A New Class of Polypyrazolylborate Ligands

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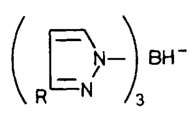
The synthesis, structures, and co-ordination chemistry of a new class of polypyrazolylborate ligands, $HB(3\text{-}Rpz)_3^-$, are presented, where R is a t-butyl or phenyl group in the 3-position of pyrazole; the structures of the cobalt complexes have been determined by *X*-ray crystallography.

In this communication we present the synthesis, structures, and co-ordination chemistry of a new class of polypyrazolylborate ligands $HB(3\text{-}Rpz)_3^-$, where R is a bulky alkyl or aryl substituent in the 3-position of the pyrazole ring. The synthesis of these new derivatives is similar to that of the original trispyrazolylborate ligands, $HB(pz)_3^-$ and $HB(3,5\text{-}Me_2pz)_3^-$, which have proven to be important ligands in co-ordination and bioinorganic chemistry,[1—4] but the co-ordination chemistry of these two groups of ligands differs in the types of complexes that can be formed. The co-ordination chemistry of the parent ligands with the first row transition metals is dominated by the formation of octahedral ML_2 complexes.[1,2,5] The number of examples of ML(X) complexes known is limited [L = $HB(pz)_3^-$ or $HB(3,5\text{-}Me_2pz)_3^-$], and these disproportionate readily to give ML_2 and MX_2.[4a,b,6] The two new ligands reported here, hydrotris(3-t-butylpyrazol-1-yl)borate, $HB(3\text{-}Bu^tpz)_3^-$ (**1**), and hydrotris(3-phenylpyrazol-1-yl)borate, $HB(3\text{-}Phpz)_3^-$ (**2**),[7] were designed to prevent bis-chelate formation and dimerization by placing bulky groups in the 3-position of the pyrazole ring. We report here stable ML(SCN) complexes [M = first row transition metal ions, L = (**1**) or (**2**)] and establish their structures crystallographically.

The syntheses of ligands and complexes are straightforward and follow the procedures used with other polypyrazolylborate ligands.[1,2] The potassium salts of (**1**) and (**2**), prepared from the appropriate pyrazole[8] and potassium borohydride in a manner analogous to that for $KHB(pz)_3$, are suitable for use in the preparation of metal complexes. Recrystallization of the thallium(I) analogues yielded white, crystalline products that gave satisfactory elemental analyses for the indicated formulations [m.p. (**1**)Tl, 190—191 °C; (**2**)Tl 185—187 °C]. Metal complexes were prepared by simply mixing the ligand with the appropriate metal salt. Two cobalt(II) complexes, the blue $Co\{HB(3\text{-}Bu^tpz)_3\}(SCN)$ (**3**), and the red $Co\{HB(3\text{-}Phpz)_3\}(SCN)$(tetrahydrofuran) (**4**), are presented as representative examples. The potassium salt of the ligand and 1 equiv. of cobalt(II) thiocyanate were mixed in methylene chloride to produce a deep blue solution, which was extracted with water and then passed down a short alumina column. Evaporation of solvent yielded a blue product with (**1**) or a red product with (**2**). Recrystallization from tetrahydrofuran (thf)–light petroleum yielded crystalline materials that gave satisfactory elemental analyses for the indicated stoicheiometries.



(1) R = Bu^t

(2) R = Ph

$Co\{HB(3\text{-}Bu^tpz)_3\}(SCN)$

(3)

$Co\{HB(3\text{-}Phpz)_3\}(SCN)(thf)$

(4)

The crystal structures of (**3**)† and (**4**)† (Figures 1 and 2) establish several important features about the co-ordination chemistry of (**1**) and (**2**). First, the t-butyl and phenyl substituents are in the 3-position of each pyrazole ring. In ligand preparations, the 3(or 5)-R-substituents assume positions to minimise steric crowding. The regiospecificity of the ligand syntheses was first demonstrated by the preparation of $H_2B(3\text{-}Mepz)_2^-$ and $HB(3\text{-}Mepz)_3^-$.[9] Secondly, (**1**) and (**2**) provide a pocket for the metal ion; formation of octahedral ML_2 or dimeric ML(X) complexes does not appear to be possible. Thirdly, tetrahedral geometries are enforced with these ligands. For (**3**), the structure (Figure 1) consists of a

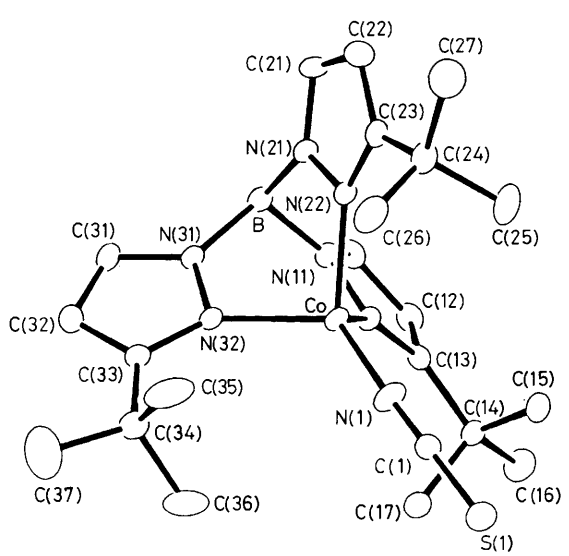


Figure 1. View of $Co\{HB(3\text{-}Bu^tpz)_3\}(SCN)$ (**3**). Thermal ellipsoids here and in Figure 2 are drawn at the 50% probability level. Selected bond distances (Å): Co–N(1), 1.911(3); Co–N(12), 2.020(3); Co–N(22), 2.024(3); Co–N(32), 2.013(3). Selected bond angles (°): N(1)–Co–N(12), 119.3(1); N(1)–Co–N(22), 121.6(1); N(1)–Co–N(32), 123.2(1); N(12)–Co–N(22), 96.3(1): N(12)–Co–N(32), 94.9(1); N(22)–Co–N(32), 95.0(1).

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† Crystals of (**3**), m.p. 276 °C, suitable for diffraction were grown from tetrahydrofuran–light petroleum at room temperature. *Crystal data:* monoclinic, space group $P2_1/n$, a = 16.466(4), b = 16.884(2), c = 9.635(2) Å, β = 95.04(2)° at −75 °C; Z = 4. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. Least-squares refinement of 289 variables led to R = 0.043 and R_w = 0.042 for 3401 reflections with $I \geqslant 3\sigma(I)$. Crystals of (**4**), m.p. 196—200 °C, suitable for diffraction were grown from tetrahydrofuran–light petroleum at room temperature. *Crystal data:* monoclinic, space group $P2_1/n$, a = 18.530(2), b = 14.177(2), c = 11.733(2) Å, β = 100.34(1)° at −100 °C; Z = 4. Intensity data were collected on a Syntex R3 diffractometer. Least-squares refinement of 388 variables led to R = 0.045 and R_w = 0.043 for 3094 reflections with $I \geqslant 3\sigma(I)$. For both structures, atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

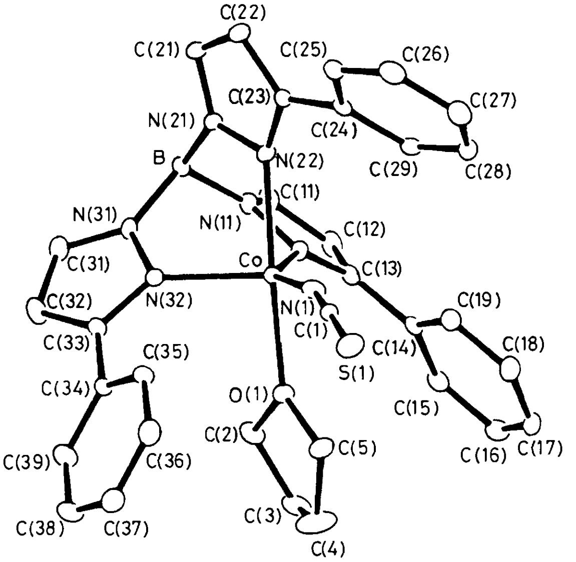

Figure 2. View of Co{HB(3-Phpz)$_3$}(SCN)(thf) (**4**). Selected bond distances (Å): Co–O, 2.143(3); Co–N(1), 1.955(4); Co–N(12), 2.054(4); Co–N(22), 2.180(4); Co–N(32), 2.079(4). Selected bond angles (°): O–Co–N(1), 89.5(1); O–Co–N(12), 91.6(1); O–Co–N(22), 175.0(1); O–Co–N(32), 91.7(1); N(1)–Co–N(12), 144.9(2); N(1)–Co–N(22), 93.7(2); N(1)–Co–N(32), 121.1(2); N(12)–Co–N(22), 83.6(1); N(12)–Co–N(32), 93.9(1); N(22)–Co–N(32), 90.0(1).

Co^{II} ion co-ordinated to three pyrazole nitrogen atoms at typical Co–N distances[4b,5a] and to an N-bound thiocyanate group. A purple Ni^{II}, a green Fe^{II}, and a white Zn^{II} analogue of (**3**) have also been prepared, the i.r. spectra of which are superimposable on that of (**3**). A tetrahedral geometry is observed with (**2**) when the cobalt complex is prepared in non-co-ordinating solvents, as shown by the deep blue colour analogous to that of (**3**) during preparation in methylene chloride. However, the complex recrystallized from thf is shown here (Figure 2) to be five-co-ordinate, with a solvent molecule bound to the metal ion to produce a trigonal bipyramidal geometry. Although the phenyl groups are clearly sterically bulky and prevent bischelate formation, they can be arranged so that the metal ion is more accessible than with t-butyl substituents.

The results presented here indicate that appropriate selection of the 3-R-group in the HB(3-Rpz)$_3^-$ ligand will permit the construction of custom-sized pockets around metal ions, allowing access only to molecules of predetermined size and/or geometry.

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