Hydrotris(indazolyl)borate, Tp<sup>4Bo</sup>, a surprisingly effective Tp ligand for supramolecular assembly

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Abstract

The assembly of TlTp<sup>4Bo</sup> and M(Tp<sup>4Bo</sup>)<sub>2</sub> (M e.g. Co, Ni) in the crystal is dictated by aromatic π-π and C-H...π interactions. This leads to the formation of chiral C<sub>2</sub>-symmetrical pairs (for Tl) or solvent-filled, about 30%-porous, non-covalent framework structures (for Co and Ni). The potassium salt KTp<sup>4Bo</sup> features a κN,η-C:C,η<sup>2</sup>-C:N cation-π coordination mode — curious for a Tp-type ligand.

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, Tp<sup>4CH<sup>"</sup>N</sup><sub>2</sub>, 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, Tp<sup>4Bo</sup>, 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.

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, K[HB(C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>]

The potassium salt of Tp<sup>4Bo</sup> was prepared following a general procedure by Trofimenko for tris(pyrazolyl)borate ligands [30]. KBH<sub>4</sub> (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<sub>2</sub> were evolved which correspond to 86.1 mmol or 96% of the theoretical amount when assuming the ideal gas law. Excess indazole is

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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]). 1H-NMR (d6-DMAC): δ = 6.85 (dddd, 3H, H-5, J4, 7.86 Hz, J5, 6.79 Hz, J7, 1.07 Hz), 6.94 (dddd, 3H, H-6, J6, 8.24 Hz, J5, 6.87 Hz, J4, 1.30 Hz), 7.15 (dt, 3H, H-7, J7, 8.40 Hz, J5, 0.92 Hz, J7, 0.86 Hz), 7.58 (dt, 3H, H-4, J4, 7.70 H, J6, 1.22 Hz, J2, 0.76 Hz), 7.86 (dd, 3H, H-3, J3, 0.91 Hz).

2.2. Thallium hydrotris(indazol-1-yl)borate, TI[HB(C2H2N2)3]2 (2)

The potassium salt of TP3Hs (0.80 g, 2.0 mol%) reacts with TlNO3 (0.53 g, 2.0 mol%) in CH3OH (10 mL) with formation of a white precipitate. This precipitate was filtered off and crystallized from dioxane with overlayering with petrol ether (50/30). The product formed as colorless crystals (yield 670 mg, 59%). 1H-NMR (d6-DMAC): δ = 7.00 (dddd, 3H, H-5, J4, 8.07 Hz, J0, 6.77 Hz, J5, 0.92 Hz), 7.26 (dddd, 3H, H-6, J6, 8.58 Hz, J7, 6.77 Hz, J4, 1.10 Hz), 7.67 (dt, 3H, H-4, J7, 8.07 Hz, J6, 1.10 Hz, J4, 0.98 Hz), 7.89 (ddq, 3H, H-7, J6, 8.58 Hz, J7, 0.93 Hz, J5, 0.92 Hz), 8.15 (d, 3H, H-3, J4, 0.93 Hz). MS (230°C): 568 (26%, [M]+). Calc. for C32H66B2TlN6: C 44.44; H 2.84; N 14.81; TI, 36.00. Found: C, 43.67; H, 2.56; N, 14.51; TI, 35.70%.

2.3. [Bis/hydrotris(indazol-1-yl)borato]cobalt(II)-CHCl3 adduct, [Co[HB(C2H2N2)3]2·3.5CHCl3 (3)

A solution of I (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(C2H2N2)3]2·1.67 dioxane (4)

A solution of I (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 (d6-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 C42H32B2CoN12Ni (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 Pbcn, a = 15.5608(3), b = 10.9574(2), c = 27.1908(5) Å, V = 4636.2(2) Å3, Z = 8, Dc = 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, Dc = 1.931, final R, wR values 0.0496, 0.1101 for 3583 reflections with I > 2σ(I); Flack parameter 0.144(15).

3: yellow rhombohedral, 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, Dc = 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, g = 120°, V = 10514.5(2) Å3, Z = 9, Dc = 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

Hydrotis(pyrrozyl)- and -(indazolyl)borato ligands have a strong preference for tris-chelation of a metal center with a C3 symmetrical N‘N,N’’ bonding mode [1,2]. Towards alkali metals such a coordination is observed in Li(PhTP3) [34], K(Tp3Mo)·3(C4H2-Me,pzH) (pz = pyrazolyl) [35] and in [NaT2]− [36], while the structures of Na(Tp)bpy·H2O [37] and KTp (CH3-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 $\text{I}(\text{CH}_3\text{OH})_2$ (Fig. 1). Yet, it is unprecedented in that the $\text{Tp}^{\text{IIb}}$ ligand combines an $\eta^2$-(C–N) and an $\eta^2$-(C–C) cation–π interaction [39–42] in its bridging coordination besides two normal K–N contacts.

The crystal structure of $\text{TI(Tp}^{\text{IIb}}\text{)}$ (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 C$_2$ 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 TI–N bond length to the π-interacting indazolyl ring is longer than the other two TI–N contacts. Such a deviation from a C$_3v$ symmetrical metal–ligand arrangement is rather unusual in tris(pyr azolyl)- 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$_{2h}$ symmetrical molecular structure of $\text{M(Tp}^{\text{IIb}}\text{)}_2$ 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 cobalt complex was crystallized from chloroform as $\text{Co(Tp}^{\text{IIb}}\text{)}_2 \cdot 3.5\text{CHCl}_3$ (3), and the nickel complex from dioxane/petrol ether as $\text{Ni(Tp}^{\text{IIb}}\text{)}_2 \cdot 1.67\text{dioxane}$ (4). The crystal packing of the $\text{M(Tp}^{\text{IIb}}\text{)}_2$ molecules is controlled by C–H···π more than by facial π–π interactions [47]. This assembly of $\text{M(Tp}^{\text{IIb}}\text{)}_2$ 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 $\text{M(Tp}^{\text{IIb}}\text{)}_2$. 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 $\text{M(Tp}^{\text{IIIb}}\text{)}_2$ 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.
CCDC-141089 (1(CH_2OH)_2), -141090 (2), -136882 (3) and -136884 (4).

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