Aust. J. Chem. 2007, 60, 72-74

Synthesis and Complexes of the New Scorpionate Ligand Tris[3-(4-benzonitrile)-pyrazol-1-yl]borate

Stuart R. Batten, A,B Martin B. Duriska, A Paul Jensen, A and Jinzhen LuA

^ASchool of Chemistry, Monash University, Clayton VIC 3800, Australia. ^BCorresponding author. Email: stuart.batten@sci.monash.edu.au

A new scorpionate ligand, hydro-tris[3-(4-benzonitrile)-pyrazol-1-yl]borate (Tp^{4bz}), was synthesized and the crystal structures of its potassium salt and its Mn^{II} , Co^{II} , Ni^{II} , and Cd^{II} complexes were determined.

Manuscript received: 5 September 2006. Final version: 6 December 2006.

The well-known tris(pyrazolyl)borates, or 'scorpionates' and their derivatives have attracted wide attention across many areas of coordination chemistry.^[1] The use of pyridyl units as the pyrazolyl C^3 substituents gives rise to a variety of different coordination modes. In the case of 2-pyridyl, a hexadentate ligand which can fully encapsulate a metal ion is formed.^[2] When 3- or 4-pyridyl substituents are employed, polymeric networks or dimeric moieties can result upon complexation, wherein a pyridyl unit coordinates to an adjacent complex unit.^[3,4]

In this communication we report the synthesis and coordination behaviour of the new ligand hydro-tris[3-(4-benzonitrile)pyrazol-1-yl]borate, $(Tp^{4bz})^-$, in which 4-benzonitrile units are used as the pyrazolyl C³ substituent. This is analogous to the $(Tp^{4py})^-$ ligand, except that the outer peripheral nitrogen atoms, i.e. the nitriles, are further from the pyrazolyl core and less sterically hindered.

The intermediate, 3-(4-benzonitrile)pyrazol-1-yl, required for the formation of KTp^{4bz} , was synthesized following the reported two-step procedure for the synthesis of 3-(2pyridyl)pyrazol-1-yl,^[2–6] using 4-acetylbenzonitrile as the starting material. An alternative synthetic route has also been reported.^[7] Reaction of 3-(4-benzonitrile)pyrazol-1-yl with KBH₄ in a melt afforded the final desired product in high yield (Scheme 1). The formation of the ligand was confirmed by ¹H and ¹³C NMR spectroscopy, electrospray mass spectrometry, microanalysis, and crystal structure determination.

The crystal structure of KTp^{4bz} is displayed in Figs 1 and 2. It shows the potassium ion coordinated in a distorted octahedral fashion to three pyrazole nitrogen atoms and three nitrile nitrogen atoms from three independent ligand units. The symmetry of the structure is such that there is one unique KTp^{4bz} unit, with 3-fold symmetry, resulting in the KTp^{4bz} unit having only one unique 'arm'. The pendant benzonitrile unit coordinates to a potassium ion of an adjacent KTp^{4bz} moiety, and in turn a pendant benzonitrile unit from this moiety coordinates back to the previous moiety. This gives rise to each KTp^{4bz} unit being connected to three further units via double bridges. This bonding mode results in the KTp^{4bz} unit behaving as a 3-connecting node, yielding a 2D coordination polymer in the form of a (6,3) sheet with corrugated topology. The sheets contain truncated, distorted triangular windows with a maximum width of 11 Å and a minimum of 7 Å. However, these windows do not lead to

porous channels within the structure due to ABC type packing blocking the windows (Fig. 2b).

In contrast, the reaction of KTp^{4bz} with either Co(II) nitrate, Ni(II) perchlorate, Mn(II) sulfate, or Cd(II) perchlorate afforded compounds with the general formula ML₂·(solv). These compounds are monomeric, with each octahedral metal coordinated to two tris-chelating ligands via the pyrazolyl nitrogens only. The nitrile groups do not coordinate.

The crystal structure of $[Co(Tp^{4bz})_2] \cdot 2MeCN$ is shown in Fig. 3. Although the Ni(II) structure contains water and methanol molecules within the asymmetric unit all four structures are otherwise isomorphous. The cobalt atom lies on an inversion centre, and thus only one ligand is unique. The coordination geometry is approximately octahedral with one of the unique Co–N sightly shorter (2.177(2) Å) than the other two (2.217(2) and 2.262(2) Å).

Although the nitrile groups did not coordinate in the binary transition metal complexes, we are currently looking at other routes to encourage coordination of the peripheral nitrile functional groups, as seen in the K^+ salt and the pyridyl analogues,^[6] in order to form larger assemblies, such as metallosupramolecules and coordination networks.

Experimental

Synthesis of 3-(4-Benzonitrile)pyrazol-1-yl (4bz)

22 g (0.15 mol) of 4-acetylbenzonitrile and 30 mL (0.23 mol) of dimethylformamide dimethylacetal was heated at 70°C and stirred for 3 h. During this time the pale yellow solution turned dark orange. The solution was cooled and the volume reduced under vacuum resulting in a dark brown precipitate. The precipitate was dissolved in 100 mL of ethanol and 50 mL of hydrazine hydrate was added. The solution was stirred and heated for 2 h after which the volume was reduced in vacuo. An orange precipitate was obtained with the addition of water. The precipitate was filtered and dissolved in toluene, insoluble by-products were removed via filtration, and the filtrate was evaporated to dryness to yield 20.3 g (79%) of the off-white product, mp 143–145°C. *m/z* (ES-MS) 169.8 (calc 170.1). ν_{max} (KBr disk)/cm⁻¹ 3280br (N–H), 2222s (–CN), 1609 (phenyl). $\delta_{\rm H}$ (200 MHz, [D₆]DMSO) 8.00 (dd, 2H, *J* 8.6, 1.8), 7.84 (dd, 2H, *J* 8.6, 1.8), 7.80 (d, 1H,



Scheme 1. Synthesis of the ligand KTp^{4bz} . Reagents and conditions: (a) *N*,*N*-dimethylformamide dimethyl acetal, 70°C; (b) hydrazine hydrate, EtOH, reflux; (c) KBH₄, 250°C.

[Tp^{4bz}]

J 2.3), 6.87 (d, 1H, *J* 2.3). (Anal. Calcd for C₁₀H₇N₃: C 70.9, H 4.2, N 24.8. Found: C 69.9, H 4.2, N 24.1.)

Synthesis of KTp^{4bz}

6.8 g (40 mmol) of 3-(4'-benzonitrile)pyrazol-1-yl and 0.54 g of potassium borohydride were ground together and heated at 250°C for 3 h. 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. X-Ray quality crystals were grown from methanol. mp 248–254°C. *m/z* (ES-MS) 516.1 (calc 516.2). ν_{max} (KBr disk)/cm⁻¹ 2403w, 2224s, 1608s, 1490m, 1457w, 1414w, 1360sh, 1339m, 1190s, 1174sh, 1112m, 1044s, 949m, 846s. $\delta_{\rm H}$ (200 MHz, [D₆]DMSO) 7.96 (d, 2H, *J* 8.6), 7.77 (d, 2H, *J* 8.6), 7.59 (d, 1H, *J* 2.2), 6.69 (d, 1H, *J* 2.2). $\delta_{\rm C}$ (200 MHz, [D₆]DMSO) 148.8, 141.1, 136.8, 133.2, 125.9, 120.3, 108.6, 102.6. (Anal. Calcd for C₃₀H₁₉N₉BK·0.5H₂O: C 63.8, H 3.5, N 22.3. Found: C 63.5, H 3.4, N 22.5.)

Synthesis of [Co(Tp^{4bz})₂]·2MeCN

25 mg (45 μ mol) of KTp^{4bz} was dissolved in 5 mL of ethanol and 19.7 mg (67 μ mol) of Co(NO₃)₂·6H₂O in 2 mL of ethanol/acetonitrile (1/1) was added. The solution was stirred and allowed to stand overnight yielding 20 mg (73%) of the Co(II) complex as large, orange-pink, X-ray quality crystals. ν_{max} (KBr disk)/cm⁻¹ 2469w, 2226s, 1609m, 1496s, 1470m, 1374s, 1335w, 1196s, 1119m, 1056s, 834s, 781s, 740s. (Anal. Calcd for C₆₀H₃₈B₂N₁₈Co·2C₂H₃N: C 65.5, H 3.8, N 23.9. Found: C 65.8, H 3.6, N 23.7.)

Synthesis of [Ni(Tp^{4bz})₂]·0.8MeOH·1.2H₂O

The Ni(II) complex was obtained using the same reaction conditions as for Co(II) using 24.7 mg (67μ mol) of Ni(ClO₄)₂·6H₂O and 5 mL of methanol. Yield 19 mg (65%).

 ν_{max} (KBr disk)/cm $^{-1}$ 2475w, 2227s, 1609m, 1495s, 1469m, 1373s, 1336m, 1196s, 1118m, 1057s, 844s, 779s, 742s. (Anal. Calcd for C_{60}H_{38}B_2N_{18}Ni: C 66.0, H 3.5, N 23.1. Found: C 65.8, H 3.6, N 23.5.)

Synthesis of [Mn(Tp^{4bz})₂]·2MeCN

The Mn(II) complex was obtained using the same reaction conditions as for Co(II) using 15.1 mg (67 μ mol) of Mn(SO₄) · H₂O. Yield 25 mg (90%). ν_{max} (KBr disk)/cm⁻¹ 2464w, 2225s, 1610m, 1496s, 1471m, 1373s, 1339w, 1196s, 1121m, 1056s, 834s, 782s, 741s. (Anal. Calcd for C₆₀H₃₈B₂N₁₈Mn: C 66.3, H 3.5, N 23.2. Found: C 66.7, H 3.8, N 22.5.)

Synthesis of [Cd(Tp^{4bz})₂]·2MeCN

The Cd(II) complex was obtained using the same reaction conditions as for Co(II) using 11.1 mg (36 μ mol) of Cd(NO₃)₂·4H₂O and 3 mL of DMF. Yield 14 mg (51%). ν_{max} (KBr disk)/cm⁻¹ 2471w, 2222s, 1611m, 1384s, 1344w, 1117m, 1089s, 1050m, 964m, 844s, 805m, 844s, 715s, 630. (Anal. Calcd for C₆₀H₃₈B₂N₁₈Cd · 1.5H₂O: C 61.5, H 3.5, N 21.5. Found: C 61.5, H 3.6, N 21.1.)

Structure Determination

Crystal data for K[Tp^{4bz}]: C₃₀H₁₉BKN₉, *M* 555.45, hexagonal, space group $R\bar{3}c$, *a* 14.1806(3), *b* 14.1806(3), *c* 50.045(1) Å, *U* 8715.3(3) Å³, *Z* 12, D_c 1.270 Mg m⁻³, μ (Mo_{Ka}) 0.219 mm⁻¹, *F*(000) 3432, *T* 123 K, 30253 reflections, 2414 unique (R_{int} 0.1170), R_1 0.0670 (1210 reflections, $I > 2\sigma(I)$), wR_2 0.2223 (all data), *S* 0.967. X-ray measurements for all structures were made using a Nonius KappaCCD diffractometer with graphite monochromated Mo_{Ka} radiation (λ 0.71073 Å). Solutions were obtained by direct methods (*SHELXS* 97)^[8] followed by successive Fourier-difference methods, and refined by full matrix least-squares on F_{obs}^2 (*SHELXL* 97).^[8] All non-hydrogen atoms



Fig. 1. Crystal structure KTp^{4bz}. Selected bond distances [Å]: K(1)–N(12) 2.811(3), K(1)–N(13) 2.831(3).





Fig. 2. (a) Top view of a single sheet of KTp^{4bz} showing the distorted triangular windows. (b) Top view of three independent sheets highlighting the ABC type stacking. (c) Side-on profile showing the corrugated nature of a single sheet.

(c)

were made anisotropic, while all hydrogens were assigned to calculated positions and not refined.

[Co(Tp^{4bz})₂]·2MeCN: C₆₄H₄₄B₂CoN₂₀, *M* 1173.74, orthorhombic, space group *Pccn*, *a* 14.8355(1), *b* 16.4618(2), *c* 24.2553(2) Å, *U* 5923.6(1) Å³, *Z* 4, *D* 1.316 Mg m⁻³, μ (Mo_{K α})



Fig. 3. Crystal structure of $[Co(Tp^{4bz})_2]$ -2MeCN. Selected bond distances [Å]: Co(1)–N(12) 2.262(2), Co(1)–N(22) 2.217(2), Co(1)–N(32) 2.177(2). For Ni (Mn) the corresponding bond lengths are 2.229(7) (2.268(2)), 2.177(7) (2.218(2)), 2.117(6) (2.176(2)).

 0.350 mm^{-1} , F(000) 2420, T 123 K, 70883 reflections, 8965 unique (R_{int} 0.1174), R_1 0.0559 (4950 reflections, $I > 2\sigma(I)$), wR_2 0.1589 (all data), S 1.065.

[Ni(Tp^{4bz})₂]·0.8MeOH·1.2H₂O: C_{60.8}H₄₂B₂N₁₈O₂Ni, *M* 1137.05, orthorhombic, space group *Pccn*, *a* 14.6742(6), *b* 16.6798(7), *c* 24.1585(13) Å, *U* 5913.1(5) Å³, *Z* 4, *D* 1.277 Mg m⁻³, μ (Mo_{K α}) 0.387 mm⁻¹, *F*(000) 2347, *T* 123 K, 44137 reflections, 6759 unique (*R*_{int} 0.2569), *R*₁ 0.0945 (2486 reflections, *I* > 2 σ (*I*)), *wR*₂ 0.2905 (all data), *S* 1.012.

[Mn(Tp^{4bz})₂]·2MeCN: C₆₄H₄₄B₂MnN₂₀, *M* 1169.75, orthorhombic, space group *Pccn*, *a* 14.8348(1), *b* 16.4475(1), *c* 24.2645(1) Å, *U*5920.43(6) Å³, *Z*4, *D* 1.312 Mg m⁻³, μ (Mo_{K α}) 0.350 mm⁻¹, *F*(000) 2412, *T* 123 K, 69465 reflections, 7316 unique (*R*_{int} 0.1165), *R*₁ 0.0542 (4355 reflections, *I* > 2 σ (*I*)), *wR*₂ 0.1408 (all data), *S* 1.021.

Unit cell data for Cd(Tp^{4bz})₂·2MeCN showed that it was isomorphous with the Co, Ni, and Mn structures, and therefore a full dataset was not collected: orthorhombic, *a* 14.9438(3), *b* 16.3799(4), *c* 24.5156(5) Å, *U* 6000.9(2) Å³.

The crystal data has been deposited with the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk; nos. 298261– 298264).

Acknowledgment

This work was supported by The Australian Research Council.

References

 (a) S. Trofimenko, Scorpionates: The Coordination Chemistry of Poly(pyrazolyl)borate Ligands 1999 (Imperial College Press: London).

(b) C. Pettinari, C. Santini, Comp. Coord. Chem. II 2004, 1, 159.

- [2] A. J. Amoroso, A. M. C. Thompson, J. C. Jeffery, P. L. Jones, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Chem. Commun.* 1994, 2751. doi:10.1039/C39940002751
- [3] G. M. Davies, J. C. Jeffery, M. D. Ward, New J. Chem. 2003, 27, 1550. doi:10.1039/B306659B
- H. Adams, S. R. Batten, G. M. Davies, M. B. Duriska, J. C. Jeffery,
 P. Jensen, J. Lu, G. R. Motson, S. J. Coles, M. B. Hursthouse,
 M. D. Ward, *Dalton Trans.* 2005, 1910. doi:10.1039/B502892B
- [5] K. L. V. Mann, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Polyhedron* 1999, 18, 721. doi:10.1016/S0277-5387(98)00345-3
- [6] J. S. Fleming, E. Psillakis, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Dalton Trans.* 1998, 4, 537. doi:10.1039/A707936B
- [7] V. K. Aggarwal, J. de Vicente, R. V. Bonnert, J. Org. Chem. 2003, 68, 5381. doi:10.1021/JO0268409
- [8] G. M. Sheldrick, *SHELX 97* **1997** (University of Göttingen: Gottingen).

Aust. J. Chem. http://www.publish.csiro.au/journals/ajc