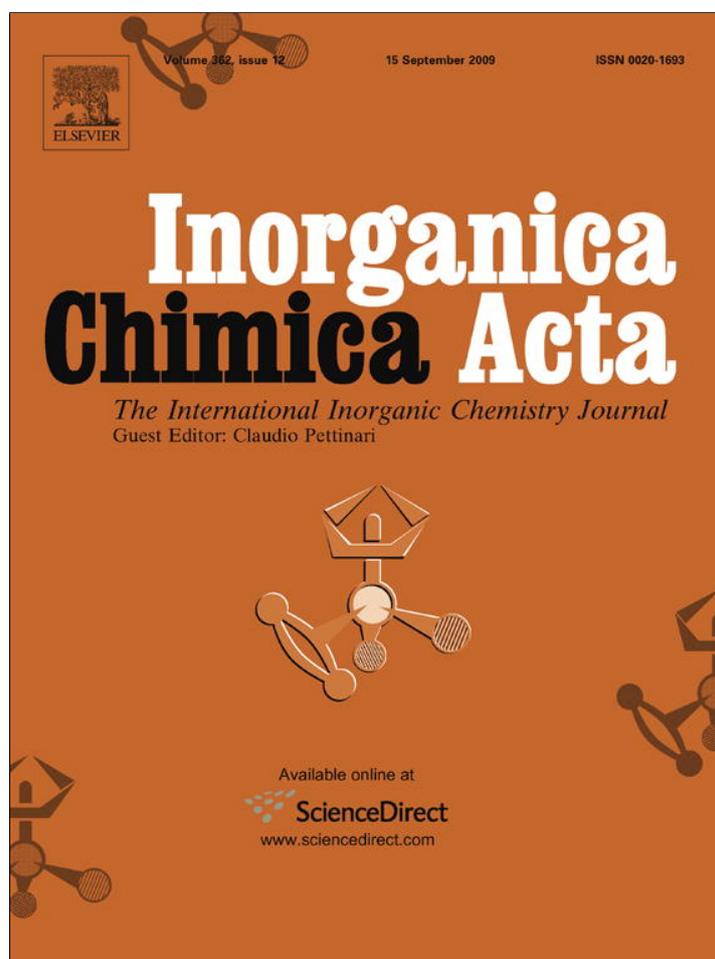


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Note

Three-centre, two-electron bonds in complexes of Mn, Ni, Co and Cd with 3-(4-benzonitrile)pyrazolyl scorpionates

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ABSTRACT

A series of complexes of the form $[M(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ containing a mixture of novel dihydrobis(3-(4-benzonitrile)pyrazolyl)borato ($\text{Bp}^{3(4\text{Bz})}$) and hydrotris(3-(4-benzonitrile)pyrazolyl)borato ($\text{Tp}^{3(4\text{Bz})}$) ligands have been synthesised and structurally characterised. The ligands, both containing 3-(4-benzonitrile)pyrazole arms, form isostructural complexes with a variety of transition metals although different crystalline solvates have been obtained depending upon the crystallisation conditions, namely $[M(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ ($M = \text{Ni}, \text{Co}$), $[\text{Ni}((\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})) \cdot 2\text{MeOH}]$ and $[\text{M}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})] \cdot \text{MeOH}$ ($M = \text{Mn}, \text{Cd}$). In all cases the metal atoms are five-coordinate with an additional agostic B–H interaction from the bis(pyrazolyl)borate ligand.

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1. Introduction

Poly(pyrazolyl)borate anions were first reported in the 1960s by Trofimenko [1]. This class of ligand, especially the hydrotris(pyrazolyl)borate derivatives, has attracted significant attention as a potential model for enzymes actions with the metal contained inside a tight binding pocket [2]. Such an environment can be viewed as an analogue of three facially orientated imidazole rings from histidine groups [3]. There has also been interest in the ligands/complexes for use in metal–ion extraction, polymerisation catalysts [4], CH-activation [5] and the stabilisation of reactive compounds [6]. Complexes of the form $[\text{Fe}(\text{Bp})_2\text{L}]$ ($L = 2,2'$ -bipyridine or 1,10-phenanthroline) have been reported to show spin-crossover behaviour that occurs both thermally and in a light-induced manner [7].¹ The initial poly(pyrazolyl)borate species contained simple pyrazole arms, however, there have been many reports since this time that incorporate substituents in the 3- and 5-positions of the pyrazole such as methyl, phenyl, *tert*-butyl, *iso*-propyl and diphenylmethyl in addition to a great variety of others [1a,b]. Variations have also been reported that contain triazole or imidazole derivatives in place of pyrazole [8].

Several of the reported complexes that contain dihydrobis(3,5-diphenylpyrazolyl)borato ligands, $\text{Bp}^{\text{Ph,Ph}}$, have been observed to

contain interactions between the metal centre and hydrogen atoms from one or both of the BH_2 groups, i.e., $\text{M} \cdots \text{H}-\text{B}$ [9]. These kinds of three-centre, two-electron interactions are well known in the literature, although there is debate surrounding what causes such interactions to occur. For example, it has been shown that the ligand containing asymmetric 3-^tBu-5-ⁱPr-pyrazole arms forms a ML_2 complex displaying trans $\text{Co} \cdots \text{H}-\text{B}$ interactions around the octahedral metal whereas related compounds with different pyrazole substituents form complexes that contain a tetrahedral metal and no agostic interactions [10]. A similar structure is observed for the $\text{Bp}^{\text{CF}_3, \text{CF}_3}$ and $\text{Bp}^{\text{COOEt, Me}}$ derived copper complexes (note, the polyfluorinated zinc complexes adopt tetrahedral coordination geometries) [11]. The $\text{Bp}^{3\text{tBu}}$ ligand also gives rise to trans-HB interactions [12] in $[\text{M}(\text{Bp}^{3\text{tBu}})_2]$ complex as does the $\text{Bp}^{\text{Me, Me}}$ ligand.

To the best of our knowledge there are only three reports of mixed Bp/Tp complexes in which the N_5 coordination environment around the transition metal is supplemented by a $\text{B}-\text{H} \cdots \text{M}$ interaction to give a distorted octahedral geometry [9,10]. There is also an example of a $[\text{Co}(\text{Tp})(\text{Tp}^*)]$ complex in which one of the Tp ligands only coordinates in a bidentate manner with a BH interaction to the octahedral metal [10]. A samarium complex is known that displays a similar agostic interaction [13].

We have previously reported the synthesis of the scorpionate ligand hydrotris[3-(4-benzonitrile)pyrazol-1-yl]borate ($\text{Tp}^{3(4\text{Bz})}$) and several complexes of this species, of the form $[\text{M}(\text{Tp}^{3(4\text{Bz})})_2]$ [14]. Herein we report the synthesis of the bispyrazolyl analogue, $\text{Bp}^{3(4\text{Bz})}$, and mixed-ligand transition metal complexes of the form $[\text{M}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ (1) ($M = \text{Mn}, \text{Ni}$,

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E-mail address: stuart.batten@sci.monash.edu.au (S.R. Batten).¹ The standard abbreviation for this class of ligand is $\text{Bp}^{\text{R,R'}}$ and $\text{Tp}^{\text{R,R'}}$ for the bis- and tris-pyrazolyl species, respectively, where R and R' represent substituents on the 3- and 5-positions of the pyrazole rings (left blank in the case of hydrogen).

Co, Cd). These compounds include the first structurally characterised example of a B–H...Ni interaction within a mixed ligand Bp/Tp scorpionate complex, and represent a rare example of an extended series of isostructural complexes with mixed Bp/Tp ligands [12,15].

2. Experimental

2.1. Synthesis

All reagents were obtained from standard commercial suppliers and used without further purification. 3-(4-benzonitrile)pyrazole was synthesised according to a previously published procedure [14]. ¹H NMR and ¹³C NMR spectra were collected using either a Bruker ADX-200 or ADX-300 spectrometer. Microanalyses were conducted at the Campbell Analytical Laboratories, University of Otago, New Zealand. Infrared spectra were obtained using a Specac Diamond ATR instrument. Note that perchlorate compounds are known to be explosive and, although no issues were found during these preparations, care should be taken.

2.1.1. KBp^{3(4Bz)}

A homogeneous solid mixture of 1.00 g of 3-(4'-benzonnitrile)pyrazol-1-yl (5.9 mmol) and 0.15 g of potassium borohydride (2.8 mol) were melted together at 170 °C for 3 hours. The melt was cooled, crushed and washed with toluene, and eventually filtered off. The solid was then dissolved in 3 mL of dry methanol. By addition of 100 mL of diethyl ether, white precipitate was formed. After drying the solid in a desiccator with P₂O₅ under vacuum, 0.805 g of KBp^{4Bz} was yielded (75%). ¹H NMR (200 MHz, d⁶-DMSO): δ 7.91 (d, 2H, *J* = 8.26 Hz), 7.73 (d, 2H, *J* = 8.28 Hz), 7.49 (d, 1H, *J* = 2.06 Hz), 6.56 (d, 1H, *J* = 2.06 Hz). ¹³C NMR (75 MHz, MeOD): δ 150.86, 141.27, 137.78, 133.37, 127.07, 120.30, 110.25, 103.38. ES-MS; *m/z* = 349.2 (calc = 349.18). *Anal. Calc.* (with 1.5 H₂O): C, 57.84; H, 4.13; N, 20.24. Found: C, 57.47; H, 4.19; N, 20.27%. IR (Nujol mull, ν/cm⁻¹): 2400w, 2346w, 2227s, 1607s, 1484m, 1459w, 1412w, 1339m, 1169s, 1142s, 1113m, 1044s, 948m, 841s, 766s.

2.1.2. KTp^{3(4Bz)}

6.80 g (40 mmol) of 3-(4'-benzonnitrile)pyrazol-1-yl and 0.54 g (10 mmol) of potassium borohydride were ground together and heated at 190–200 °C for 3 hours. The melt was cooled, crushed up and washed with chloroform. The remaining solid was collected via filtration and dried in vacuo to yield 3.8 g (68%) of the desired borate as the potassium salt. ¹H NMR (200 MHz, d⁶-DMSO): δ 7.96 (d, 2H, *J* = 8.6 Hz), 7.77 (d, 2H, *J* = 8.6 Hz), 7.59 (d, 1H, *J* = 2.2 Hz), 6.69 (d, 1H, *J* = 2.2 Hz). ¹³C NMR (50 MHz, d⁶-DMSO): δ 148.8, 141.1, 136.8, 133.2, 125.9, 120.3, 108.6, 102.6. ES-MS; *m/z* = 516.1 (calc = 516.2). *Anal. Calc.*: C, 64.9; H, 3.45; N, 2.7. Found: C, 63.5; H, 3.37; N, 22.5%. IR (KBr disk, ν/cm⁻¹): 2403w, 2224s, 1608s, 1490m, 1457w, 1414w, 1360sh, 1339m, 1190s, 1174sh, 1112m, 1044s, 949m, 846s.

2.1.3. [Co(Bp^{3(4Bz)})(Tp^{3(4Bz)})]

Co(ClO₄)₂·6H₂O (14 mg, 0.0383 mmol) was dissolved in 2 mL of H₂O/EtOH (1:1). Above this was layered a 1:1 solution of KBp^{3(4Bz)} (15 mg, 0.0386 mmol) and KTp^{3(4Bz)} (21.5 mg, 0.0386 mmol) in MeOH (2 mL) with a buffer layer of H₂O/EtOH (1:1, 2 mL). After 24 hours, 15 mg (42%) of thin purple crystals were isolated by filtration. IR (ν/cm⁻¹): 3136w, 2472m, 2323w, 2225s, 1610s, 1490s, 1468s, 1371s, 1334s, 1277m, 1179vs, 1117s, 1053s, 1019s, 1002s, 954m, 841vs, 774vs, 731vs, 697vs, 661vs, 644vs. *Anal. Calc.* for dehydrated complex, C₅₀H₃₃B₂CoN₁₅: C, 64.96; H, 3.60; N, 22.73. Found: C, 65.19; H, 3.50; N, 22.94%.

2.1.4. [Ni(Bp^{3(4Bz)})(Tp^{3(4Bz)})]

Small green crystals were obtained by an analogous synthesis to the Co complex. Insufficient product could be obtained for further analysis.

2.1.5. [Ni(Bp^{3(4Bz)})(Tp^{3(4Bz)})]·2MeOH

A solution of KBp^{3(4Bz)} (15 mg, 0.0386 mmol, 3 mL) and KTp^{3(4Bz)} (21.5 mg, 0.0386 mmol) in methanol (3 mL) was gently heated and stirred. To this was added a hot methanolic solution of NiCl₂ (5 mg, 0.0386 mmol, 5 mL). The resulting solution was heated and stirred for a few minutes before being left to cool to room temperature and allowed to stand. After 48 hours, 23.5 mg (66%) of green crystals were recovered by filtration. IR (ν/cm⁻¹): 3140m, 2475m, 2226vs, 1610s, 1490vs, 1468s, 1373vs, 1337s, 1278m, 1181vs, 1117s, 1054vs, 1019s, 1003s, 955m, 842vs, 788vs, 774vs, 734vs, 696s, 662s, 646s. *Anal. Calc.* for de-solvated sample, C₅₀H₃₃B₂N₁₅Ni: C, 64.98; H, 3.60; N, 22.73. Found: C, 65.45; H, 3.71; N, 22.72%.

2.1.6. [Cd(Bp^{3(4Bz)})(Tp^{3(4Bz)})]·MeOH

Twelve milligrams (0.0385 mmol) of Cd(ClO₄)₂·6H₂O was dissolved with 2 mL of H₂O/EtOH (1:1). After adding a mixture of H₂O/EtOH (1:1) as a buffer layer on the top, 15 mg (0.0386 mmol) of KBp^{3(4Bz)} mixed with 21.5 mg (0.0387 mmol) of KTp^{3(4Bz)} dissolved in 2 mL of MeOH was added slowly. One day later, 22 mg (57%) of small, colourless block crystals was yielded. IR (ν/cm⁻¹): 2441w, 2387w, 2227s, 1611s, 1488s, 1470s, 1414m, 1368s, 1344s, 1175s, 1145s, 1116s, 1059s, 1003s, 954m, 867m, 841s, 773s, 720s, 684s, 640m. *Anal. Calc.* (with 4 H₂O): C, 56.61; N, 19.42; H, 4.19. Found: C, 56.71; N, 19.62; H, 3.51%.

2.1.7. [Mn(Bp^{3(4Bz)})(Tp^{3(4Bz)})]·MeOH

Small colourless crystals were obtained by an analogous synthesis to the Cd complex. Insufficient product could be obtained for further analysis.

2.2. Crystallography

Single crystals were mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected using either a Bruker X8 APEX II CCD (1Mn·MeOH) or Nonius Kappa-CCD (1Co, 1Ni, 1Ni·2MeOH, 1Cd·MeOH) diffractometer, both equipped with monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections were maintained at 123 K using an open-flow N₂ cryostream. Data were initially processed using DENZO [16] or the APEX II program suite [17] for the respective instruments. Structures were solved by direct methods using SHELXS-97 [18]. Refinement was carried out by conventional alternating least squares cycles against F² using SHELXL-97 and the program X-SEED as a graphical interface [19]. Where possible hydrogen atoms attached to oxygen or boron were experimentally located from the Fourier difference map and allowed to refine freely (see individual structure data for details). Hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model to the atom to which they are attached.

2.2.1. Crystal Data for 1Co

C₅₀H₃₃B₂CoN₁₅, *M* = 924.46, pink block, 0.20 × 0.16 × 0.10 mm³, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 13.4630(4), *b* = 17.6714(6), *c* = 19.6608(7) Å, α = 82.2490(10), β = 89.7130(10), γ = 82.6270(10)°, *V* = 4596.1(3) Å³, *Z* = 4, *D*_c = 1.336 g/cm³, *F*₀₀₀ = 1900, 2θ_{max} = 50.0°, 21341 reflections collected, 12309 unique (*R*_{int} = 0.1273). Final *GoF* = 0.849, *R*₁ = 0.0727, *wR*₂ = 0.1841, *R* indices based on 8281 reflections with *I* > 2σ(*I*), 1249 parameters, 0 restraints. *Lp* and absorption corrections applied, μ = 0.428 mm⁻¹. There is a small

residual electron density peak, suggestive of a substoichiometric amount of solvent, however, this could not be accurately modelled.

2.2.2. Crystal data for 1Ni

$C_{50}H_{33}B_2N_{15}Ni$, $M = 924.24$, green block, $0.20 \times 0.18 \times 0.18 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.4791(8)$, $b = 17.7740(14)$, $c = 19.6101(17) \text{ \AA}$, $\alpha = 82.225(4)$, $\beta = 89.653(6)$, $\gamma = 82.798(3)^\circ$, $V = 4617.9(6) \text{ \AA}^3$, $Z = 4$, $D_c = 1.329 \text{ g/cm}^3$, $F_{000} = 1904$, $2\theta_{\text{max}} = 50.0^\circ$, 47993 reflections collected, 16228 unique ($R_{\text{int}} = 0.2626$). Final GoF = 0.959, $R_1 = 0.0999$, $wR_2 = 0.1638$, R indices based on 5434 reflections with $I > 2\sigma(I)$, 1249 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.474 \text{ mm}^{-1}$. There is a small residual electron density peak, suggestive of a substoichiometric amount of solvent, however, this could not be accurately modelled.

2.2.3. Crystal data for 1Ni·2MeOH

$C_{52}H_{41}B_2N_{15}NiO_2$, $M = 988.33$, green block, $0.16 \times 0.15 \times 0.12 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.719(3)$, $b = 13.938(3)$, $c = 14.454(3) \text{ \AA}$, $\alpha = 75.63(3)$, $\beta = 71.11(3)$, $\gamma = 74.66(3)^\circ$, $V = 2481.5(9) \text{ \AA}^3$, $Z = 2$, $D_c = 1.323 \text{ g/cm}^3$, $F_{000} = 1024$, $2\theta_{\text{max}} = 55.0^\circ$, 35623 reflections collected, 11346 unique ($R_{\text{int}} = 0.0706$). Final GoF = 0.942, $R_1 = 0.0551$, $wR_2 = 0.1216$, R indices based on 6285 reflections with $I > 2\sigma(I)$, 661 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.449 \text{ mm}^{-1}$.

One of the methanol molecules is disordered over three positions (1:1:2). These disordered positions were refined using an isotropic model with the hydrogen atoms omitted.

2.2.4. Crystal data for 1Cd·MeOH

$C_{51}H_{37}B_2CdN_{15}$, $M = 1009.98$, colourless block, $0.20 \times 0.20 \times 0.13 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 18.6254(5)$, $b = 14.3035(4)$, $c = 18.9040(6) \text{ \AA}$, $\beta = 106.244(1)^\circ$, $V = 4835.1(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.387 \text{ g/cm}^3$, $F_{000} = 2056$, $2\theta_{\text{max}} = 55.0^\circ$, 26774 reflections collected, 11041 unique ($R_{\text{int}} = 0.0958$). Final GoF = 0.987, $R_1 = 0.0627$, $wR_2 = 0.1072$, R indices based on 5232 reflections with $I > 2\sigma(I)$, 645 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 0.507 \text{ mm}^{-1}$.

The BH bonds within the Bp^{4Bz} ligand were restrained using DFIX restraints.

2.2.5. Crystal data for 1Mn·MeOH

$C_{51}H_{37}B_2MnN_{15}O$, $M = 952.52$, colourless block, $0.14 \times 0.14 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 18.7059(8)$, $b = 14.3354(6)$, $c = 18.7493(7) \text{ \AA}$, $\beta = 107.078(1)^\circ$, $V = 4806.1(3) \text{ \AA}^3$,

$Z = 4$, $D_c = 1.316 \text{ g/cm}^3$, $F_{000} = 1964$, $2\theta_{\text{max}} = 55.0^\circ$, 24975 reflections collected, 10591 unique ($R_{\text{int}} = 0.0312$). Final GoF = 1.045, $R_1 = 0.0530$, $wR_2 = 0.0995$, R indices based on 7371 reflections with $I > 2\sigma(I)$, 645 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.330 \text{ mm}^{-1}$.

The OH hydrogen atom of the methanol was refined using a DFIX restraint.

3. Results and discussion

The poly(pyrazolyl)borate ligands, $Bp^{3(4Bz)}$ and $TP^{3(4Bz)}$, were synthesised using an adaptation of a literature procedure via a melt reaction of 3-(4-benzonitrile)pyrazole with $K(BH_4)$ (see experimental details). Temperature control during the reaction is crucial in determining the product, i.e., whether two, three or four pyrazolyl arms are added to the borate. Higher reaction temperatures yield the more highly substituted products. Obtaining a non-statistical mixture of products is well-known for similar reactions [20]. The use of nitrile-containing arms in pyrazolylborate species is rare with the only previous examples reported being a ligand with the CN substituent in the 4-position of the pyrazole ring [21] and our own $TP^{3(4Bz)}$ species [14].

Reactions of a 1:1 mixture of the $KBp^{3(4Bz)}/KTP^{3(4Bz)}$ starting materials with transition metal salts gave three different crystalline products depending on the solvents and counter-anion used in the synthesis. All products contain the same metal complex, $[M(Bp^{3(4Bz)})(TP^{3(4Bz)})]$ (1) but are differently solvated. In all cases only the mixed Bp/TP complex was formed, confirmed by elemental analysis, with no homoleptic species observed during our studies. Overall five crystalline products were obtained, namely $[M(Bp^{3(4Bz)})(TP^{3(4Bz)})]$ ($M = Co$ and Ni), $[Ni(Bp^{3(4Bz)})(TP^{3(4Bz)})] \cdot 2MeOH$ and $[M(Bp^{3(4Bz)})(TP^{3(4Bz)})] \cdot MeOH$ ($M = Cd$ and Mn). The metal complexes within these crystalline structures are very similar (see Table 1) and the differences in solvation appear to play no role in influencing the structure of the scorpionate species (see below).

The complexes of $[M(Bp^{3(4Bz)})(TP^{3(4Bz)})]$ contain the $Bp^{3(4Bz)}$ and $TP^{3(4Bz)}$ ligands chelating to the metal via two or three pyrazolyl nitrogen atoms, respectively (Fig. 1), in a similar arrangement to previously observed complexes with a Bp/TP ligand combination [9,10]. The range of the M–N distances is unremarkable in all cases (Table 1). If only the N_5 coordination environment of the metal is considered (i.e., discounting the $BH \cdots M$ interaction) then the geometry is distorted square-pyramidal with the metal atom lying

Table 1
Selected bond lengths (Å) and angles (°) for all complexes herein and previous literature reports of related compounds.

	N(Tp)-trans ^b	N(Tp)-cis	N(Bp)	M–H	B–H–M	B–M	M-plane ^c		
1Co·xH ₂ O ^a	2.150(4)	2.142(4)	2.175(4)	2.124(4)	2.120(4)	2.15	105.9	2.66	0.23
	2.148(4)	2.149(4)	2.188(4)	2.123(4)	2.120(4)	2.23	103.2	2.65	0.23
1Ni·xH ₂ O ^a	2.099(5)	2.130(6)	2.106(6)	2.106(6)	2.119(6)	1.93(5)	112.7	2.65	0.22
	2.078(6)	2.117(5)	2.112(6)	2.105(6)	2.112(6)	1.95(5)	111.7	2.66	0.22
1Ni·2MeOH	2.109(2)	2.101(2)	2.102(2)	2.086(2)	2.129(2)	2.28	102.8	2.68	0.25
1Mn·MeOH	2.234(2)	2.230(2)	2.285(2)	2.258(2)	2.241(2)	2.37(2)	103.6	2.87	0.31
1Cd·MeOH	2.312(4)	2.315(3)	2.372(3)	2.322(3)	2.314(3)	2.52(4)	103.2	2.97	0.32
CoMixed ^d [9b]	2.103(3)	2.091(3)	2.153(3)	2.113(3)	2.140(3)	2.03	109.5	2.71	0.22
[Co(η^2 TP ^{ph})(η^3 TP ^{ph})] [9c]	2.103(2)	2.138(2)	2.199(2)	2.124(2)	2.201(2)	2.17(2)	106.0	2.73	0.24
[Co(Bp)(TP ₃)] [10] ^e	2.117(6)	2.145(6)	2.167(6)	2.142(6)	2.120(6)	2.37	101.5	2.72	0.26
[Co(Tp)(Tp)] [10] ^f	2.087(10)	2.164(9)	2.152(9)	2.117(9)	2.149(10)	2.26	109.1	2.77	0.32
[Cd(Tp ^{3ph})(Bp ^{MeMe})] [9a]	2.327(3)	2.319(3)	2.381(4)	2.254(4)	2.241(3)	2.69	103.1	3.15	0.30

^a Two crystallographically unique complexes per ASU.

^b The coordinating nitrogen atom in the trans-position relative to the BH–M interaction.

^c Distance of metal from plane of basal nitrogen atoms (assuming square-pyramidal).

^d [Co(H₂B(3,5-Ph₂p_z)₂)(HB(3,5-Me₂p_z)₂(3,5-Ph₂p_z))].

^e [Co(HB(3⁴Pr⁴BrPz)₃)(H₂B(3PhPz)₂)].

^f [Co(HB(3-i-Pr-4-Br-pz)₃)(HB(3-Phpz)₃)].

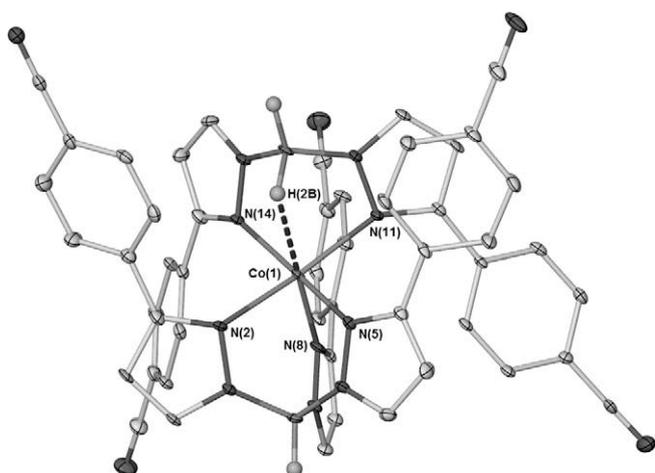


Fig. 1. Molecular structure of one crystallographically unique complex in the structure of $[\text{Co}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$. Ellipsoids shown at 25% probability, CH hydrogen atoms are omitted for clarity. All $[\text{M}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ complexes are essentially isostructural.

slightly above the plane of the basal nitrogen atoms. The apical coordinating nitrogen atom (i.e., that which is *trans* to the BH...M interaction) is supplied by the $\text{Tp}^{3(4\text{Bz})}$ ligand.

A space-filling representation of the complex highlights the manner in which the pyrazolyl arms of the ligands stack with each other around the metal (Fig. 2). The arrangement of the arms is such that they are interdigitating around the metal with face-to-face π -interactions between them. The π -interactions are arranged with two pairs of arms (one from each ligand) on either 'side' of the complex and with the third arm from the $\text{Tp}^{3(4\text{Bz})}$ ligand potentially able to 'lean' towards either the left- or right-hand pair. The asymmetric unit of 1 contains two unique complexes, one each of both the left- and right-handed species. The structures of 1·2MeOH and 1·MeOH are centrosymmetric and contain only a single complex in the ASU. Interestingly, the asymmetric nature of the $\text{Tp}^{3(4\text{Bz})}$ ligand appears to have a small but noticeable effect on the N–M bond

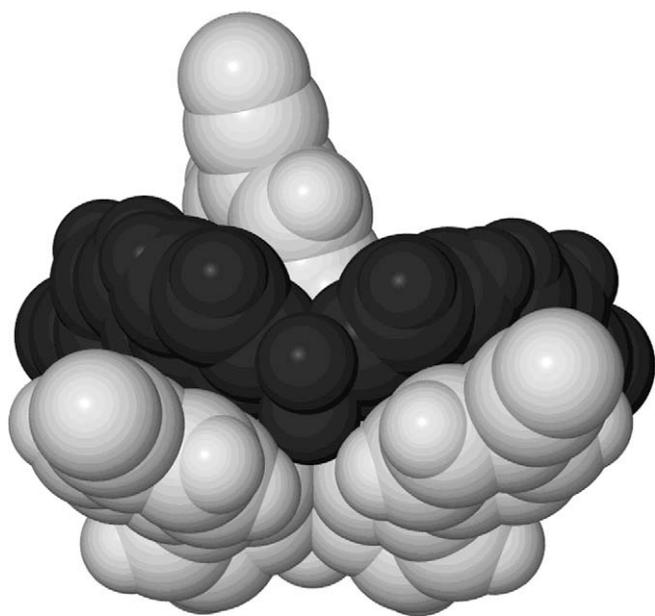


Fig. 2. Space filling model of a $[\text{Co}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ complex ($\text{Tp}^{3(4\text{Bz})}$ shown in light grey). At the bottom of the picture is the pocket in which the B–H...M interaction occurs.

lengths with the M–N bond furthest from the 'twisted' arm being marginally longer than the others in the majority of cases (Table 1).

The spatial arrangement of the ligands around the metal provides a small pocket in which the BH–M interaction resides. The three-centre, two-electron bond is observed in all of the complexes, with the H–M distance of the interaction varying in accordance with the radius of the metal atom (Table 1). B–M distances are also quoted to reduce the errors that can be associated with the refinement of hydrogen atoms (especially when located close to atoms with large electron density). The fact that the heteroleptic complex 1 forms with a variety of different metal ions suggests that the species is preferred over the potential homoleptic complexes. In this instance there is also the issue of potential nitrile coordination, which was not observed, unlike pyridyl-substituted Tp ligands [22] which have recently been used to form nano-scale 'balls' using the extra coordinating group [23]. The behaviour of the scorpionates is also in sharp contrast to related ligands that contain a bridging alkyl spacer between pyridyl–pyrazolyl arms, which coordinate in a ditopic fashion through the pyridyl arms rather than utilising the vacant pyrazolyl nitrogen atom [24].

The different degrees of solvation between the structures do not appear to play any role in influencing the geometric arrangement of the molecular complexes. In the structure of 1Ni·2MeOH there is one well-ordered methanol molecule that forms a hydrogen bond to one of the terminal nitrile groups of the $\text{Tp}^{3(4\text{Bz})}$ ligand ($\text{O} \cdots \text{N} = 3.03 \text{ \AA}$). The second methanol molecule is disordered over three positions, close to a nitrile group of the $\text{Bp}^{3(4\text{Bz})}$ ligand, however given the disorder it cannot be conclusively determined if there is any intermolecular interaction. In the structures of 1Mn·MeOH and 1Cd·MeOH the methanol molecule forms a hydrogen bond to a nitrile group of the $\text{Bp}^{3(4\text{Bz})}$ ligand ($\text{O} \cdots \text{N} = 2.89 \text{ \AA}$ in both instances).

4. Conclusions

A series of complexes of the form $[\text{M}(\text{Bp}^{3(4\text{Bz})})(\text{Tp}^{3(4\text{Bz})})]$ have been synthesised and structurally characterised. The five-coordinate metal atoms within the isostructural complexes have an additional three-centre, two-electron bond from one of the BH groups of the $\text{Bp}^{3(4\text{Bz})}$ ligand. Interestingly, despite the addition of terminal nitrile groups that are capable of further metal coordination, only the discrete mixed-ligand complexes formed – a testament to the stability of scorpionate ligands.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2009.05.068](https://doi.org/10.1016/j.ica.2009.05.068).

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