

Synthesis and Characterisation of Transition Metal Complexes with 5-Methylindazolyl Borates

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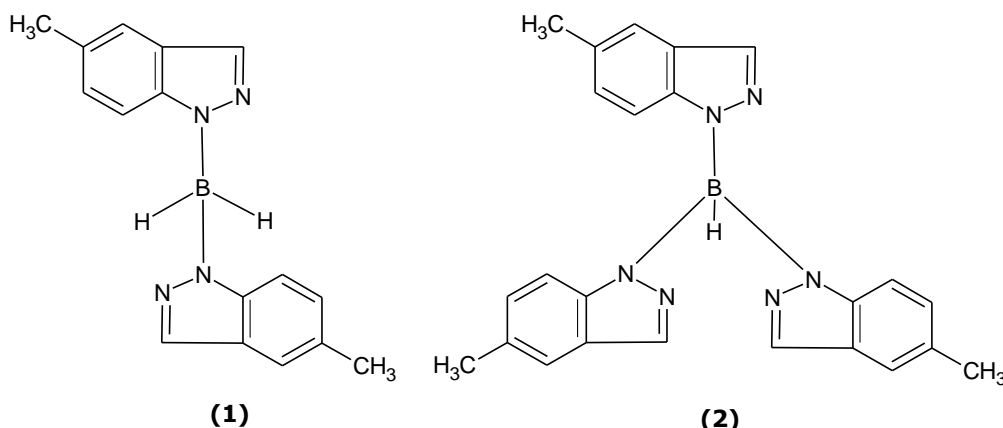
Abstract: The nucleophilicity of the nitrogen atoms and their steric accessibility may however be varied through appropriate ring substitution mainly in the 1 or 3(5) position. A number of reports have appeared where, with suitable substitution pyrazole has been made to function as a bidentate, tridentate and tetradentate ligand⁽³⁻¹²⁾. Here we report the synthesis and characterization of some transition metal complexes with dihydrobis (5-methylindazolyl)-borate (I) and hydro tris-(5-methyl indazolyl) borate(II).

Keyword: dihydrobis (5-methyl indazolyl)-borate, hydro tris-(5-methyl indazolyl) borate(II).

I. Introduction

The coordinating capacity of pyrazole as a monodentate or bidentate ligand was known as early as 1890^(1,2). In the latter case pyrazole acts through both the nitrogen atoms and functions as an 'exobidentate' ligand having C_{2v} symmetry. The nucleophilicity of the nitrogens and their steric accessibility may be varied through appropriate ring substitution. Due to these attractive features and the vigorous development of pyrazole chemistry in general, the coordination chemistry of pyrazole and of its derivatives has attracted much attention during the last several decades.

A substituent in the 3 positions introduces steric hindrance and makes it difficult to have six 3-substituted pyrazoles coordinated via the 2-N to a metal. This difficulty can be circumvented by coordination through a tautomeric 5-substituted structure, where steric hindrance is minimized. Several substituted pyrazoles both at 3 and 3,5-positions have been synthesized and some are given below 3-tert-butylpyrazole⁽²⁾, 3-tert-butyl-5-isopropylpyrazole⁽³⁾, 3-tert-butyl-5-methylpyrazole, 3-isopropyl-4-bromopyrazole^(4,5) 3-isopropylpyrazole⁽⁶⁾, 3-isopropyl-5-methylpyrazole⁽⁷⁾, 3,5-diisopropylpyrazole⁽⁸⁾, 3-neopentyl-pyrazole⁽⁹⁾, 3-thienylpyrazole⁽¹⁰⁾, 3-phenylpyrazole⁽²⁾, 3-phenyl-5-methyl-pyrazole⁽¹¹⁾, 3,5-diphenylpyrazole⁽⁸⁾, 3-p-tolylpyrazole⁽¹²⁾, 3-p-anisyl-pyrazole⁽⁴⁾, 3,5-di-tert-butylphenylpyrazole⁽¹³⁾, 3-anthrylpyrazole⁽¹⁴⁾, 3-mesityl-pyrazole, 3-cumyl-5-methylpyrazole⁽¹⁵⁾. Most of the synthesized substituted pyrazoles have been used for the synthesis of their dihydrobis-, hydrotris- and tetrakispyrazolylborate salts which have wide application in coordination chemistry, bioinorganic and organometallic chemistry.



II. Experimental

5-Methylindazolyl (Koch-Light), m.p., 170°C, was recrystallized from methanol. Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and Hg(II) chlorides (BDH) were used as such. The metals were estimated by complexometric titrations against EDTA. The IR spectra were recorded in nujol and KBr in the 4000–200 cm^{-1} region on a Perkin-Elmer 621 spectrophotometer. The diffuse reflectance spectra were recorded on a Carl Zeiss VSU-2P spectrophotometer using MgO as the calibrant. Magnetic susceptibility measurements were done at room temperature with a vibration sample magnetometer model 155.

Potassium dihydrobis (5-methylindazolyl)borate

Potassium borohydride (1.0 g) and 5-methylindazole (4.92 g) were mixed together in 1:2 molar ratio and the mixture was stirred and heated at < 100°C. After 12 hr, when evolution of hydrogen gas stopped, the melt was poured into 250 ml of hot toluene and the resulting mixture was filtered. The filtrate containing traces of KBH₄ was rejected and the solid was washed twice with hot toluene and recrystallized from hexane, m.p. 184–186°C. It was soluble in hexane and ethanol. Potassium hydrotris (5-methylindazolyl) borate(II) was synthesized similarly except that the ratio of KBH₄ to 5-methylindazole was kept 1:3.

Preparation of the complexes: Dihydrobis (5-methylindazolyl)borate copper(II)

An ethanolic solution of copper (II) chloride (1.0 g) was added to the ligand (1.27 g) solution in the same solvent. A dark blue solid was obtained after keeping the solution for a few hours. It was filtered and washed with absolute ethanol and dried in an oven at 100°C. All other complexes of ligands I and II were synthesized in the manner described above (Tables 8.1C and 8.2C).

III. Results And Discussion:

The complexes of (I) and (II) have a 1:2 (metal:ligand) ratio and are stable at room temperature. The molar conductances of the complexes (43–45 ohm⁻¹ cm² mol⁻¹) in DMSO are lower than that required for a 1:1 electrolyte.

In the formation of the ligand, the hydrogen atoms at position 1 in the 5-methylindazole molecule are removed, together with the hydrogen atoms of potassium borohydride. The –CH₃ group remains intact as the νCH bands in the IR spectra of both the free and complexed ligand remain unaltered.⁽¹⁵⁾ The IR spectra of ligands show a weak band in 2385–2422 cm⁻¹ region due to νB–H. The other characteristic frequencies of 5-methylindazole also appear in the ligand. The ν(C=C) and ν(C=N) (1500–1620 cm⁻¹) bands are similar to those observed in the free indazole and 5-methylindazole.⁽¹⁶⁾ The ν(M–N) frequency lies in the 410–450cm⁻¹ region. A comparison of the far IR spectra of the ligands with those of Zn(II), Cd(II) and Hg(II) complexes reveals the appearance of a new band at 410, 435 and 438 cm⁻¹ respectively. This band is presumably due to the M–N stretching vibrations suggesting coordination through the imine nitrogen atom.

Pyrazole and its derivatives show a change in ν(NH) after complex formation. It has been shown to coordinate via pyridyl nitrogen^(17–19) although a clear cut assignment has not been made in such cases.

Table 8.1(C): Analytical Colour and melting point data of potassium hydrotris (5-methylindazolyl)borate and its complexes

S.No.	Complexes	Colour (m.p.°C)	Found (Calc.), %			
			C	H	N	M
1.	[HB(5-MlnZ) ₃]K ⁺	Black (200)	64.70 (64.89)	4.80 (4.95)	18.80 (18.92)	–
2.	Cu[HB(5-MlnZ) ₃] ₂	Dark blue (270–272)	65.80 (65.96)	4.85 (5.03)	19.12 (19.24)	2.10 (7.27)
3.	Ni[HB(5-MlnZ) ₃] ₂	Lila (360)	66.20 (66.33)	4.90 (5.06)	19.10 (19.34)	6.60 (6.76)
4.	Co[HB(5-MlnZ) ₃] ₂	Chocolate (360)	66.15 (66.31)	4.90 (5.06)	19.10 (19.34)	6.60 (6.78)
5.	Mn[HB(5-MlnZ) ₃] ₂	Light yellow (360)	66.50 (66.62)	5.0 (5.08)	19.30 (19.43)	6.10 (6.35)
6.	Fe[HB(5-MlnZ) ₃] ₂	Colourless (360)	66.40 (66.55)	5.0 (5.08)	19.20 (19.41)	6.32 (6.45)
7.	Zn[HB(5-MlnZ) ₃] ₂	Colourless (360)	65.70 (65.82)	4.90 (5.02)	19.02 (19.20)	7.30 (7.47)
8.	Cd[HB(5-MlnZ) ₃] ₂	Colourless (360)	62.30 (62.47)	4.60 (4.70)	18.0 (18.22)	12.0 (12.19)
9.	Hg[HB(5-MlnZ) ₃] ₂	Colourless	56.80 (57.0)	4.15 (4.35)	16.50 (16.63)	19.68 (19.81)

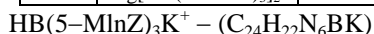
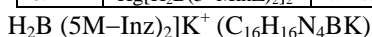


Table 8.2(C): Analytical data, colour and melting points of potassium dihydrobis (5-methylindazolyl)borate and its complexes

S. No.	Complexes	Colour	Melting Point (°C)	Found (Calc.), %			
				C	H	N	M
1.	[H ₂ B(5-MlnZ) ₂]K ⁺	Black	185–187	61.0 (61.18)	4.90 (5.09)	17.70 (17.84)	–
2.	Cu[H ₂ B(5-MlnZ) ₂] ₂	Dark blue	254–255	55.40 (55.55)	4.50 (4.62)	16.04(16.20)	9.0 (9.19)
3.	Ni[H ₂ B(5-MlnZ) ₂] ₂	Brownish red	>360	55.80 (55.94)	4.50 (4.66)	16.20 (16.31)	8.40 (8.55)
4.	Co[H ₂ B(5-MlnZ) ₂] ₂	Chocolate	>360	55.80 (55.93)	4.50 (4.66)	16.15 (16.31)	8.40 (8.58)
5.	Mn[H ₂ B(5-MlnZ) ₂] ₂	White	>360	56.13 (56.26)	4.52 (4.60)	16.15 (16.40)	7.90 (8.04)
6.	Fe[H ₂ B(5-MlnZ) ₂] ₂	White	>360	56.02 (56.18)	4.50 (4.68)	16.23 (16.38)	8.0 (8.17)
7.	Zn[H ₂ B(5-MlnZ) ₂] ₂	White	>360	55.30 (55.41)	4.50 (4.61)	16.0 (16.16)	9.30 (9.43)
8.	Cd[H ₂ B(5-MlnZ) ₂] ₂	White	>360	51.72 (51.89)	4.20 (4.32)	15.0 (15.13)	15.0 (15.18)
8.	Hg[H ₂ B(5-MlnZ) ₂] ₂	White	>360	46.20 (46.36)	3.72 (3.86)	13.40 (13.52)	24.10 (24.21)



Electronic spectra and magnetic susceptibilities:

The absorption bands observed in the ranges 36,460–35,550 cm⁻¹ and 34,550–33,980 in all the complexes are attributed to the intra-ligand transitions.

The reflectance spectra of Cu(II) complexes with I and II show one absorption band (12430–12560 cm⁻¹) corresponding to ²T_{2g} ← ²E_g transition in addition to a weak band around 15,200 cm⁻¹ which may be due to spin forbidden transition. The magnetic moment value is indicative of a distorted octahedral geometry, like that for other Cu(II) complexes with similar ligands^(20,21).

The reflectance spectra (29300, 17500, 10110 cm⁻¹) corresponding to the transitions ³A₂(F) ← ³T₁(P), ³A₂(F) ← ³T₁(F), ³A₂(F) ← ³T₂(F) respectively and the magnetic moment values (2.90 B.M.) are in consonance with an octahedral geometry for Ni(II) ion.

The magnetic moment values of Co[H₂B(5-MlnZ)₂]₂ and Co[HB(5-MlnZ)₂]₂ (4.92–4.95 BM) and the reflectance spectral bands (19850, 17300, 8200 cm⁻¹) assigned to the transitions ⁴T_{1g}(F) ← ⁴T_{1g}(P), ⁴T_{1g}(F) ← ⁴A_{2g}(F) and ⁴T_{1g}(F) ← ⁴T_{2g}(F) are typical of an octahedral Co(II) complex in high spin state.

The magnetic moment (5.90 BM) and electronic spectral bands in the region 25550–19000 cm⁻¹ corresponding to the transitions ⁶T_{1g} ← ⁴T_{1g}(G), ⁶T_{1g} ← ⁴E_g(G), ⁶A_{1g} ← ⁴T_{1g}(G) are indicative of an octahedral stereochemistry for Mn(II) ion.^(22–27)

IV. Zn/Cd/Hg-Complexes

The infra red spectra of these complexes are comparable to those of Ni(II), Co(II), Fe(III), Mn(II) complexes, almost band for band (± 5 cm⁻¹). In view of such similarity in the infrared spectra, these complexes are also considered to be pseudo-octahedral with the ligands functioning as tridentate.

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