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Synthesis and structure of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$: a bis(pyrazolyl)hydroborato cobalt(II) complex with *trans* [Co···H–B] interactions

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The bis{bis(3-*tert*-butyl-5-isopropylpyrazolyl)hydroborato}cobalt(II) complex $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ has been synthesized by reaction of $\mathrm{Tl}[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]$ with $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$; the molecular structure of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is based on a square planar array of pyrazolyl groups with two axial [Co···H–B] interactions, in marked contrast to those of other $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$ derivatives which have tetrahedral structures and are devoid of such interactions.

It is well known that transition metal complexes with electronically unsaturated metal centers may supplement their bonding by participating in three-center–two-electron interactions, *e.g.* [M···H–B] and [M···H–C].[1] The factors which influence the occurrence of these interactions, however, may be quite complex.[2] In this paper, we describe how modifying the substituents in bis{bis(pyrazolyl)hydroborato}cobalt(II) complexes $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$[3] has a dramatic effect on the existence of three-center–two-electron [Co···H–B] interactions.

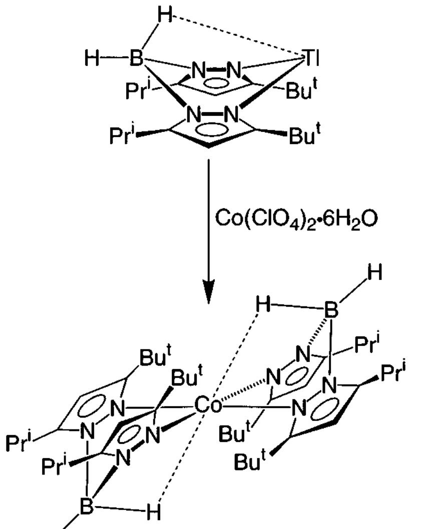
The bis{bis(3-*tert*-butyl-5-isopropylpyrazolyl)hydroborato}cobalt(II) complex $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is readily synthesized by treatment of the thallium derivative $\mathrm{Tl}[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]$ with $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ (Scheme 1). Despite the fact that other $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$ complexes have been synthesized (Table 1),[4] the successful isolation of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is noteworthy because the related complex, $[\mathrm{Bp}^{\mathrm{Bu^t}}]_2\mathrm{Co}$, which also incorporates *tert*-butyl substituents in the 3-positions of the pyrazolyl groups, has been reported to be unstable.[5]

The most interesting feature of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is concerned with its molecular structure (Fig. 1),[6] which is strikingly different from those of all other $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$ complexes. Thus, rather than adopting the tetrahedral array of nitrogen donors typical for other $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$ derivatives, the cobalt center of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is co-ordinated in a square planar manner to the four pyrazolyl groups.[7] Furthermore, the bonding to cobalt is augmented by three-center–two-electron [Co···H–B] interactions, such that the overall co-ordination environment about cobalt is pseudo-octahedral.[8] Although [Co···H-B] interactions in poly(pyrazolyl)borate complexes have been observed previously, the Co···H distance of 1.95 Å in $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is significantly shorter than those in other derivatives (Table 1).[9,10]

Excellent support for the presence of a [Co···H-B] interaction is provided by IR spectroscopy. Thus, $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ exhibits two distinct sets of ν(B–H) absorptions in the IR spectrum at 2486 $\mathrm{cm^{-1}}$ and 2099/2071 $\mathrm{cm^{-1}}$,[11,12] of which the lower energy set is assigned to that of the [Co···H–B] interaction. Significantly, the ν(B–H) absorptions attributed to the [Co···H–B] interaction in $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ are lower in energy than those of other poly(pyrazolyl)borato cobalt complexes (Table 1).[9]

Whereas $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is unique in being the only bis(pyrazolyl)hydroborato cobalt derivative to exhibit a square planar rather than tetrahedral array of nitrogen donors,[7] the former co-ordination is common in other transition metal complexes for which the ligand field stabilization energies of a d^n configuration ($0 < n < 10$) may favor a square planar over tetrahedral geometry.[13] For example, the chromium, nickel, and copper complexes $[\mathrm{Bp}^{\mathrm{RR'}}]_2\mathrm{M}$ (M = Cr, Ni or Cu; Table 1) all adopt a square planar array of nitrogen donors. In contrast, the zinc and cadmium complexes $[\mathrm{Bp}^{\mathrm{RR'}}]_2\mathrm{M}$ (M = Zn or Cd; Table 1) adopt tetrahedral co-ordination since d^{10} metal centers show no ligand field preference for square planar geometries.

The X-ray diffraction and IR spectroscopic studies described above indicate that the Co···H bonds in $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ represent a significant interaction. An important issue, however, is concerned with the extent to which the [Co···H–B]



Scheme 1

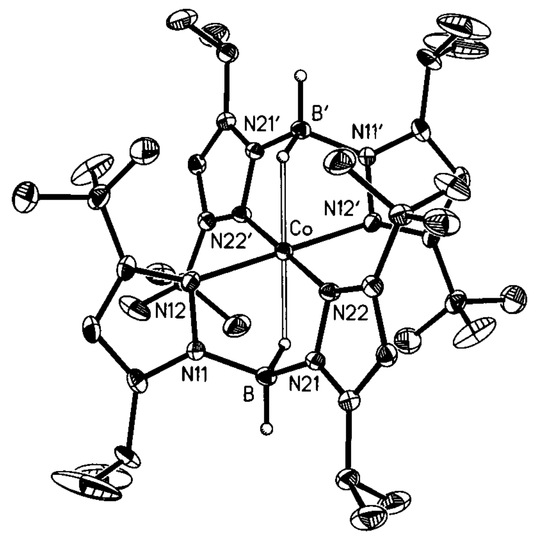


Fig. 1 Molecular structure of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$. Selected bond lengths (Å) and angles (°): Co–N12 2.131(5), Co–N22 2.138(5); N12–Co–N12′ 180.0, N12–Co–N22 86.4(2), N12′–Co–N22 93.6(2).

Table 1 Comparison of metrical and IR data for $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{M}$ transition metal complexes

	M[N$_4$] Co-ordination	d(M···H)/Å	d(M···B)/Å	d(M–N)/Å range	ν(B–H)/cm^{-1} range	Ref.
$[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$	Square planar	1.95	2.59	2.13–2.14	2486–2071	This work
$[\mathrm{Bp}]_2\mathrm{Co}$	Tetrahedral	3.06	3.01	1.93–1.98	—	T1
$[\mathrm{Bp}^{\mathrm{Me_2}}]_2\mathrm{Co}$	Tetrahedral	3.15	3.14	1.991–1.992	—	T2
$[\mathrm{Bp}^{\mathrm{Ph}}]_2\mathrm{Co}$	Tetrahedral	—	—	—	2450–2295	T3
$[\mathrm{Bp}]_2\mathrm{Cr}$	Square planar	3.12	3.22	2.06–2.07	—	T4
$[\mathrm{Bp}]_2\mathrm{Ni}$	Square planar	3.05	3.14	1.89–1.90	—	T5
$[\mathrm{H_2B(pz)(pz^{Me_2})}]_2\mathrm{Ni}$	Square planar	2.90	3.05	1.88–1.89	—	T2
$[\mathrm{Bp}^{\mathrm{Me_2}}]_2\mathrm{Ni}$	Square planar	2.81	2.99	1.888–1.893	—	T2
$[\mathrm{Bp}^{\mathrm{Ph}}]_2\mathrm{Ni}$	Square planar	—	—	—	2424	T3
$[\mathrm{Bp}^{\mathrm{(CF_3)_2}}]_2\mathrm{Cu}$	Square planar	2.58	2.87	1.997–2.004	2572, 2970	T6
$[\mathrm{Bp}^{\mathrm{Ph}}]_2\mathrm{Zn}$	Tetrahedral	—	—	—	2470–2315	T3
$[\mathrm{H_2B(pz^{Me_2})(pz^{Ph_2})}]_2\mathrm{Zn}$	Tetrahedral	3.28	3.22	1.98–2.02	2497, 2400	T7
$[\mathrm{Bp}^{\mathrm{Me_2}}]_2\mathrm{Zn}$	Tetrahedral	3.09	3.17	2.001–2.007	—	T6
$[\mathrm{Bp}^{\mathrm{(CF_3)_2}}]_2\mathrm{Zn}$	Tetrahedral	2.98	3.17	2.014–2.039	2937–2487	T6
$[\mathrm{Bp}]_2\mathrm{Cd}$	Tetrahedral	2.91	3.13	2.181–2.243	—	T8

T1 L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko and J. P. Jesson, *Inorg. Chem.*, 1973, **12**, 508; T2 ref. 14. T3 ref. 5. T4 P. Dapporto, F. Mani and C. Mealli, *Inorg. Chem.*, 1987, **17**, 1323. T5 H. M. Echols and D. Dennis, *Acta Crystallogr.*, *Sect. B*, 1976, **32**, 1627. T6 H. V. R. Dias and J. D. Gordon, *Inorg. Chem.*, 1996, **35**, 318. T7 M. V. Capparelli and G. J. Agrifoglio, *Crystallogr. Spectrosc. Res.*, 1992, **6**, 651. T8 D. L. Reger, S. S. Mason and A. L. Rheingold, *Inorg. Chim. Acta*, 1995, **240**, 669.

interactions are responsible for promoting the structural change from tetrahedral, since it is also possible that the observed [Co···H–B] interactions are a result of conformational changes due to interligand steric interactions. Thus, one possible reason for $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ adopting a square planar rather than tetrahedral array of nitrogen donors is to minimize interligand steric interactions between *tert*-butyl substituents:[14] a square planar geometry allows the 3-*tert*-butyl groups of each ligand to be located on opposite sides of the [CoN$_4$] plane, whereas a tetrahedral geometry would require the 3-*tert*-butyl groups on one ligand to mesh with those of the other. It is, therefore, possible that the [Co···H–B] interactions in $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ may be sterically promoted as a result of a conformational change.[15] However, since the Co···H distance of 1.95 Å is substantially shorter than the M···H separations in other square planar $[\mathrm{Bp}^{\mathrm{RR'}}]_2\mathrm{M}$ derivatives, *e.g.* 3.05 Å for $[\mathrm{Bp}]_2\mathrm{Ni}$ (Table 1), it is evident that the [Co···H–B] interactions are important in influencing the structure of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$.[16] A further observation which supports this notion is that square planar Co(II) complexes are uncommon, with tetrahedral and octahedral complexes being preferentially favored; as such, there is a clear electronic preference for square planar Co(II) to bind two additional ligands.[1] In contrast, square planar co-ordination for Ni(II) is common,[1] such that the nickel centers in square planar $[\mathrm{Bp}^{\mathrm{RR'}}]_2\mathrm{Ni}$ derivatives do not partake in three-center–two-electron [Ni···H–B] interactions (Table 1).

In summary, the molecular structure of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$, based on a square planar array of pyrazolyl groups with two axial [Co···H–B] interactions, provides a striking contrast with those of other $[\mathrm{Bp}^{\mathrm{R,R'}}]_2\mathrm{Co}$ derivatives which adopt tetrahedral co-ordination geometries and are devoid of [Co···H–B] interactions.

Acknowledgements

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Notes and references

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1998.

2 See, for example: A. Haaland, W. Scherer, K. Ruund, G. S. McGrady, A. J. Downs and O. Swang, *J. Am. Chem. Soc.*, 1998, **120**, 3762.

3 Bis- and Tris-(pyrazolyl)hydroborato ligands are represented by the abbreviations $[\mathrm{Bp}^{\mathrm{R,R'}}]$ and $[\mathrm{Tp}^{\mathrm{R,R'}}]$, with the 3- and 5-alkyl substituents listed respectively as superscripts. Additional substituents on boron (other than hydrogen) are represented by a prefix, *e.g.* [R$_2$Bp]. See: S. Trofimenko, *Chem. Rev.* 1993, **93**, 943; G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291.

4 The compounds $[\mathrm{Bp}^{\mathrm{Me_2}}]_2\mathrm{Co}$[4a] and $[\mathrm{Bp}^{\mathrm{Et_2}}]_2\mathrm{Co}$[4b] have also been synthesized, but IR and metrical data have not been reported. (*a*) S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288; (*b*) S. Trofimenko, *Inorg. Chem.*, 1970, **9**, 2493.

5 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507.

6 $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}\cdot 2\mathrm{CHCl_3}$: $\mathrm{C_{42}H_{74}B_2Cl_6CoN_8}$, $M = 984.34$, monoclinic, $P2_1/n$ (no. 14), $a = 10.398(2)$, $b = 20.473(3)$, $c = 12.839(2)$ Å, $\beta = 101.342(8)°$, $U = 2679.7(6)$ Å^3, $Z = 2$, $\mu = 0.655$ mm^{-1}, $T = 293$ K. Independent reflections 3493, $R1 = 0.0722$, $wR_2 = 0.1407$ for $I > 2\sigma(I)$. CCDC reference number 186/1088. The hydrogen atoms attached to boron were located and refined isotropically, giving the following bond lengths (Å) and angles (°): B–H$_{\mathrm{term}}$ 1.13, B–H$_{\mathrm{bridge}}$ 1.15; H–B–H 111 (Found: C, 51.4; H, 7.7; N, 11.5. Calc. for $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}\cdot 2\mathrm{CHCl_3}$: C, 51.3; H, 7.6; N, 11.4%).

7 The compound [RBp]$_2$Co (R = cyclooctane-1,5-diyl) does, however, have a similar co-ordination geometry with [Co···H–C] agostic interactions [d(Co···H) = 2.16 Å and ν(C–H) of 2690 cm^{-1}]. See: S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 205; S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1992, **31**, 974.

8 The UV/VIS electronic spectrum of $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ in CHCl$_3$ indicates that the pseudo-octahedral geometry is also maintained in solution. Specifically, $[\mathrm{Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$ is pale pink and is characterized by absorptions (λ/nm and ε/M^{-1} cm^{-1}) at 310 (2600), 540 (28) and 594 (33). The intensities of these absorptions are much more similar to that of yellow octahedral [Tp]$_2$Co [459 (13), 515 (1.3), 641 (0.1)] than that of violet tetrahedral [Bp]$_2$Co [525 (301), 552 (406), 585 (340)] in the visible range.[8a] For further comparison, low-spin ($S = \frac{1}{2}$) [RBp]$_2$Co (R = cyclooctane-1,5-diyl) is also pink [472 (sh), 500, 562 (sh), 769 nm].[8b] (*a*) J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Am. Chem. Soc.*, 1967, **89**, 3148; (*b*) S. Trofimenko, F. B. Hulsbergen and J. Reedijk, *Inorg. Chim. Acta*, 1991, **183**, 203.

9 For example, $[\mathrm{Tp}^{\mathrm{3\text{-}Pr^i,4\text{-}Br}}]\mathrm{Co}[\mathrm{Bp}^{\mathrm{Ph}}]$ exhibits Co···H and Co···B separations of 2.37 and 2.72 Å, respectively, and ν(B–H) absorptions in the range 2480–2160 cm^{-1}. Likewise, $[\mathrm{Tp}^{\mathrm{3\text{-}Pr^i,4\text{-}Br}}]\mathrm{Co}[\mathrm{Tp}^{\mathrm{Ph}}]$ exhibits Co···H and Co···B separations of 2.26 and 2.77 Å, respectively (for the $[\mathrm{Tp}^{\mathrm{Ph}}]$ ligand), and ν(B–H) absorptions in the range 2490–2175 cm^{-1}. See: J. C. Calabrese, P. J. Domaille, J. S. Thompson and S. Trofimenko, *Inorg. Chem.*, 1990, **29**, 4429.

10 For further comparison, the mean terminal Co–H bond length for complexes listed in the Cambridge Structural Database is 1.45 Å, with a range of 1.12–1.71 Å. CSD Version 5.14. *3D Search and Research Using the Cambridge Structural Database*, F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, pp. 1 and 31–37.

11 Assignments for ν(B–H) absorptions have been confirmed by studies on the deuterium labelled isotopomer, $[\mathrm{D_2Bp}^{\mathrm{Bu^t,Pr^i}}]_2\mathrm{Co}$: thus ν(B–D) absorptions are observed at 1859 and 1575 cm^{-1}, corresponding to ν(B–H)/ν(B–D) ratios of 1.34 and 1.33/1.32.

12 The IR spectra of $\{[\mathrm{Bp}^{\mathrm{R,R'}}]\mathrm{M}\}$ derivatives are often surprisingly complicated and frequently exhibit more than two ν(B–H) absorptions. For example, Trofimenko has reported six ν(B–H) absorptions for $\mathrm{Tl}[\mathrm{Bp}^{\mathrm{Bu^t}}]$, at 2410, 2355, 2290, 2275, 2218 and 2178

cm^{-1} (ref. 5). Trofimenko has also noted that pyrazabole exhibits a complex set of absorptions in both the solid state and solution. See: S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3165.

13 In fact, the preference for Co(II) to adopt tetrahedral co-ordination is so high that it is cited as forming more tetrahedral complexes than that of any other transition metal. See ref. 1.

14 In this regard, Kokusen has suggested that the subtle conformation changes between $[Bp]_2Co$ and $[Bp^{Me_2}]_2Co$ are a result of interligand steric interactions between the 3-methyl substituents. See: H. Kokusen, Y. Sohrin, M. Matsui, Y. Hata and H. Hasegawa, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 195.

15 Trofimenko has also noted that interligand steric interactions have the effect of forcing six-membered $[M(N_2)_2B]$ fragments into a "deep boat" conformation which may have the effect of forcing the B–H groups closer to a metal. See ref. 9.

16 Furthermore, the observation that $[RBp]_2Co$ (R = cyclooctane-1,5-diyl), which is devoid of bulky pyrazolyl substituents, adopts a similar octahedral geometry with agostic [Co···H–C] interactions (ref. 7), also suggests that the strengths of these three-center–two-electron [Co···H–X] interactions are important in influencing the geometrical preferences of $[R''_2Bp^{R,R'}]_2Co$ derivatives.

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