

Synthesis and Physico-chemical and Spectroscopic Investigations of Sodium Dihydrobis(1,2,3-benzotriazolyl)borate Ligand and Its Transition Metal Complexes

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The title ligand, sodium dihydrobis(1,2,3-benzotriazolyl)borate, Na[H₂B(BTz)₂], was synthesized by refluxing 1 mole of sodium borohydride with 2 moles of 1,2,3- benzotriazole in toluene. The ligand shows ample reactivity towards Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions and forms stable complexes. The ligand and its metal complexes were characterized by physico-chemical and spectroscopic techniques. All the complexes of divalent metal ions are tetrahedral except for Cu(II), which has been proposed to have a square-planar geometry. The complexes of Cr(III) and Fe(III) appear to have an octahedral geometry. The magnitude of molar conductance of 10⁻³ M solution indicates that all the complexes are non-electrolytic.

Key Words: Dihydrobis(1,2,3-benzotriazolyl)borate ligand, metal complexes, spectral studies, electronic spectra.

Introduction

Boron attached to nitrogen heterocycles yields ligands, and this has a unique place in organoborate chemistry. Such ligands containing B-N bonds have been extensively exploited in coordination chemistry.¹⁻³ Polypyrazolyl borates are versatile multidentate ligands used in bioinorganic, organometallic and coordination chemistry.⁴⁻¹³ The numerous scorpionate-type pyrazolyl borates known have limited use of parent pyrazole or ligands with -CH₃, -C₃H₇, -C₄H₉ and -C₆H₅ substituents on the pyrazole ring.¹⁴⁻¹⁶ Substitution on the pyrazole ring controls the steric environment of the binding site. Thus, a relationship between

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structure and reactivity in metal complexes is exhibited.¹⁷ Although the dipyrazolyl borate anion has a formal analogy to the β -diketonate ions due to steric requirements, the bis-types of ligands always exhibited monomeric structures.^{4,5}

Many azole ligands are easily synthesized by condensation and ring closure reactions. By contrast, only a few poly(azolyl)borate ligands and their complexes withazolyl groups other than pyrazole have been investigated, although the chemistry of poly(azolyl)borate complexes may critically be dependent upon the pattern of ring substitution.^{18,19} The different coordination characteristics of poly(benzotriazolyl)borate species offer the prospect of new and interesting chemistry, parallel to that of pyrazolyl, imidazolyl, indazolyl and triazolyl borates.²⁰⁻²² We report here the synthesis and characterization of sodium dihydrobis(1,2,3-benzotriazolyl)borate and its complexes with Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions with a view to study the nature of bonding of the ligand to the metal ions and their geometry.

Experimental

Materials

Sodiumborohydride (BDH), 1,2,3-benzotriazole (Loba Chemie), hydrated metal chlorides (Merck), DMSO (Merck) and toluene (Merck) were used as received without further purification. Methanol was distilled before use.

Measurements

IR spectra ($4000-200\text{ cm}^{-1}$) were recorded on a RXI FT-IR spectrometer with a KBr disk and UV-Visible spectra were recorded on a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were obtained with a 155 Allied Research vibrating sample magnetometer at room temperature. The electrical conductivities of 10^{-3} M solutions in DMSO were carried out on a digital CM-82T Elico conductivity bridge. Elemental analysis (C, H, N) was carried out with a Thomas and Coleman analyzer.

Preparation of the sodium dihydrobis(1,2,3-benzotriazolyl)borate, $\text{Na}[\text{H}_2\text{B}(\text{BTz})_2]$

1,2,3-Benzotriazole (6.32 g, 53.5 mmol) was mixed with the suspension of NaBH_4 (1.00 g, 26.5 mmol) in toluene (75 mL) and refluxed for 12 h under dry (anhydrous) conditions. Two moles of hydrogen gas was evolved, which was collected over water. When the hydrogen gas ceased to evolve and the temperature did not rise, the reaction mixture was cooled to room temperature, which formed a white powder-like product. It was filtered, washed with cold diethyl ether (20 mL) and dried in vacuo. The ligand was soluble in DMF, DMSO, THF, acetone, water and methanol.

Preparation of metal (II) complexes, $\text{M}[\text{H}_2\text{B}(\text{BTz})_2]_n$ [$\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}$ and Hg(II)]

A methanolic solution (20 mL) of $\text{Na}[\text{H}_2\text{B}(\text{BTz})_2]$ (0.49 g, 2.0 mmol) was added to a continuously stirred methanolic solution (20 mL) of metal(II) chlorides [$\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}$ and Hg(II)] in 2:1 molar ratio. Immediate precipitation occurred at room temperature. The precipitate was

filtered off, washed with methanol and anhydrous diethyl ether and dried in vacuo. The complexes were air stable and soluble in DMSO only.

Preparation of metal(III) complexes [M = Cr(III) and Fe(III)]

Methanolic solution (20 mL) of Na[H₂B(BTz)₂] (0.75 g, 3.0 mmol) was added dropwise, with continuous stirring to a methanolic solution (20 mL) of trivalent metal chlorides in 3:1 molar ratio. The mixture was then refluxed on a water-bath for about 30 min and left overnight. The precipitate thus obtained was filtered, washed with methanol and anhydrous diethyl ether and dried in vacuo. The complexes obtained were soluble only in DMSO.

Results and Discussion

The reaction of NaBH₄ with 1,2,3-benzotriazole (BTz) in 1:2 molar ratio in toluene under reflux conditions yields sodium dihydrobis(1,2,3-benzotriazolyl)borate. The completion of the reaction was ascertained by the release of the requisite volume of the hydrogen gas according to the following equation shown in Figure 1 and was further supported by various physico-chemical and spectroscopic studies presented in Tables 1 and 2.

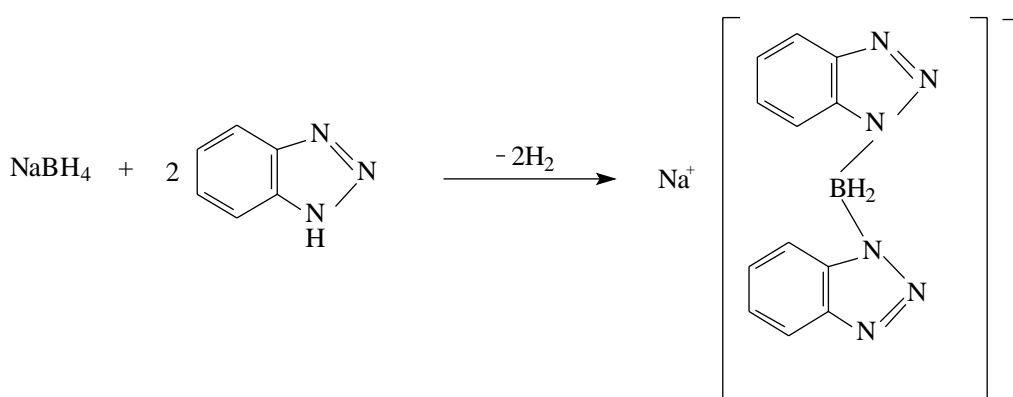
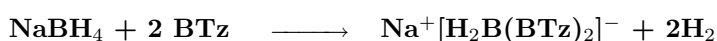


Figure 1. Preparation of the ligand Na⁺[H₂B(BTz)₂]⁻.



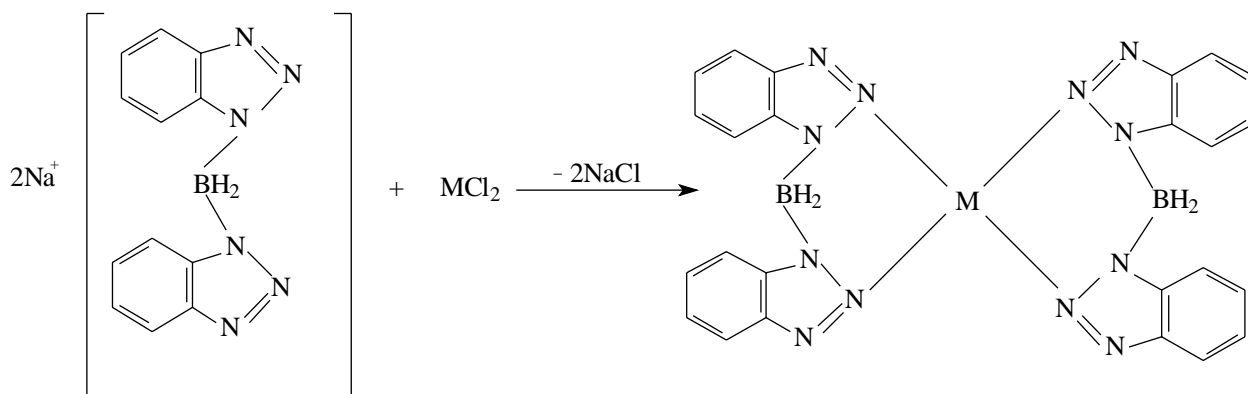
When $n = 2$ (i.e. for divalent metal ions), $M = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}, \text{Hg(II)}$ (Figure 2) and $n = 3$ (i.e. for trivalent metal ions), $M = \text{Cr(III)}$ and Fe(III) (Figure 3) resulted in $M[\text{H}_2\text{B}(\text{BTz})_2]_n$ complexes whose physico-chemical and analytical data are consistent with the proposed molecular formulae (Table 1).

IR Spectra

IR spectra of the ligand show the absence of ν (N-H) in the 3400-3000 cm^{-1} region, and the appearance of a new band of medium intensity at 1450 cm^{-1} indicated the replacement of the hydrogen atom from N-H of 1,2,3-benzotriazole by a B-N bond in Table 2. The dihydrobis(organyl)borates generally exhibit 2 ν (B-H) bands in the 2400-2500 cm^{-1} region, which is strongly influenced by the substituents on the

ring. We observed a doublet at 2436 and 2496 cm^{-1} due to 2 B-H bonds in sodium dihydrobis(1,2,3-benzotriazolyl)borate.^{23,24} Since ν (B-H) is insensitive to the nature of the metal ions bonded, it did not shift even after complexation.²⁵⁻²⁸ The IR spectra of the metal complexes exhibited bands that are only slightly shifted from those characteristic of the ligand in Table 2.

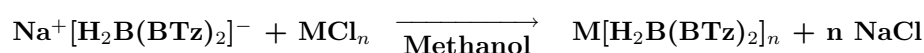
The C-N stretching frequency is slightly shifted to lower wave number (5-15 cm^{-1}) in all the complexes.²⁵⁻²⁸ The weak intensity (N=N) stretching frequency has also been observed to show a small shift (5-12 cm^{-1}) to lower wave numbers.²⁹⁻³¹



M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

Figure 2. Preparation of the complexes $\text{M}[\text{H}_2\text{B}(\text{BTz})_2]_2$.

The sodium dihydrobis(1,2,3-benzotriazolyl)borate ligand exhibited considerable reactivity towards metal salts MCl_2 [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)] and MCl_3 [M = Cr(III) and Fe(III)] as shown by the following equation (Figures 2 and 3):



Conductance measurements

The molar conductivities (Λ_m) of the complexes were measured in DMSO at room temperature. The magnitudes of Λ_m in Table 1 indicate a non-electrolytic nature for these complexes,³² which further supported the suggested molecular formulae of the complexes.

Electronic spectra and magnetic moments

The electronic spectral bands and the magnetic moments of the complexes are listed in Table 3. The electronic spectrum of the dark brown Cr(III) complex exhibits weak broad bands at 25,316 and 17,513 cm^{-1} , which have been assigned to ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{A}_{2g}(\text{F})$ transitions, respectively, with charge transfer bands. The magnetic behavior of octahedral Cr(III) is independent of the field strength of the ligand. It is expected that the magnetic moment for all Cr(III) complexes should be approximately equal to the calculated spin value only. The Cr(III) complex under consideration has the value of 3.91 B.M., which matches the calculated value of 3.88 B.M. Thus, the ligand field bands and magnetic moment value support an octahedral geometry^{33,34} around the metal ion in $\text{Cr}[\text{H}_2\text{B}(\text{BTz})_2]_3$ complex.

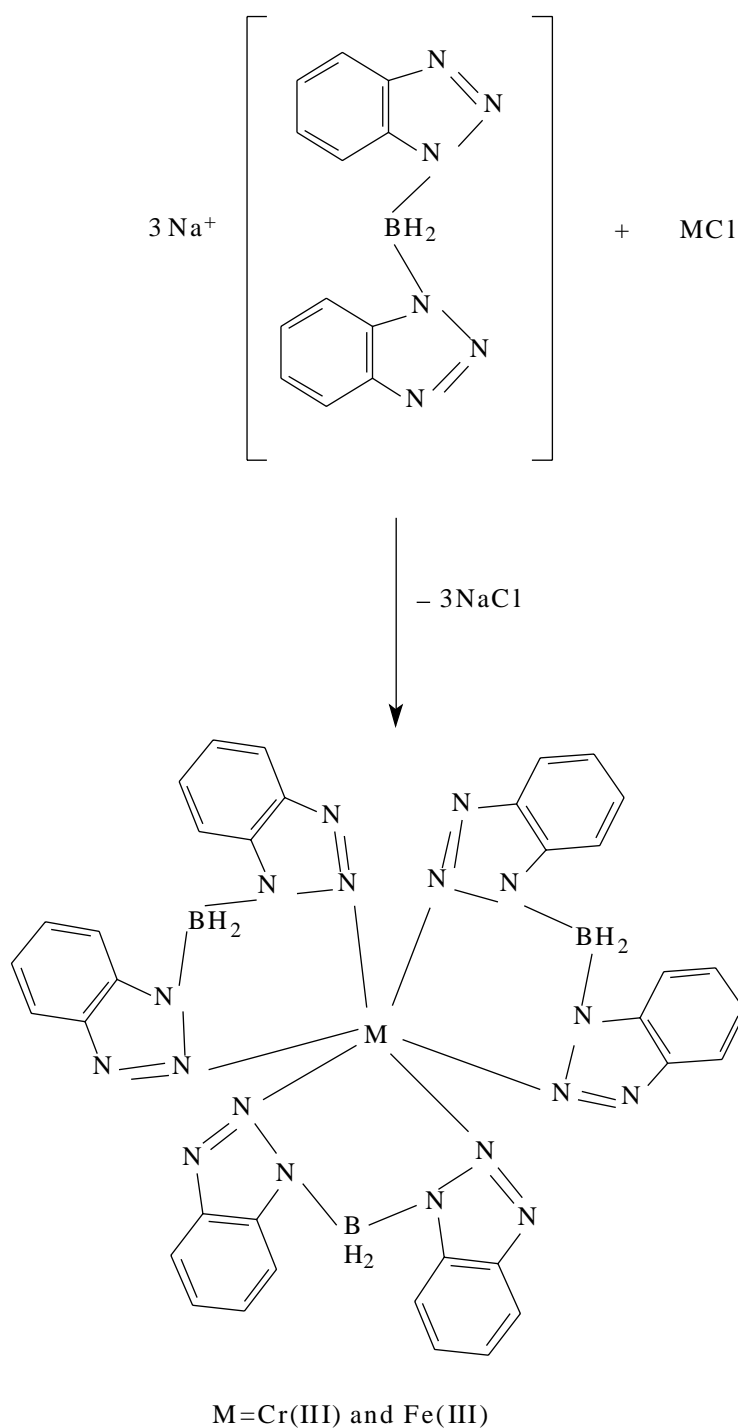


Figure 3. Preparation of the complexes $\text{M}[\text{H}_2\text{B}(\text{BTz}_2)]_3$.

The electronic spectrum of Fe(III) complex was not studied in detail because of the tendency of the trivalent ion to exhibit charge transfer bands in the UV region with low energy shoulders in the visible region. All the iron(III) complexes are generally high spin and exhibit 2 closely spaced bands at 23,696 and 23,148 cm^{-1} assigned to ${}^4\text{T}_{2g} \leftarrow {}^6\text{A}_{1g}$ and ${}^4\text{T}_{1g} \leftarrow {}^6\text{A}_{1g}$ transitions, respectively.^{35,36} In the complex $\text{Fe}[\text{H}_2\text{B}(\text{BTz})_2]_3$ only one broad band at 23,148 cm^{-1} was observed, which may be assigned to ${}^4\text{T}_{1g} \leftarrow {}^6\text{A}_{1g}$ transition. The

Table 1. Physical properties, conductivity and analytical data of the ligand and its metal complexes.

Compounds	Color	mp (°C)	Yield (%)	Λ_m ($\text{ohm}^{-1}\text{cm}^2$ mol^{-1})	Analysis (%), found (Calculated), %			
					C	H	N	M
$[\text{C}_{12}\text{H}_{10}\text{N}_6\text{B}]^-$ $\text{Na}^+[\text{L}]$ (249.063)	White	210- 212	59	--	58.31 (57.80)	4.50 (4.01)	33.48 (33.75)	--
$\text{C}_{36}\text{H}_{30}\text{N}_{18}\text{B}_3\text{Cr}$ $[\text{L}]_3.\text{Cr}$ (799.19)	Dark brown	> 300	62	21.7	54.51 (54.10)	3.41 (3.78)	32.61 (31.55)	6.08 (6.51)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Mn}$ $[\text{L}]_2.\text{Mn}$ (553.06)	White	> 300	66	19.9	51.82 (52.10)	3.40 (3.60)	29.90 (30.40)	10.21 (9.94)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Fe}$ $[\text{L}]_2.\text{Fe}$ (553.93)	Brownish red	> 300	64	34.2	52.35 (52.00)	3.50 (3.60)	30.56 (30.35)	10.48 (10.08)
$\text{C}_{36}\text{H}_{30}\text{N}_{18}\text{B}_3\text{Fe}$ $[\text{L}]_3.\text{Fe}$ (803.04)	Coffee	> 300	61	27.9	53.70 (54.10)	4.02 (3.78)	32.12 (31.55)	7.35 (6.98)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Co}$ $[\text{L}]_2.\text{Co}$ (557.06)	Light gray	> 300	73	39.7	52.30 (51.8)	3.48 (3.59)	29.78 (30.18)	10.91 (10.58)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Ni}$ $[\text{L}]_2.\text{Ni}$ (556.82)	Green	> 300	74	40.1	50.90 (51.80)	3.63 (3.59)	29.80 (30.19)	10.93 (10.54)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Cu}$ $[\text{L}]_2.\text{Cu}$ (561.67)	Bluish green	> 300	69	38.3	51.70 (51.30)	3.51 (3.56)	30.30 (29.93)	11.61 (11.32)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Zn}$ $[\text{L}]_2.\text{Zn}$ (563.52)	White	> 300	63	42.7	50.80 (51.20)	3.43 (3.55)	30.11 (29.84)	12.02 (11.61)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Cd}$ $[\text{L}]_2.\text{Cd}$ (610.54)	White	> 300	61	31.6	47.60 (47.21)	3.70 (3.30)	27.91 (27.53)	17.86 (18.41)
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Hg}$ $[\text{L}]_2.\text{Hg}$ (698.72)	Dark gray	> 300	57	4.3	40.85 (41.26)	3.02 (2.88)	24.46 (24.06)	28.24 (28.70)

Table 2. Characteristic IR bands (cm^{-1}) observed for the ligand and its metal complexes.

Compounds	$\nu(\text{B-H})$	$\nu(\text{B-N})$	$\nu(\text{C-N})$	$\nu(\text{C=C})$	$\nu(\text{N-N})$	$\nu(\text{N=N})$
$\text{Na}^+[\text{C}_{12}\text{H}_{10}\text{N}_6\text{B}]^-$ [L] (249.063)	2436 w 2496 w	1450 w	1489 w	1661 s	1007 s	1590 w
$\text{C}_{36}\text{H}_{30}\text{N}_{18}\text{B}_3\text{Cr}$ [L] ₃ .Cr (799.19)	2445 w 2370 w	1453 w	1488 w	1618 s	996 s	1580 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Mn}$ [L] ₂ .Mn (553.06)	2434 w 2368 w	1447 w	1489 w	1602 s	997 s	1585 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Fe}$ [L] ₂ .Fe (553.93)	2459 w 2369 w	1445 w	1491 w	1618 s	945 s	1578 w
$\text{C}_{36}\text{H}_{30}\text{N}_{18}\text{B}_3\text{Fe}$ [L] ₃ .Fe (803.04)	2448 w 2371 w	1459 w	1493 w	1611 s	991 s	1589 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Co}$ [L] ₂ .Co (557.06)	2450 w 2371 w	1446 w	1490 w	1617 s	998 s	1579 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Ni}$ [L] ₂ .Ni (556.82)	2453 w 2365 w	1448 w	1490 w	1619 s	998 s	1582 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Cu}$ [L] ₂ .Cu (561.67)	2441 w 2369 w	1448 w	1492 w	1613 s	994 s	1578 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Zn}$ [L] ₂ .Zn (563.52)	2440 w 2371 w	1449 w	1495 w	1612 s	993 s	1579 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Cd}$ [L] ₂ .Cd (610.54)	2438 w 2358 w	1447w	1490 w	1620 s	995 s	1589 w
$\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{B}_2\text{Hg}$ [L] ₂ .Hg (698.72)	2436 w 2365 w	1473 w	1495 w	1613 s	993 s	1587 w

Table 3. Magnetic susceptibility, electronic spectra and ligand field parameters of the complexes.

Compounds	Magnetic moment (B.M.)	Electronic band positions (cm ⁻¹)	Log ϵ (mol ⁻¹ cm ²)	Possible assignments	10 Dq (cm ⁻¹)	B (cm ⁻¹)	β
C ₃₆ H ₃₀ N ₁₈ B ₃ Cr [L] ₃ .Cr	3.91	30,675 25,316 17,513	2.8 2.4 2.1	Charge Transfer ⁴ T _{1g} (F) ⁴ A _{2g} (F) ⁴ T _{2g} (F) ⁴ A _{2g} (F)	17,513	876	0.85
C ₂₄ H ₂₀ N ₁₂ B ₂ Mn [L] ₂ .Mn	5.55	33,783 32,467 25,316	3.4 2.9 2.6	Charge Transfer Charge Transfer ⁴ T _{1g} ⁶ A _{1g}	---	---	---
C ₂₄ H ₂₀ N ₁₂ B ₂ Fe [L] ₂ .Fe	5.28	30,303 27,397 22,624	2.9 2.9 3.1	Charge Transfer Charge Transfer ⁵ E _g ⁵ T _{2g}	---	---	---
C ₃₆ H ₃₀ N ₁₈ B ₃ Fe [L] ₃ .Fe	5.84	30,864 25,641 23,148	2.9 2.7 2.8	Charge Transfer Charge Transfer ⁴ T _{1g} (G) ⁶ A _{1g}	---	---	---
C ₂₄ H ₂₀ N ₁₂ B ₂ Co [L] ₂ .Co	4.74	31,250 27,027 24,390 14,925	3.1 3.0 2.8 2.1	Charge Transfer Charge Transfer ⁴ T ₁ (F) ⁴ A ₂ (F) ⁴ T ₂ (F) ⁴ A ₂ (F)	15,625	520	0.46
C ₂₄ H ₂₀ N ₁₂ B ₂ Ni [L] ₂ .Ni	3.86	30,395 27,027 24,570 18,315 16,393	3.0 2.8 2.7 2.6 2.6	Charge Transfer Charge Transfer ³ T ₁ (P) ³ T ₁ (F) ³ A ₂ (P) ³ T ₁ (F) ³ T ₂ (F) ³ T ₁ (F)	4,250	346	0.32
C ₂₄ H ₂₀ N ₁₂ B ₂ Cu [L] ₂ .Cu	1.82	28,011 27,777 26,109 11,547	3.2 3.1 2.6 2.2	Charge Transfer Charge Transfer Charge Transfer ² T _{2g} ² E _g	---	---	---
C ₂₄ H ₂₀ N ₁₂ B ₂ Zn [L] ₂ .Zn	Dia- magnetic	---	---	---	---	---	---
C ₂₄ H ₂₀ N ₁₂ B ₂ Cd [L] ₂ .Cd	Dia- magnetic	---	---	---	---	---	---
C ₂₄ H ₂₀ N ₁₂ B ₂ Hg [L] ₂ .Hg	Dia- magnetic	---	---	---	---	---	---

second band was not observed, even when the concentrated solution of the compound was run. The magnetic moment for high spin octahedral Fe(III) ion ranges from 5.7 to 6.0 B.M. The observed magnetic moment value is well within the accepted range and hence an octahedral geometry³⁷ for the Fe(III) ion in Fe[H₂B(BTz)₂]₃ is proposed.

The tetrahedral Mn(II) complexes were generally yellow, pale yellow or yellow green. These colors are an effective, simple and reliable criterion to confirm that the formed manganese(II) complexes have tetrahedral geometry rather than octahedral.³⁸ The Mn[H₂B(BTz)₂]₂ complex is pale yellow in solution and

shows intense absorption bands in the visible region at $25,316\text{ cm}^{-1}$ assigned to ${}^4\text{T}_{1g} \leftarrow {}^6\text{A}_{1g}$ transition. It also shows 2 strong charge transfer bands at $33,783$ and $32,467\text{ cm}^{-1}$. The tetrahedral Mn(II) complex gives an essentially spin-only magnetic moment value of 5.9 B.M., which does not vary much since the magnetic moment is temperature independent. The observed magnetic moment value 5.55 B.M. in Mn(II) complex is appreciably close to the calculated spin value only. The observed magnetic moment value and electronic spectrum suggest a tetrahedral geometry³⁷ for the Mn(II) complex. The tetrahedral high-spin Fe(II) shows only one spin allowed d-d transition in the visible region. The brownish red $\text{Fe}[\text{H}_2\text{B}(\text{BTz})_2]_2$ complex gives only one spin allowed d-d band at $22,624\text{ cm}^{-1}$ assigned to ${}^5\text{E}_g \leftarrow {}^5\text{T}_{2g}$ transition. The magnetic moments of tetrahedral Fe(II) species are normally in the range of 5.0-5.5 B.M., owing to the spin of the 4 unpaired electrons and a small second-order orbital contribution. The observed magnetic moment case is 5.84 B.M., which is in the range of tetrahedral species. The ligand field bands and magnetic moment value indicate a tetrahedral structure³⁹ for $\text{Fe}[\text{H}_2\text{B}(\text{BTz})_2]_2$ complex.

For the tetrahedral Co(II) complexes, there are 2 orbital forbidden absorptions, which are seldom observed. There is a complex absorption in the visible region and the intensity of the band is due to spin-orbit coupling.⁴⁰ For $\text{Co}[\text{H}_2\text{B}(\text{BTz})_2]_2$, few d-d transitions were observed around 500-600 nm. Two bands at $14,925$ and $24,390\text{ cm}^{-1}$ assigned to ${}^4\text{T}_2(\text{F}) \leftarrow {}^4\text{A}_2(\text{F})$ and ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2(\text{F})$ transitions, respectively, in addition to 2 charge transfer bands at $27,027\text{ cm}^{-1}$ and $31,250\text{ cm}^{-1}$, were noted. The effective magnetic moment for a tetrahedral Co(II) species is 4.74 B.M., while the calculated value is 3.89 B.M. It slightly varies with the field strength of the ligand. The observed magnetic moment value is 4.74 B.M., which supports a high-spin tetrahedral structure for the Co(II) ion similar to the crystal structure⁴¹ found for the complex cumyl peroxy TptBu.iPr.Co- η^1 -OOCMe₂.Ph.

The tetrahedral complexes of the Ni(II) ion are generally blue or green, unless the ligands also have absorptions in the visible region. The green $\text{Ni}[\text{H}_2\text{B}(\text{BTz})_2]_2$ in DMSO shows 2 shoulders in the visible region, at $16,393\text{ cm}^{-1}$ and $18,315\text{ cm}^{-1}$, assigned to ${}^3\text{T}_2(\text{F}) \leftarrow {}^3\text{T}_1(\text{F})$ and ${}^3\text{A}_2(\text{F}) \leftarrow {}^3\text{T}_1(\text{F})$ transitions, respectively, besides 1 sharp band at $24,570\text{ cm}^{-1}$ corresponding to ${}^3\text{T}_1(\text{P}) \leftarrow {}^3\text{T}_1(\text{F})$ transition. Two strong bands at $30,395$ and $27,027\text{ cm}^{-1}$ have also been observed in the UV region.⁴² The magnetic moment of a regular tetrahedral Ni(II) should be approximately 4.2 B.M. at room temperature but it is reduced appreciably if distortion occurs. Thus, for a regular tetrahedral Ni(II) ion, the magnetic moment lies between 3.5 and 3.2 B.M. The observed magnetic moment value was found to be 3.86 B.M. which is within the specified limits.⁴³ The electronic spectra and the magnetic moment support a tetrahedral structure for $\text{Ni}[\text{H}_2\text{B}(\text{BTz})_2]_2$ complex.

In the case of Cu(II) complex, only one band of lower energy was assigned to the d-d transition, which is considered very sensitive to the ligand field strength and changes in the molecular geometry and corresponds to the ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$ transition.⁴⁴ On the basis of d-d transitions, it is difficult to distinguish between a square-planar and a tetrahedral Cu(II) ion because it occurs in the same region for both the geometries. The magnetic moment value extends over a range of 1.78-1.99 B.M. for Cu(II) complexes, as has been shown in the crystal structure of dimeric hydroxamate complex of Cu(II) ion with a magnetic moment value⁴⁵ of 1.78 B.M. In our case, the experimental magnetic moment for Cu(II) ion is 1.82 B.M., which is in the range for a square-planar Cu(II) ion for the complex $\text{Cu}[\text{H}_2\text{B}(\text{BTz})_2]_2$.

Conclusion

Synthesis of a sodium dihydrobis(1,2,3-benzotriazolyl)borate ligand using sodium borohydride and 1,2,3-benzotriazole in 1:2 molar ratio in toluene and its metal complexes with Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions is reported here. The magnitudes of molar conductance of these complexes were recorded in DMSO solution, and the results suggested that the products obtained have a non-electrolytic character. The elemental analyses of the complexes show their exact compositions, while IR studies suggest their nature of bonding. The definite geometries of the complexes were established by the magnitude of magnetic moment values and their electronic spectra. Finally, the ligand field parameters such as $10 Dq$, B and β were also evaluated and the value of β indicates a considerable orbital overlap in metal-ligand complexes.

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