

## Synthesis, characterization and spectroscopic studies of the dihydrobis(1,2,3-benzotriazolyl)borate anion and its complexes with $MCl_2 \cdot py_2$

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*Abstract:* The preparation of sodium dihydrobis(1,2,3-benzotriazolyl)borate was realised by refluxing one mole of sodium borohydride with two moles of 1,2,3-benzotriazole in toluene over a period of 12 h. Its complexes with  $MCl_2 \cdot py_2$  [where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and py = pyridine] were characterized by elemental analysis as well as magnetic, spectroscopic and conductivity measurements. On the basis of these studies, it is proposed that the geometry of all the complexes is octahedral. The ligand field parameters  $10 Dq$ ,  $B$  and  $\beta$  show extensive overlap between the M–L orbital. The molar conductance of  $10^{-3}$  M solutions of the complexes in DMSO suggest them to be non-ionic in nature.

*Keywords:* borate, transition metal complexes, spectroscopy.

### INTRODUCTION

Boron attached to nitrogen heterocycles yields novel ligands, which occupy a unique place in coordination chemistry.<sup>1</sup> Polypyrazolyl borate gave rise to a tremendous amount of chemistry<sup>2</sup> with amazing diversity. These anions may be considered as a subgroup of a wider class of ligands, which are potentially accessible *via* the reaction of  $BH_4^-$  with nitrogen heterocycles. Pyrazolyl borate derivatives are multidentate ligands used in bioinorganic, organometallic and coordination chemistry.<sup>3–9</sup>

The known scorpionate type pyrazolyl borates are either limited to the use of parent ligands or with substituents such as  $-CH_3$ ,  $-C_3H_7$ ,  $-C_4H_9$  and  $-C_6H_5$ . Considerable work with perfluorinated substituents of polypyrazolyl borate has also been reported.<sup>10,11</sup> Substitution on the pyrazolyl ring allows control over the steric environment of the binding site.<sup>12,13</sup> The dipyrazolyl anions have a formal analogy to  $\beta$ -diketonates and they mimic them in complex formation.<sup>2</sup>

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Only a few poly(azolyl)borate ligands and their complexes other than pyrazole have been reported, although the chemistry of poly(azolyl)borate complexes may critically depend on the pattern of the ring substitution.<sup>14,15</sup> It prompted us to investigate the behaviour of metal complexes of analogous ligand systems with modified steric and/or electronic properties.<sup>16</sup>

In this communication, the preparation and characterization of a new poly(azolyl)borate ligand derived from 1,2,3-benzotriazole and its complexes with  $MCl_2py_2$  [where  $M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)$  and  $py =$  pyridine] is described.

## EXPERIMENTAL

### General consideration

Sodium borohydride (BDH), 1,2,3-benzotriazole (Loba Chemie), hydrated metal chlorides (Merck), toluene (Ranbaxy) and pyridine (CDH) were used as received.  $MCl_2py_2$  was synthesized by a literature method.<sup>17</sup> Methanol was distilled before use. Elemental analysis (C, H, N) was carried out with a Thomas and Coleman analyzer. The metals were estimated by complexometric titration.<sup>18</sup> The IR spectra ( $4000-400\text{ cm}^{-1}$ ) were recorded on a RXI FT-IR spectrometer as KBr discs. The conductivity measurements were carried out on a CM-82T Elico conductivity bridge in DMSO. The UV-Vis spectra were recorded on a Cintra 5GBC spectrometer in DMSO. Magnetic susceptibility measurements were performed with a 155 Allied Research vibrating sample magnetometer at room temperature.

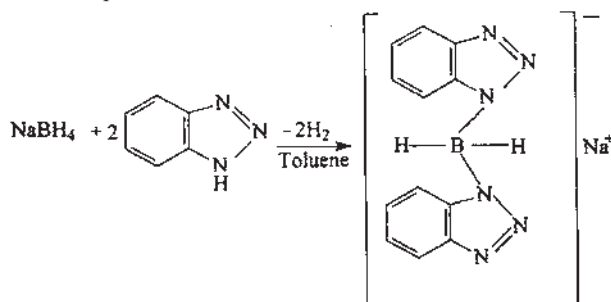
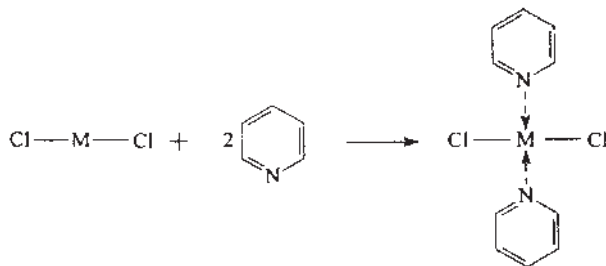


Fig. 1. Preparation of the ligand  $Na[H_2B(BTz)_2]$ .

### Synthesis of $Na[H_2B(BTz)_2]$

1,2,3-Benzotriazole (6.32 g, 53.5 mmol) was mixed with a suspension of  $NaBH_4$  (1.0 g, 26.5 mmol) in toluene (75 mL) and refluxed for 12 h under dry condition. Two moles of evolved hydrogen gas were collected over water. When the gas evolution ceased and the temperature did not rise, the reaction mixture was cooled to room temperature, which afforded a white product (Fig. 1). This was filtered, washed with cold diethyl ether (20 mL) and dried *in vacuo*.



$M = Mn(II), Fe(II), Co(II), Ni(II)$  and  $Cu(II)$

Fig. 2. Preparation of the  $MCl_2py_2$  complexes.

*Synthesis of complexes*

A methanolic solution of MCl<sub>2</sub>py<sub>2</sub> (20 mL) (Fig. 2) was added to a methanolic solution of Na[H<sub>2</sub>B(BTz)<sub>2</sub>] (20 mL) in a 1:2 mole ratio with continuous stirring over about 1 h. The reaction mixture was left overnight, which yielded the required compound (Fig. 3). This was isolated, washed with methanol and dried in *vacuo*.

## RESULTS AND DISCUSSION

The ligand is soluble in DMF, DMSO, THF, acetone, methanol and water. The complexes are thermally stable and decompose above 300 °C. They are soluble in DMSO. Their molar conductance of 10<sup>-3</sup> M in DMSO are given in Table I. They fall well below those reported for univalent electrolyte at room temperature, indicating their non-electrolytic nature.<sup>19</sup>

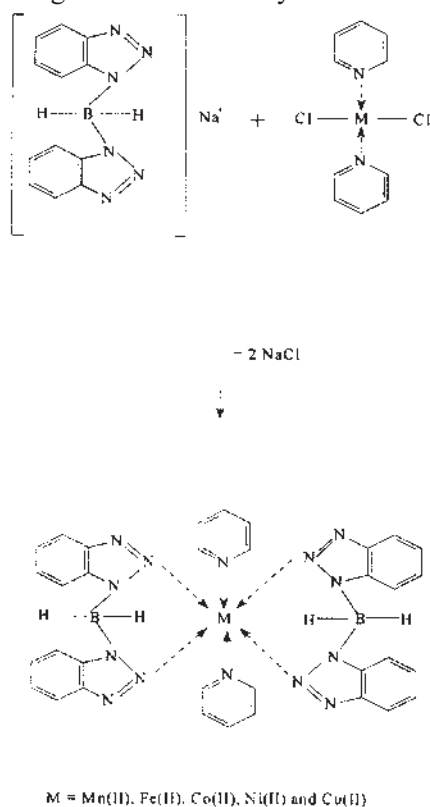


Fig. 3. Preparation of the complexes  
M[H<sub>2</sub>B(BTz)<sub>2</sub>]<sub>2</sub>py<sub>2</sub>.

*IR Spectra*

The ligand showed the absence of  $\nu(\text{N-H})$  in the 3400–3000 cm<sup>-1</sup> region and the appearance of a new band at 1450 cm<sup>-1</sup>, indicating the substitution of hydrogen by boron (Table II). Dihydrobis(organyl)borates generally exhibit two  $\nu(\text{B-H})$  in the 2350–2500 cm<sup>-1</sup> region, which are strongly influenced by the substituents on the ring. A doublet at 2436 and 2496 cm<sup>-1</sup> due to the presence of two B-H bonds in



TABLE II. Characteristic infrared bands ( $\text{cm}^{-1}$ ) for the complexes

Compounds	B-H stretching	B-N stretching	C-N stretching	C=N stretching	C=C stretching	N-N stretching	N=N stretching	M-N stretching
$[\text{C}_{12}\text{H}_{10}\text{N}_6\text{B}]^-\text{Na}^+$	2436 w 2496 w	1450 w	1489 w	—	1661 s	1007 s	1590 w	—
$\text{C}_{34}\text{H}_{30}\text{N}_{14}\text{B}_2\text{Mn}$	2463 w 2352 w	1453 w	1490 w	1595 s	1608 w	947 s	1578 w	445 w
$\text{C}_{34}\text{H}_{30}\text{N}_{14}\text{B}_2\text{Fe}$	2413 w 2348 w	1459 w	1492 w	1595 s	1610 w	945 s	1595 w	462 w
$\text{C}_{34}\text{H}_{30}\text{N}_{14}\text{B}_2\text{Co}$	2444 w 2359 w	1447 w	1488 w	1546 s	1606 w	943 s	1580 w	462 w
$\text{C}_{34}\text{H}_{30}\text{N}_{14}\text{B}_2\text{Ni}$	2450 w 2364 w	1440 w	1490 w	1595 s	1612 w	945 s	1595 w	437 w
$\text{C}_{34}\text{H}_{30}\text{N}_{14}\text{B}_2\text{Cu}$	2389 w 2358 w	1440 w	1496 w	1564 s	1615 w	951 s	1589 w	443 w

TABLE III. Magnetic susceptibility, electronic spectra and ligand field parameters of the complexes

Compounds	Magnetic moment/ $\mu_B$	Electronic bands/cm <sup>-1</sup>	$\log \epsilon/\text{mol}^{-1} \text{cm}^2$	Possible assignments	10Dq/cm <sup>-1</sup>	B/cm <sup>-1</sup>	$\beta$
$C_{34}H_{30}N_{14}B_2Mn$ [L] <sub>2</sub> ·Mn·py <sub>2</sub>	5.8	26,041	2.23	C.T.	-	-	-
		22,075	1.92	$4T_{2g}(G) \leftarrow {}^6A_{1g}$			
$C_{34}H_{30}N_{14}B_2Fe$ [L] <sub>2</sub> ·Fe·py <sub>2</sub>	5.3	16,639	1.83	$4T_{1g}(G) \leftarrow {}^6A_{1g}$	-	-	-
		34,965	3.54	C.T.			
		25,316	2.93	C.T.			
$C_{34}H_{30}N_{14}B_2Co$ [L] <sub>2</sub> ·Co·py <sub>2</sub>	4.4	11,642	2.20	${}^5E_g \leftarrow {}^5T_{2g}$	20,102	437	0.84
		24,691	2.5	$4T_{1g}(P) \leftarrow 4T_{1g}(F)$			
		22,075	2.1	$4A_{2g}(F) \leftarrow 4T_{1g}(F)$			
		19,230	1.8	$4T_{2g}(F) \leftarrow 4T_{1g}$			
$C_{34}H_{30}N_{14}B_2Ni$ [L] <sub>2</sub> ·Ni·py <sub>2</sub>	3.2	30,675	2.0	C.T.	16,639	520	0.48
		26,809	1.8	C.T.			
		21,276	1.3	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$			
$C_{34}H_{30}N_{14}B_2Cu$ [L] <sub>2</sub> ·Cu·py <sub>2</sub>	1.9	16,639	1.5	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	-	-	-
		16,639	2.0	${}^2E_g \leftarrow {}^2B_{1g}$			
		11,274	2.2	${}^2A_{1g} \leftarrow {}^2B_{1g}$			

sodium dihydrobis(1,2,3-benzotriazolyl)borate has been observed.<sup>20</sup> The complexes, M[H<sub>2</sub>B(BTz)<sub>2</sub>]py<sub>2</sub> show identical bands. Different absorptions bands appear in the 1620–1520 cm<sup>-1</sup> range, indicating the presence of  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$ , confirming the presence of the pyridine ring in the complexes.<sup>21</sup> The  $\nu(\text{M}-\text{N})$  band may appear in the lower frequency region (470–400 cm<sup>-1</sup>) for nitrogen ligands.<sup>22</sup> It has been found on the basis of normal coordinate analysis of first row transition metal compounds with nitrogen containing donor groups that the  $\nu(\text{M}-\text{N})$  generally increases with increasing nuclear charge in the metal.<sup>23</sup> It was observed that the  $\nu(\text{M}-\text{N})$  band appears in the 462–443 cm<sup>-1</sup> region.

#### *Electronic Spectra and Magnetic Moments*

The Mn(II) complex in octahedral environment gives spin forbidden as well as parity forbidden bands. In addition to the  $n-\pi^*$  transition, the Mn(II) complex in DMSO exhibits two additional bands at 22,075 and 16,639 cm<sup>-1</sup>, which have been assigned to  ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$  and  ${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$  transitions, respectively (Table III). The d<sup>5</sup> configuration gives an essentially spin-only magnetic moment of  $\sim 5.9 \mu_{\text{B}}$ . In the present work, the value of  $5.84 \mu_{\text{B}}$  supports an octahedral structure for the Mn(II) ion in a high spin state.<sup>24</sup>

The brown coloured Fe(II) complex exhibits a charge transfer and a band in the visible region at 11,642 cm<sup>-1</sup>, which may be assigned as  ${}^5\text{E}_g \leftarrow {}^5\text{T}_{2g}$ .<sup>25</sup> The magnetic moment value for the Fe(II) complex ( $5.28 \mu_{\text{B}}$ ) is very close to that of high spin octahedral Fe(II) complexes.

Octahedral Co(II) complexes are typically pale red or purple in colour with three spin allowed electronic transitions to the excited quartet state; the  ${}^4\text{A}_{2g}$  level is usually close to the  ${}^4\text{T}_{1g}(\text{P})$  level and the transitions to these two levels are close together. Three absorption bands at 24,691, 22,075 and 19,230 cm<sup>-1</sup> were observed, corresponding to  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ;  ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  transitions, respectively.<sup>26</sup> These bands in the visible region are consistent with spin allowed d-d transitions for an octahedral Co(II) ion. The observed magnetic moment ( $4.40 \mu_{\text{B}}$ ) is consistent with the predicted high-spin value for an octahedral Co(II) complex, with a considerable orbital contribution to the overall magnetic moment.<sup>27,28</sup>

In case of the Ni(II) complex, two bands<sup>29</sup> at 21,276 and 16,639 cm<sup>-1</sup> were assigned to  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$  and  ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$  transitions, respectively. The magnetic moment for octahedral Ni(II) complexes generally lies between 2.9–3.4  $\mu_{\text{B}}$ . The found value of  $3.2 \mu_{\text{B}}$  is well within the specified limit and a regular octahedral geometry for the Ni(II) ion is, therefore, proposed.<sup>30</sup>

The electronic spectrum of the Cu(II) complex shows two d-d transitions in the visible region.<sup>31</sup> A broad hump at 11,274 cm<sup>-1</sup> and a band at 16,639 cm<sup>-1</sup> may reasonably be assigned as  ${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{1g}$  and  ${}^2\text{E}_g \leftarrow {}^2\text{B}_{1g}$  transitions, respectively. It has been

reported that the magnetic moments of octahedral Cu (II) complexes fall in the region 1.73 to 2.20  $\mu_B$ .<sup>24</sup> The observed magnetic moment (1.91  $\mu_B$ ) supports a tetragonally distorted octahedral environment around the Cu(II) ion in the Cu[H<sub>2</sub>B(BTz)<sub>2</sub>]py<sub>2</sub> complex.

#### CONCLUSION

A novel ligand sodium dihydrobis(1,2,3-benzotriazolyl)borate and its complexes with another complex MCl<sub>2</sub>py<sub>2</sub> have been synthesized. All the complexes are stable, nonionic and paramagnetic. An octahedral geometry is proposed for all of them.

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#### ИЗВОД

#### СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И СПЕКТРОСКОПСКО ИЗУЧАВАЊЕ ДИХИДРОБИС(1,2,3-БЕНЗОТРИАЗОЛИЛ)БОРАТНОГ АНЈОНА И ЊЕГОВИХ КОМПЛЕКСА СА MCl<sub>2</sub>py<sub>2</sub>

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Рефлуковањем једног мола натријум-борхидрида са два мола 1,2,3-бензотриазола у толуену у току 12 часова добијен је и окарактерисан натријум-дихидробис(1,2,3-бензотриазолил)борат. Његови комплекси са MCl<sub>2</sub>py<sub>2</sub> [где је M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) и py = пиридин] су окарактерисани елементалном анализом, магнетним, спектроскопским и мерењима проводљивости. На основу тог проучавања претпостављена је октаедарска геометрија за све комплексе. Параметри лигандног поља 10Dq, V и  $\beta$  показују значајно преклапање између M-L орбитала. Моларна проводљивост 10<sup>-3</sup> M раствора комплекса у DMSO указује на њихову нејонску природу.

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