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A New Binding Mode of the Anionic Ligand Dihydrobis(1-pyrazolyl)borate, $H_2BPz_2^-$, towards Iron(II), Cobalt(II) and Nickel(II)

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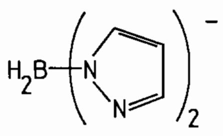
The polypyrazolylborate ligands of the general formula $(H_nBPz_{4-n})^-$ ($n = 0, 1, 2$) have been extensively studied since 1966 [1] and they are still of great interest in the coordination chemistry of the transition metals [2].

As far as the bidentate ligand dihydrobis(1-pyrazolyl)borate, $H_2BPz_2^-$ (I), is concerned, only one example of tris-complex has been characterized in the solid state so far, namely $K[V(H_2BPz_2)_3]\cdot EtOH$ [3]. All of the dipositive and tripositive 3d metal ions have been reported to form complexes with 1:2 metal-to-ligand ratio. The formation of tris-chelates of cobalt(II) and nickel(II) was only supposed to occur in acetonitrile solution in the presence of an excess of the $H_2BPz_2^-$ ligand [4].

In this note, the synthesis and characterization of iron(II), cobalt(II) and nickel(II) tris-chelates having the general formula $Et_4N[M(H_2BPz_2)_3]$ is reported.



I

Experimental

$K(H_2BPz_2)$ was prepared by the literature method [5]. Solutions in ethanol of $Et_4N(H_2BPz_2)$ were prepared immediately before their use by metathetical reaction of Et_4NCl and $K(H_2BPz_2)$. The iron(II) complex was synthesized under nitrogen atmosphere using deoxygenated solvents. All of the complexes were prepared at room temperature by adding a solution of $Et_4N(H_2BPz_2)$ (3×10^{-3} mol) in ethanol (20 cm^3) to the appropriate metal(II) chloride (10^{-3} mol) dissolved in 20 cm^3 of ethanol. Crystalline compounds were obtained in a short time and immediately filtered off. In the case of the nickel complex, the presence of a few drops of acetone in the reactant mixture improved the size of the crystals. The compounds were washed with warm benzene in order to remove traces of the bis-complexes, which may sometimes contaminate the tris-complexes. Compounds of adequate purity were thus obtained. *Anal.* Found: C, 49.3; H, 7.19; N, 28.7. $C_{26}H_{44}N_{13}B_3Fe$ requires: C, 49.8; H, 7.08; N, 29.0. Found: C, 49.4; H, 7.43; N, 28.5. $C_{26}H_{44}N_{13}B_3Co$ requires: C, 49.6; H, 7.05; N, 28.9. Found: C, 49.7; H, 7.05; N, 29.1. $C_{26}H_{44}N_{13}B_3Ni$ requires: C, 49.6; H, 7.05; N, 28.9%.

ν_{max} (BH_2) 2400s, 2360sh and 2300s cm^{-1} are identical in the three complexes.

Magnetic and spectrophotometric measurements were carried out with the apparatus and techniques already described [6].

Results and Discussion

The reaction of the tetraethylammonium salt of the bidentate ligand dihydrobis(1-pyrazolyl)borate, $Et_4N(H_2BPz_2)$, with iron(II), cobalt(II) and nickel(II) in ethanol, affords complexes with 1:3 metal-to-ligand ratio having the general formula $Et_4N[M(H_2BPz_2)_3]$ (M = Fe, Co, Ni). The cobalt and nickel complexes are stable in air. The iron complex is slowly oxidized by atmospheric oxygen, but it is indefinitely stable under inert atmosphere. The complexes are paramagnetic with magnetic moment values close to those expected for high-spin d^6, d^7 and d^8 configurations, respectively (Table I). The reflectance spectra of the complexes are typical of octahedral species, thus indicating that the three molecules of the bidentate ligand are coordinated to each metal as chelates.

In solution, the three complexes behave in different ways with respect to each other. The nickel complex in acetone and acetonitrile solutions still gives the same tris-chelates which are present in the solid state, as indicated by the strict similarity of their electronic spectra (Table I). The cobalt complex in ethanol exhibits an electronic spectrum characteristic of the tetrahedral bis-chelate $[Co(H_2BPz_2)_2]$ [1b]. The electronic spectrum in acetonitrile is similar to that in ethanol apart from the lower molar absorptivity. This feature indicates that the six-coordinated species, presumably $[Co(H_2BPz_2)_3]^-$, are in equilibrium with the tetrahedral species $[Co(H_2BPz_2)_2]$ in acetonitrile solution. The iron(II) complex in acetonitrile solution exhibits an electronic spectrum different from that of the solid compound, indicating six-coordinated species which may be bis-solvent adducts of the type $Fe(H_2BPz_2)_2\cdot 2CH_3CN$.

When an excess of the ligand $H_2BPz_2^-$ is present in the acetonitrile solution of either cobalt(II) or iron(II) tris-chelates, only the octahedral species $[M(H_2BPz_2)_3]^-$ can be identified from the electronic spectra.

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TABLE I. Some Physical Data for the Complexes

Compound	Colour	μ_{eff} (μ_B) (300 K)	State (molar concentration for solutions in parentheses)	Absorption maxima (nm) (ϵ_{molar} for solutions in parentheses)
$Et_4N[Fe(H_2BPz_2)_3]$	white	5.42	R[a]	850
			CH_3CN (4.1×10^{-3})	680(12)
			+ ligand (7.1×10^{-3} + 1.1×10^{-2})[b]	830(11)
$Et_4N[Co(H_2BPz_2)_3]$	pink	4.86	R	450, 500, 535, 570, 950, 1500
			C_2H_5OH (1.9×10^{-3})	500(232), 550(282), 585(237), 1070(50), 1230(50)
			CH_3CN (1.9×10^{-3})	500(60), 550(62), 590(47), 1000(13), 1200 sh,
			+ ligand (5.0×10^{-3} + 1.1×10^{-2})	490(26), 530 sh, 590 sh, 1025(8)
$Et_4N[Ni(H_2BPz_2)_3]$	turquoise	3.17	R	360, 565, 1100
			$(CH_3)_2CO$ (9.4×10^{-3})	360(19), 565(10), 925(9)
			CH_3CN (2.6×10^{-3})	360(15), 565(8), 875(8)
			+ ligand (2.5×10^{-3} + 6.1×10^{-3})	360(16), 565(9), 950(10)

[a] R = diffuse reflectance spectra. [b] The first concentration refers to the complex and the second concentration to the added ligand.

The easy formation of crystalline tris-chelates when the $Et_4N(H_2BPz_2)$ salt is used in the place of the $K(H_2BPz_2)$, even in the case of cobalt(II) which strongly favours the bis-chelate over the tris-chelate in ethanol solution, may be due to favourable solid state packing forces which make the $Et_4N[M(H_2BPz_2)_3]$ compounds less soluble than the neutral bis-chelates in ethanol solution.

It has been previously shown that steric hindrance exerted by the $H_2BPz_2^-$ ions in a tris-chelate may be partially released through a rearrangement of the ligand conformation towards planarity and through a lengthening of the metal-donor linkages [3]. In this regard we may note that the six-coordinated complex $Et_4N[Fe(H_2BPz_2)_3]$ is high-spin, in agreement with the proposed expansion of the metal-to-ligand bond lengths. In contrast, it was reported that the six-coordinated complex bis(hydrotris(1-pyrazolyl)-borato)iron(II), $Fe(HBPz_3)_2$, is low-spin and exhibits relatively short metal-to-ligand bond distances [7].

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