text{H}_{10}\text{BKN}_6$ (252.13): calculated C 42.87, H 4.00, N 33.33; found 41.35, H 3.66, N 33.29%.

Synthesis of $[\text{Hydrotris(imidazolyl)boratothallium(I)}] \text{3}$: TlNO_3 (530 mg, 2.0 mmol) were dissolved in methanol (5 ml) and water (5 ml). This solution was overlaid with a solution of K [**2**] (500 mg, 2.0 mmol) in methanol (10 ml).

Slow diffusion of both 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 one week (yield 520 mg, 63%). – m.p. 268–270 °C. – $^1\text{H-NMR}$ (d_6 -DMSO): δ/ppm = 6.80 (s, 2H, H-4 and H-5), 7.24 (s, 1H, H-2). – $^{13}\text{C-NMR}$ (d_6 -DMSO): δ/ppm = 120.60 (C-4), 127.98 (C-5), 139.65 (C-2). – IR: ν/cm^{-1} = 2430 m, 2412 m (νBH), 1477 s, 1207 s, 1119 s, 1073 s, 924 s. – $\text{C}_9\text{H}_{10}\text{BN}_6\text{Tl}$ (417.41): calculated C 25.90, H 2.41, N 20.13; found 25.96, H 2.40, N 20.07%.

Crystal structure determination of 3: Crystal data: Molecular formula $\text{C}_9\text{H}_{10}\text{BN}_6\text{Tl}$, formula mass 417.41 g mol^{-1} , a = 8.706(1), b = 9.192(1), c = 15.261(2) Å, β = 94.740(3)°, V = 1217.0(3) Å³, Z = 4, D_{calc} = 2.278 g cm^{-3} , $F(000)$ = 768, monoclinic, space group $\text{P2}_1/\text{n}$. Data collection: Bruker AXS with CCD area detector, Mo-K α radiation (λ = 0.71073 Å), graphite monochromator, crystal size $0.24 \times 0.047 \times 0.047$ mm³, 298(2) K, double-pass method ϕ - ω -scan, $5.2^\circ \leq 2\theta \leq 50.0^\circ$, $-10 \leq h \leq 10$, $-10 \leq k \leq 8$, $-18 \leq l \leq 15$, 6084 reflections measured, 2136 independent, R_{int} = 0.064, $\mu(\text{Mo-K}\alpha)$ 13.26 mm^{-1} . Data collection and cell refinement with SMART [18], data reduction with SAINT [18]. An experimental absorption correction (SADABS) [19] was performed with $T_{\text{min}}/T_{\text{max}}$ of 0.408/1.000. Structure Analysis and Refinement: Structure solution was performed by direct methods using SHELXS-97 [20]. Refinement: Full-matrix least-squares on F^2 (SHELXL-97) [20]; all non-hydrogen atomic positions found and refined anisotropically, the hydrogen atoms were placed at calculated positions, using appropriate riding models with $d_{\text{C-H}}$ = 0.96 Å and a refined isotropic temperature factor of B_{eq} = 0.037. 167 refined parameters, final $R1$ = 0.0345, $wR2$ = 0.0730 for 1618 reflections with $I > 2\sigma I$, $R1$ = 0.0489, $wR2$ = 0.0771 for all reflections, goodness-of-fit on F^2 = 0.923, largest difference peak and hole 0.969/–1.361 e^{-3} in the vicinity of the thallium atom. Graphics were computed with ORTEP3 for Windows [21]. The structural data have been deposited with the Cambridge Crystallographic Data Center (No. 135180).

Acknowledgements: Our work is supported by the Deutsche Forschungsgemeinschaft (grant Ja466/4-2, 4-3) and the Fonds der Chemischen Industrie.

- [1] S. Trofimenko, *Scorpionates – Polypyrazolylborate Ligands and Their Coordination Chemistry*, Imperial College Press, **1999**; S. Trofimenko, *Chem. Rev.* **1993**, 93, 943.
- [2] N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, 43, 419.
- [3] P. K. Byers, A. J. Canty, R. T. Honeyman, *Adv. Organomet. Chem.* **1992**, 34, 1; G. Parkin, *Adv. Inorg. Chem.* **1995**, 42, 291; D. L. Reger, *Coord. Chem. Rev.* **1996**, 147, 571; M. Etienne, *Coord. Chem. Rev.* **1997**, 156, 201.
- [4] C. Janiak, T. G. Scharmann, J. C. Green, R. P. G. Parkin, M. J. Kolm, E. Riedel, W. Mickler, J. Elguero, R. M. Claramunt, D. Sanz, *Chem. Eur. J.* **1996**, 2, 992; C. Janiak, T. G. Scharmann, W. Günther, W. Hinrichs, D. Lentz, *Chem. Ber.* **1996**, 129, 991; C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow, R. Macdonald, *J. Am. Chem. Soc.* **1996**, 118, 6307; C. Janiak, T. G. Scharmann, W. Günther, F. Girgsdies, H. Hemling, W. Hinrichs, D. Lentz, *Chem. Eur. J.* **1995**, 1, 637; C. Janiak, T. G. Scharmann, H. Hemling, D. Lentz, J. Pickardt, *Chem. Ber.* **1995**, 128, 235; C. Janiak, T. G. Scharmann, K.-W. Brzezinka, P. Reich, *Chem. Ber.* **1995**, 128, 323, and references therein.
- [5] T. A. Khan, S. A. A. Zaidi, S. A. Shaheer, S. R. A. Zaidi, *Synth. React. Inorg. Met.-Org. Chem.* **1992**, 22, 673; S. A. A. Zaidi, T. A. Khan, S. A. Shaheer, S. R. A. Zaidi, Z. A. Siddiqi, *Bull. Soc. Chim. Fr.* **1986**, 536; S. A. A. Zaidi, T. A. Khan, S. R. A. Zaidi, Z. A. Siddiqi, *Polyhedron* **1985**, 4, 1163; S. A. A. Zaidi, T. A. Khan, Z. A. Siddiqi, *Synth. React. Inorg. Met.-Org. Chem.* **1984**, 14, 717.
- [6] An exception is the ionic lithium salt of tetrakis(imidazolyl)borate: O. Knop, P. K. Bakshi, *Can. J. Chem.* **1995**, 73, 151.
- [7] C. Santini, G. G. Lobbia, C. Pettinari, M. Pellei, G. Valle, S. Calogero, *Inorg. Chem.* **1998**, 37, 890; M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975; G. J. A. A. Koolhaas, W. L. Driessen, J. Reedijk, H. Kooijman, A. L. Spek, *Chem. Commun.* **1995**, 517; R. Gregorzik, U. Hartmann, H. Vahrenkamp, *Chem. Ber.* **1994**, 127, 2117; U. Hartmann, R. Gregorzik, H. Vahrenkamp, *Chem. Ber.* **1994**, 127, 2123; W. E. Lynch, D. M. Kurtz, S. Wang, R. A. Scott, *J. Am. Chem. Soc.* **1994**, 116, 11030; S. Chen, J. F. Richardson, R. M. Buchanan, *Inorg. Chem.* **1994**, 33, 2376.
- [8] C. Janiak, *Main Group Met. Chem.* **1998**, 21, 33; C. Janiak, *Coord. Chem. Rev.* **1997**, 163, 107.
- [9] J. L. Kisko, T. Hascall, C. Kimblin, G. Parkin, *J. Chem. Soc., Dalton Trans.* **1999**, 1929.
- [10] A. L. Rheingold, L. M. Liable-Sands, S. Trofimenko, *J. Chem. Soc., Chem. Commun.* **1997**, 1691.
- [11] C. Janiak, R. Hoffmann, *J. Am. Chem. Soc.* **1990**, 112, 5924.
- [12] According to a nomenclature suggested by Trofimenko (ref. [1]) the tris(pyrazolyl)borato ligand is abbreviated as Tp with the 3- and 5-alkyl substituents (R, R') given respectively as superscripts. If the fourth substituent on boron is different from the hydrogen atom, this substituent is added as a prefix, e.g. [MeTp^{MeMe}] for tris(3,5-dimethylpyrazolyl)methylborato.
- [13] C. Janiak, S. Temizdemir, T. G. Scharmann, *Z. Anorg. Allg. Chem.* **1998**, 624, 755.
- [14] C. Janiak, L. Braun, F. Girgsdies, *J. Chem. Soc., Dalton Trans.* **1999**, 3133.
- [15] F. Jäckle, K. Polborn, M. Wagner, *Chem. Ber.* **1996**, 129, 603.
- [16] C. Janiak, H. Hemling, *J. Chem. Soc., Dalton Trans.* **1994**, 2947; C. Janiak, L. Esser, *Z. Naturforsch.* **1993**, 48 b, 394; C. Janiak, *J. Chem. Soc., Chem. Commun.* **1994**, 545.
- [17] R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Pitman, London, **1983**, Chap. 5–14, pp. 138–141.
- [18] SMART, Data Collection Program for the CCD Area-Detector System; SAINT, Data Reduction and Frame Integration Program for the CCD Area-Detector System. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, **1997**.
- [19] R. H. Blessing, *Acta Crystallogr. A* **1995**, 51, 33.
- [20] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Göttingen **1997**; SHELXS-97, Program for Crystal Structure Solution, Göttingen, **1997**.
- [21] M. N. Burnett, C. K. Johnson, ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge National Laboratory Report ORNL-6895, **1996**; L. J. Farrugia, ORTEP3 for Windows, version 1.0.1 β , University of Glasgow, Scotland, **1997**.