

Hydrotris(indazolyl)borate, $\text{Tp}^{4\text{Bo}}$, a surprisingly effective Tp ligand for supramolecular assembly¹

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Abstract

The assembly of $\text{TiTp}^{4\text{Bo}}$ and $\text{M}(\text{Tp}^{4\text{Bo}})_2$ (M e.g. Co, Ni) in the crystal is dictated by aromatic π – π and C–H $\cdots\pi$ interactions. This leads to the formation of chiral C_2 -symmetrical pairs (for Ti) or solvent-filled, about 30%-porous, non-covalent framework structures (for Co and Ni). The potassium salt $\text{KTp}^{4\text{Bo}}$ features a $\kappa\text{N},\eta\text{-C-C},\eta^2\text{-C-N}$ cation– π coordination mode — curious for a Tp-type ligand. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; π – π interactions; Framework structures; Indazolylborate ligand; Transition metal complexes; Supramolecular assembly

1. Introduction

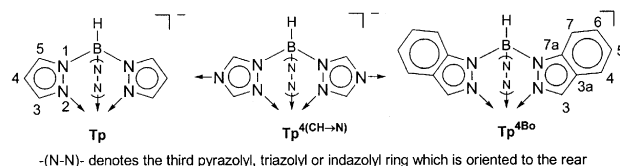
Poly(pyrazolyl)borate ligands (scorpionates) are highly popular and versatile ligands in physico-chemically, bio-inorganic and structurally oriented coordination chemistry [1–15]. The various hydrogen-substituted derivatives of the prototypical Tp ligand are much valued for their control on the metal coordination sphere. Tp derivatives are engineered mostly for a strictly molecular and mononuclear Tp–metal chemistry [16–21]. Only very seldom, e.g. with the hydrotris(triazolyl)borate ligand, $\text{Tp}^{4(\text{CH}\rightarrow\text{N})}$ ², or similarly functionally substituted Tp ligands, was the formation of coordination polymeric structures or non-covalent hydrogen-bonding interactions seen and exploited [22–27].

The hydrotris(indazolyl)borate ligand, $\text{Tp}^{4\text{Bo}}$, is known, [28,29], yet little studied up to now [1,2], and is presented here as surprisingly prone to supramolecular assembly. This could open the field of supramolecular chemistry and in particular crystal engineering to Tp–metal complexes which, thus far, may not have been viewed as accessible to Tp ligands.

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¹ Dedicated to Professor Dr Rolf W. Saalfrank on the occasion of his 60th birthday.

² The abbreviation $\text{Tp}^{4\text{R}}$ follows the suggested nomenclature by Trofimenko [1,2] to indicate a substituent in the 4-position. ‘CH \rightarrow N’ means the substitution of CH by a nitrogen atom; ‘4Bo’ indicates the 4,5-fusion of the benzo ring in the poly(indazolyl)borate ligand.



2. Experimental

The solvent methanol was dried over CaO by refluxing for 4 h under inert gas followed by distillation. NMR spectra were collected on a Bruker ARX300 or ARX400 and calibrated against the solvent signal. Mass spectra were obtained on a Varian MAT 311A/AMD in solid-probe EI mode at an ionization energy of 70 eV.

2.1. Potassium hydrotris(indazol-1-yl)borate, $\text{K}[\text{HB}(\text{C}_7\text{H}_5\text{N}_2)_3]$ (**1**)

The potassium salt of $\text{Tp}^{4\text{Bo}}$ was prepared following a general procedure by Trofimenko for tris(pyrazolyl)borate ligands [30]. KBH_4 (1.6 g, 30.0 mmol) and indazole (11.3 g, 95.9 mmol) were heated to 220°C in a Schlenk flask which was connected to a volumetric gas measurement system. A strong gas evolution starts upon melting and ceases towards the end of the reaction. After 4 h, 2.1 L of H_2 were evolved which correspond to 86.1 mmol or 96% of the theoretical amount when assuming the ideal gas law. Excess indazole is

separated by sublimation (160°C bath temperature, 1.5 mbar) to leave the product as a yellow powder (yield 10.57 g, 88%). Crystals could be grown from methanol through slow evaporation. M.p. 256–258°C (Refs. [28,29] 256–258°C). ¹H-NMR (d₆-DMSO): δ = 6.85 (ddd, 3H, H-5, $J_{5,4} = 7.86$ Hz, $J_{5,6} = 6.79$ Hz, $J_{5,7} = 1.07$ Hz), 6.94 (ddd, 3H, H-6, $J_{6,7} = 8.24$ Hz, $J_{6,5} = 6.87$ Hz, $J_{6,4} = 1.30$ Hz), 7.15 ('dt', 3H, H-7, $J_{7,6} = 8.40$ Hz, $J_{7,5} = 0.92$ Hz, $J_{7,3} = 0.86$ Hz), 7.58 ('dt', 3H, H-4, $J_{4,5} = 7.70$ Hz, $J_{4,6} = 1.22$ Hz, $J_{4,7} = 0.76$ Hz), 7.86 (d, 3H, H-3, $J_{3,7} = 0.91$ Hz).

2.2. Thallium hydrotris(indazol-1-yl)borate, Tl[HB(C₇H₅N₂)₃] (2)

The potassium salt of Tp^{4Bo} (0.80 g, 2.0 mmol) reacts with TlNO₃ (0.53 g, 2.0 mmol) in CH₃OH (10 mL) with formation of a white precipitate. This precipitate was filtered off and crystallized from dioxane through overlaying with petrol ether (50/30). The product formed as colorless crystals (yield 670 mg, 59%). ¹H-NMR (d₆-DMSO): δ = 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). MS (230°C): 568 (26%, [M]⁺). Calc. for C₂₁H₁₆BN₆Tl (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%.

2.3. [Bis{hydrotris(indazol-1-yl)borato}cobalt(II)-CHCl₃ adduct, [Co{HB(C₇H₅N₂)₃}₂] · 3.5CHCl₃ (3)

A solution of **1** (0.40 g, 1.0 mmol) in CH₃OH (10 ml) is added to a slurry of CoCl₂ · 6H₂O (0.12 g, 0.5 mmol) in CH₃OH (5 mL) under stirring. The precipitate formed is filtered and dried in air. An initial crystallization from dioxane/petrol ether yielded red–brown needles and a yellow solid. The brown impurity could be removed after treatment of a CHCl₃ solution with Al₂O₃. This changed the relative solubility of the two phases. After evaporation of CHCl₃ in vacuum, the remaining solid was treated again with CHCl₃ (5 mL) which led to the dissolution of the brown impurity leaving a citrus-yellow solid behind. The yellow solid was crystallized from hot–cold CHCl₃ to give initially yellow needle shaped crystals and after longer standing yellow rhombic crystals (yield 220 mg, 56%). Most of the CHCl₃ solvent of crystallization is rapidly lost when the crystals are removed from the mother liquor. M.p. > 300°C. ¹H-NMR (CDCl₃) corresponds to Refs. [28,29]. MS (438°C): 785 (83%, [M]⁺). Calc. for C₄₂H₃₂B₂CoN₁₂ · 4/3(CHCl₃) (944.5): C, 55.10; H, 3.56; N, 17.80. Found: C, 55.63; H, 3.56; N, 17.89%.

2.4. [Bis{hydrotris(indazol-1-yl)borato}nickel(II)-dioxane adduct, [Ni{HB(C₇H₅N₂)₃}₂] · 1.67 dioxane (4)

A solution of **1** (0.40 g, 1.0 mmol) in CH₃OH (10 ml) is added to a slurry of anhydrous NiCl₂ (65 mg, 0.5 mmol) in CH₃OH (5 mL) under stirring. The precipitate formed is filtered and dried in air. Light pink crystals could be obtained from dioxane/petrol ether (yield 250 mg, 64%). M.p. > 300°C. ¹H-NMR (d₈-THF): 2.04 (s, 1H, H-3), 2.44 (s, 1H, H-4), 3.58 (s, 1H, H-5) 8.79 (br, s, 1H, H-6), 15.09 (br, s, 1H, H-7). MS (428°C): 784 (11%, [M]⁺). Calc. for C₄₂H₃₂B₂N₁₂Ni (785.1): C, 64.25; H, 4.11; N, 21.41. Found: C, 63.89; H, 3.68; N, 20.01%.

2.5. X-ray structure determination

Data collection by the ω-scan method, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, at 173 K on a Bruker AXS CCD diffractometer. Structure solution by direct methods; refinement by full-matrix least-squares on F² using the SHELXTL program package (Version 5.1, Bruker AXS). All non-hydrogen positions found and refined with anisotropic temperature factors. Graphics were computed with ORTEP3 for Windows [31–33].

2.5.1. Crystal data

1: (CH₃OH)₂: colorless blocks, orthorhombic, space group *Pbca*, *a* = 15.5608(3), *b* = 10.9574(2), *c* = 27.1908(5) Å, *V* = 4636.2(2) Å³, *Z* = 8, *D*_c = 1.336, final *R*, *wR* values 0.0506, 0.1022 for 3752 reflections with *I* > 2σ(*I*).

2: colorless blocks, monoclinic, space group *C2*, *a* = 26.6043(2), *b* = 7.1280(1), *c* = 11.0435(2) Å, β = 111.179(1)°, *V* = 1952.79(5) Å³, *Z* = 4, *D*_c = 1.931, final *R*, *wR* values 0.0496, 0.1101 for 3583 reflections with *I* > 2σ(*I*); Flack parameter 0.144(15).

3: yellow rhombohedra, monoclinic, space group *C2/c*, *a* = 23.2237(2), *b* = 19.9395(3), *c* = 23.0847(4) Å, β = 101.084(1)°, *V* = 10490.4(3) Å³, *Z* = 8, *D*_c = 1.524, final *R*, *wR* values 0.0842, 0.1631 for 5502 reflections with *I* > 2σ(*I*).

4: pink blocks, trigonal, space group *R-3*, *a* = *b* = 30.2345(2), *c* = 13.2816(2) Å, γ = 120°, *V* = 10514.5(2) Å³, *Z* = 9, *D*_c = 1.317, final *R*, *wR* values 0.0699, 0.1526 for 2799 reflections with *I* > 2σ(*I*).

See also Section 4.

3. Results and discussion

Hydrotris(pyrazolyl)- and -(indazolyl)borato ligands have a strong preference for tris-chelation of a metal center with a C₃ symmetrical κ³N,N',N'' bonding mode [1,2]. Towards alkali metals such a coordination is observed in Li(PhTp^{tBu}) [34], K(Tp^{Me3}) · 3(3,4,5-Me₃pzH) (pz = pyrazolyl) [35] and in [NaTp₂][−] [36], while the structures of NaTp · H₂O [37] and KTp^{4(CH→N)} · 2H₂O [38] exhibit polymeric ribbons through a bridging action of the ligands.

A ligand bridging action is also observed in the coordination polymeric structure of **1**(CH₃OH)₂ (Fig. 1). Yet, it is unprecedented in that the Tp^{4B_o} ligand combines an η²-(C–N) and an η²-(C–C) cation–π interaction [39–42] in its bridging coordination besides two normal K–N contacts.

The crystal structure of Tl(Tp^{4B_o}) (**2**) is built from pairs of molecules. These pairs are held together by face-to-face π-stacking of two indenyl moieties as shown in Fig. 2. The π-stacking is such that the two thallium centers are pointing in the same direction. The molecular units of each pair are related through a C₂ symmetry operation. There is no mirror plane or center of inversion. Hence, each pair represents a chiral entity. Most remarkably, 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. The Tl–N bond length to the π-interacting indazolyl ring is longer than the other two Tl–N contacts. Such a deviation from a C_{3_v} symmetrical metal–ligand arrangement is rather unusual in tris(pyrazolyl)- and -(indazolyl)borato-thallium complexes [34,43–46]. The solution NMR spectra of **1** and **2** show that all rings are equivalent due to loose or solvent-separated cation–anion contacts and to the absence of neighboring π-contacts, respectively.

The D_{3_d} symmetrical molecular structure of M(Tp^{4B_o})₂ in **3** and **4** is schematically depicted in Fig. 3. M–N bond lengths are as expected. Solvent molecules are incorporated into the crystal structure and influence the molecular packing. The

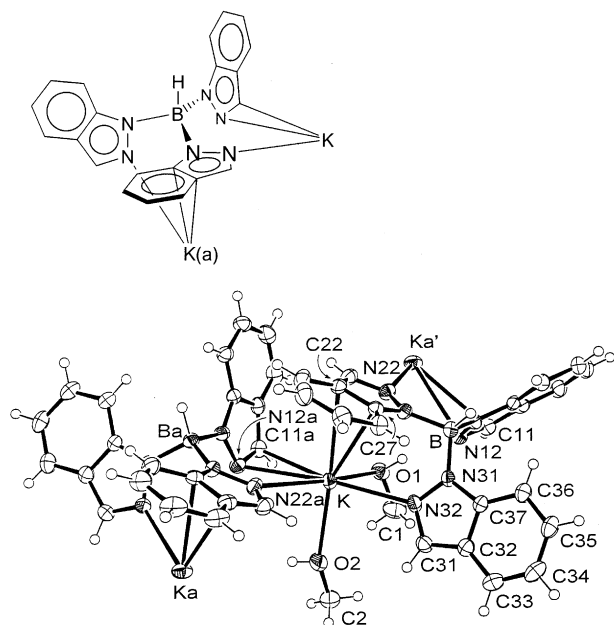


Fig. 1. Schematic drawing of the ligand bridging mode in K(Tp^{4B_o})(**1**)(CH₃OH)₂ (top) and section of the polymeric ribbon (bottom). The methanol molecules on Ka and Ka' are not shown for clarity. Selected distances (Å): K–N32 2.796(2), K–N22a 2.944(2), K–N21a 3.126(2), K–C11a 3.251(2), K–C22 3.225(2), K–C27 3.159(2), K–O1 2.825(2), K–O2 2.716(2). Symmetry relation: a = 1.5 – x, y – 0.5, z; a' = 1.5 – x, y + 0.5, z.

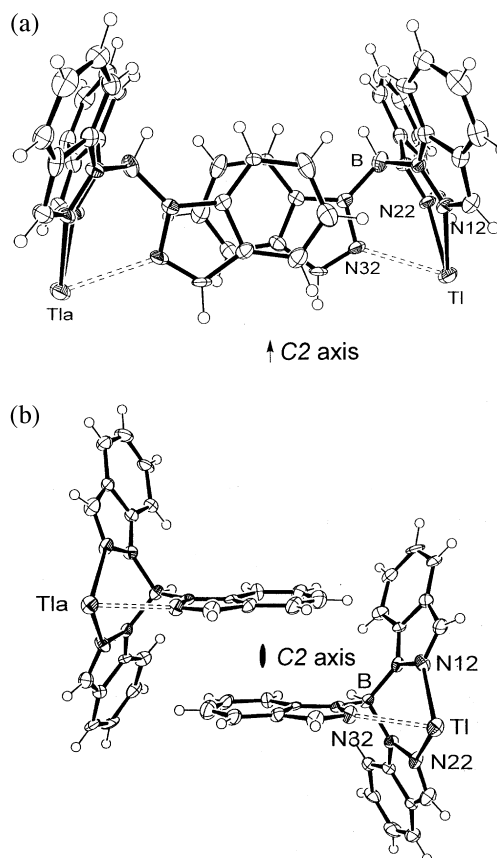


Fig. 2. π–π-stacked pairs of molecular Tl(Tp^{4B_o}) (**2**) units in the solid state, (a) top view, (b) front view. Selected distances (Å): Tl–N12 2.590(9), Tl–N22 2.584(8), Tl–N32 2.747(8), π···π 3.58. Symmetry relation: a = 1 – x, y, 1 – z.

cobalt complex was crystallized from chloroform as Co(Tp^{4B_o})₂·3.5CHCl₃ (**3**), and the nickel complex from dioxane/petrol ether as Ni(Tp^{4B_o})₂·1.67 dioxane (**4**). The crystal packing of the M(Tp^{4B_o})₂ molecules is controlled by C–H···π more than by facial π–π interactions [47]. This assembly of M(Tp^{4B_o})₂ complexes gives rise to large non-covalent framework structures with voids and channels of about 38% (M = Co) and 29% (M = Ni) of the unit cell volume. This volume was computed with the program PLATON [48,49] as the potential solvent area in the solvent-depleted structures. Fig. 3 provides example views of these open spaces in M(Tp^{4B_o})₂. Most of the potential solvent areas are built as channels. The open space is filled by solvent molecules. Because of the weak host–guest interactions the solvent molecules are prone to disorder. The solvent-incorporating structures of M(Tp^{4B_o})₂ indicate that even the very weak intermolecular C–H···π interactions could be a basis for porous framework structures [50,51].

4. Supplementary material

Crystallographic data are deposited with the Cambridge Structural Database as supplementary publication Nos.

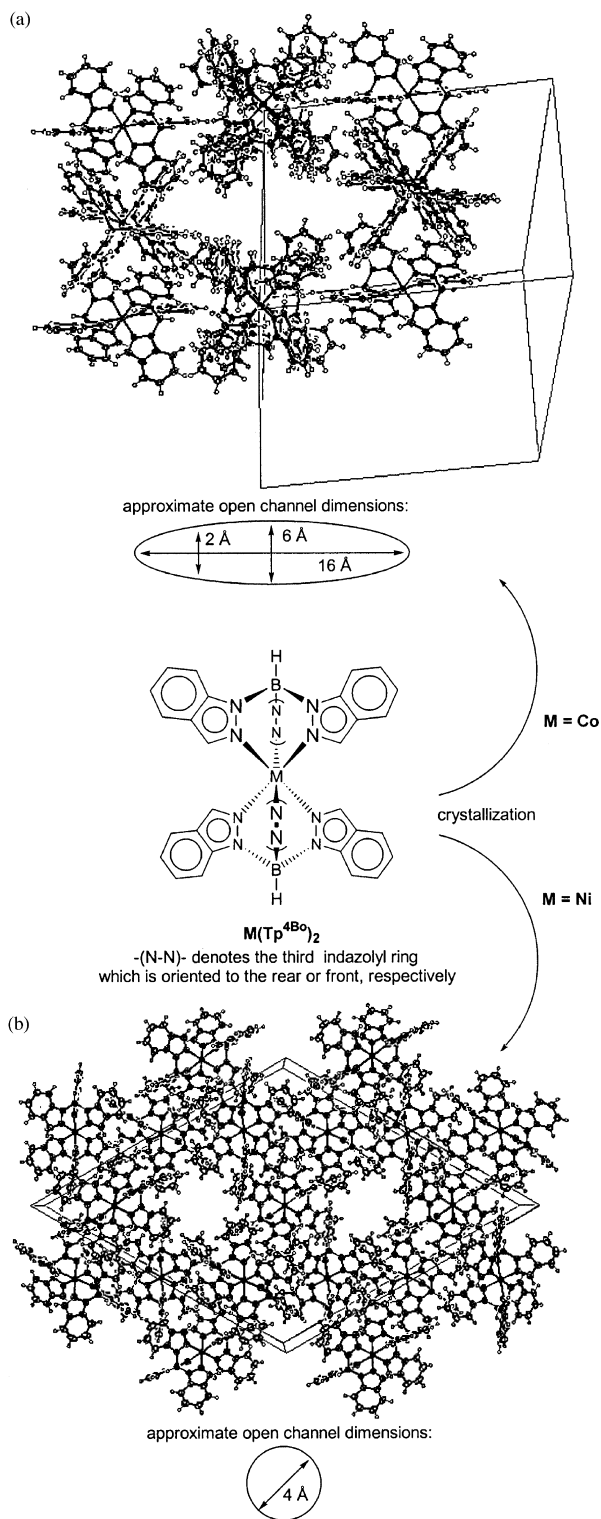


Fig. 3. Solvent-depleted crystal structure of (a) $\text{Co}(\text{Tp}^{4\text{Bo}})_2 \cdot 3.5\text{CHCl}_3$ (**3**) to illustrate the channel formation along the *ab*-diagonal and of (b) $\text{Ni}(\text{Tp}^{4\text{Bo}})_2 \cdot 1.67$ dioxane (**4**) with the channel formation along *c*. In the middle is a schematic structure for $\text{M}(\text{Tp}^{4\text{Bo}})_2$ depicted. The indicated open channel dimensions take into account the van-der-Waals radius of the surrounding hydrogen atoms. 'Open channel' means that the channel dimensions are even wider in-between the molecular layers. Additional channels and voids are present which are not shown.

CCDC-141089 (**1**(CH_3OH)₂), -141090 (**2**), -136882 (**3**) and -136884 (**4**).

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