



Spectral studies of transition metal complexes of dihydrobis(1-pyrazolyl)borate with some Lewis bases

Adediran M. Mesubi^a, Uche B. Eke^{b,*}, Oyedele M. Oyeku^c, Samson O. Owalude^b

^a Department of Physical Sciences, College of Science and Technology, Covenant University, Ota, Ogun State, Nigeria

^b Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Kwara State, Nigeria

^c Federal Institute for Industrial Research Oshodi, Lagos, Nigeria

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Abstract

Co(II), Ni(II) and Cu(II) complexes of dihydrobis(1-pyrazolyl)borate and their adducts with some Lewis bases have been prepared and characterized by elemental analyses, IR and UV–vis spectroscopic techniques. The adducts were either 1:1 or 1:2 complexes depending on whether the Lewis base was bidentate or monodentate. The results indicate that adducts with 1,10-phenanthroline were the most stable due to the chelating effect of the Lewis base. The order of reactivity of the complexes was determined to be $\text{Ni}(\text{H}_2\text{BPz}_2)_2 > \text{Cu}(\text{H}_2\text{BPz}_2)_2 > \text{CoH}_2(\text{BPz}_2)_2 > \text{Co}(\text{H}_2\text{BPz}_2)_2$. The effects of various solvents (i.e., benzene, chloroform and DMF) on the structure were studied. The solvents appear to minimally affect the visible spectra of $\text{Co}(\text{H}_2\text{BPz}_2)_2$. The $\text{Ni}(\text{H}_2\text{BPz}_2)_2$ and $\text{Cu}(\text{H}_2\text{BPz}_2)_2$ adducts exhibit a four-coordinate structure in non-coordinating solvents. However, in coordinating solvents, such as DMF, the adducts exhibit six-coordinate structures.

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1. Introduction

Poly(1-pyrazolyl)borates are a class of uninegative ligands with excellent ligating properties. These ligands are sometimes referred to as “Scorpionate” ligands with “pinch and sting” capabilities [1]. Poly(1-pyrazolyl)borates function as bidentate ($[\text{H}_2\text{B}(\text{Pz})_2]^-$ (I)), tridentate ($[\text{HB}(\text{Pz})_3]^-$ (II)) and tetradentate

($[\text{B}(\text{Pz})_4]$ (III)) chelating ligands [2]. Depending on the number of pyrazole groups attached to the boron atom, these scorpionates (I, II and III) are typically referred to as dihydrobispyrazolylborates, hydrotrispyrazolylborates and tetrakispyrazolylborates, respectively [2,3]. Poly(1-pyrazolyl)borates form a variety of stable coordination compounds with transition metal ions and organometallic compounds [1–6].

The syntheses and characterization of transition metal complexes of poly(1-pyrazolyl)borate have continued to be of much interest since its discovery nearly four decades ago. For example, shortly after its discovery, the syntheses and characterization of several metal complexes of the $[\text{H}_2\text{B}(\text{Pz})_2]_2\text{M}$, $[\text{HB}(\text{Pz})_3]\text{M}$ and $[\text{B}(\text{Pz})_4]_2\text{M}$ (where $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Pb}$ and Hg) type were reported [2]. In addition,

* Corresponding author. Tel.: +234 8033795414.

E-mail address: ekeub@yahoo.co.uk (U.B. Eke).

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several studies of the coordination chemistry of various hydrotrispyrazolylborates have been reported [7–14]. The reaction of poly(1-pyrazolyl)borate metal complexes with other ligating compounds has also attracted much attention. With lanthanides and actinides, poly(1-pyrazolyl)borates form air and moisture stable complexes [15–18]. The solid-state structures of this group of compounds exhibit interesting structural geometries. For example, uranylhydrotris(3,5-dimethylpyrazolyl)boratotrichlorotetrahydrofuran (μ [HB(3,5-Me₂Pz)₃]Cl₃(THF)) exhibits a capped octahedral geometry with a seven coordinate uranium centre [10]. When the three chloro and THF ligands were replaced with cyclopentadienide and alkoxide/aryloxy, respectively, the resulting product adopted an asymmetric metal centre [3,7–10].

Many transition metal complexes are known to form adducts with Lewis bases [19–21] due to the ability of transition metal ions in these complexes expanding their coordination shells. For example, a tetrahedral or square planar complex can expand its coordination shells to form a five-coordinate 1:1 adduct or a six-coordinate 1:2 adduct depending on the type and number of Lewis base molecules involved in the adduct formation. For example, the coordination number of a low-spin square planar nickel(II) complex can be increased by the addition of two molecules of a monodentate Lewis base to form a high-spin octahedral adduct [19]. Transition metal complexes of poly(1-pyrazolyl)borates and Lewis base ligands have been extensively studied. However, studies of metal compounds containing a mixture of these two ligands are rare in the literature. Gunnoe and co-workers have pioneered adduct formation chemistry of transition metal-poly(1-pyrazolyl)borates with π -bonding ligands, such as phosphines, phosphates and carbon monoxide [22,23]. Here, we have expanded this pioneering effort by incorporating Lewis base ligands into the coordination sphere of transition metal-poly(pyrazolyl)borate complexes. The resulting adducts were characterized using physical, infrared and electronic spectroscopic techniques.

2. Experimental

Potassium borohydride, pyrazole, transition metal salts and the Lewis bases were obtained from commercial sources and used without further purification. Reagent grade solvents were used without further purification. The melting points were determined in open capillaries using an electrothermal melting point apparatus and are uncorrected. The UV-visible absorption spectra of the adducts were recorded on a Pye Uranium

SP 80-150 UV-visible spectrophotometer in the Department of Chemistry, University of Ilorin, Nigeria. The infrared spectra were recorded using KBr pellets from 4000 to 400 cm⁻¹. The mass spectra were measured by introducing the sample at room temperature into the ion source of the mass spectrometer (70 eV). The ion source temperature was varied to obtain good quality spectra. The infrared mass spectral analysis and microanalysis (C, H, N) were performed at the Institute für Anorganische und Analytische Chemie, Technische Universität, Berlin, Germany.

2.1. Preparation of Ni(II), Co(II) and Cu(II) dihydrobis(1-pyrazolyl)borate complexes

The complexes were prepared using the same general method described here for nickel(II)bis(1-pyrazolyl)borate. Nickel(II) chloride (0.71 g, 0.0055 mole) and potassium dihydrobis(1-pyrazolyl)borate (KH₂B(Pz)₂), (2 g, 0.011 mole), which was obtained according to a previously published procedure [2], were separately dissolved in 15 cm³ of distilled water. The two clear solutions were mixed together at room temperature and stirred for several minutes until a copious amount of precipitate was formed. Then, the resulting precipitate was washed with distilled water, dried in air and recrystallized from hot toluene.

The general equation for the reaction is shown in Scheme 1, and the physical and electronic data are listed in Table 1.

2.2. Preparation of the adducts

The nickel(II), cobalt(II) and copper(II) bis(1-pyrazolyl)borate adducts were prepared by reacting the transition metal complexes with a general formula of M[H₂B(Pz)₂]₂ with Lewis bases. The bidentate and monodentate Lewis bases were reacted with M[H₂B(Pz)₂]₂ at room temperature in a 1:1 and 1:2 ratio, respectively. Each reactant was dissolved in a minimum quantity of benzene, and the two solutions were mixed together and stirred. The resulting solution was allowed to stand at room temperature with occasional stirring for approximately thirty to sixty minutes. The resulting solids were filtered under suction and recrystallized from an appropriate solvent. The adduct solutions that did result in immediate precipitates were allowed to evaporate slowly at room temperature while unstable solutions were stored in a refrigerator. The resulting precipitates were filtered under suction. The physical and analytical data for the adducts are reported in Table 2.

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