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COMPLEXES OF POTASSIUM HYDRIDOTRIS (4-AMINO-1,2,4-TRIAZOLYL)BORATE WITH SOME TRANSITION METAL IONS

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ABSTRACT

Potassium hydridotris(4-amino-1,2,4-triazolyl)borate has been synthesized and employed as a versatile tridentate ligand for the preparation of transition metal complexes with Co(II), Ni(II), Cu(II), Fe(III), and Mn(II). The complexes were characterized by elemental analysis, IR spectroscopy, magnetic susceptibility, and electronic reflectance measurements. Spectral data confirm coordination through the N-2 nitrogen of the triazolyl ring, while magnetic moment values and electronic transitions suggest octahedral geometries for Co(II), Ni(II), Fe(III), and Mn(II) complexes, and a square planar geometry for Cu(II). The study highlights the structural diversity and magneto-structural correlations of triazolylborate-based complexes, underscoring their potential relevance in coordination chemistry and materials science.

KEYWORDS: Triazolylborate Ligands, Metal Complexes, Magneto-Structural Corelation

Heterocyclic compounds constitute one of the largest and classical divisions of organic chemistry. Depending upon the heteroatom(s) available within the ring, heterocycles can be divided as oxygen, nitrogen or sulfur based and for every class; compounds are further classified on the basis on ring size which is estimated by the total atoms present in the ring structure. Basically, the type and size of the ring framework, along with the attached substituents have strong impact on the physicochemical properties (Broughton and Watson, 2004). Besides, possessing various useful clinical applications, heterocyclic compounds significantly plays prominent role in anti-bacterial (Azab *et al.*, 2013, anti-viral (Salem *et al.*, 2013) anti-fungal (Cao *et al.*, 2014), anti-inflammatory (Mabkhot *et al.*, 2013), and anti-cancer drugs (Gomtsyan, 2012). In coordination chemistry, 1,2,4-triazole derivatives have emerged as particularly valuable ligands. Polynuclear transition metal complexes containing triazole bridges have been extensively studied for their magneto-structural correlations. For instance, binuclear Cu(II) complexes bridged by N1,N2-1,2,4-triazole ligands exhibit cooperative magnetic behavior, with exchange interactions mediated through the $d_{x^2-y^2}$orbitals of copper and the nitrogen orbitals of the bridging ligand (Janiak, 1994; Edelmann, 2001). The strength of isotropic exchange (J) is highly sensitive to structural parameters, particularly the N–Cu–N bond angles, which approach maximum values near 90° (Hanson, 1999; Navon *et al.*, 2000; Ibrahim and Soliman, 1994). Deviations from this geometry, often due to asymmetric bridging, result in diminished exchange interactions, paralleling trends observed in dihydroxo-bridged Cu(II) systems (Santini *et al.*, 1998; Santini *et al.*, 1998; Effendy *et al.*, 2001; Pellei *et al.*, 2000; Lobbia *et al.*, 2004).

Beyond their magnetic properties, triazoles are of pharmacological importance, being widely utilized in pharmaceuticals and agrochemicals due to their favorable geometry and coordination capabilities. Motivated by these considerations, we have synthesized potassium hydridotris(4-amino-1,2,4-triazolyl)borate and explored its coordination chemistry with several transition metal ions. This study aims to elucidate the structural, spectral, and magnetic features of these complexes, thereby contributing to the broader understanding of triazolylborate ligands in transition metal coordination.

EXPERIMENTAL

4-Amino-1,2,4-triazole (Merck), N,N-dimethylactamide (Merck), potassium tetrahydridoborate, and transition metal chlorides (all BDH) were commercially obtained.

Synthesis of [hydridotris(4-amino-1,2,4-triazolyl)borato]metal(II) Complexes:

Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]cobalt(II)

A methanolic solution of cobalt(II) chloride (0.22 g, 0.93 mmol) and potassium hydridotris(4-amino-1,2,4-triazolyl)borate (0.50 g, 1.63 mmol) was refluxed for about 2 h. The orange product which precipitated out after cooling the reaction mixture to room temperature was filtered off, washed thoroughly with methonal and finally dried *in vacuo*.

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Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]nickel (II)

The nickel(II) chloride (0.50 g, 1.63 mmol) solution in methanol and the potassium hydridotris(4-amino-1,2,4-triazolylborate) (0.13 g, 0.81 mmol)suspension in the same solvent were mixed togather in a round bottom flask. The flask was heated at reflux for about 2 h. The reaction mixture was allowed to cool to room temperature. The resulting blue solid product was filtered off, washed with methanol and dried *in vacuo*.

Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]copper(II)

The compound was obtained by mixing a methanolic solution of copper(II) chloride (0.50 g, 1.63 mols) to a solution of potassium hydrotris(4-amino-1,2,4-triazolylborate) (0.13 g, 0.81 mmol) in the same solvent. The resulting mixture was refluxed for about 2 h, after which time it was allowed to cool to room temperature. The resulting green solid product was filtered off, washed with methanol and finally dried *in vacuo*.

Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]iron(III)

Preparation of this complex was achieved by refluxing a mixture of solutions of potassium hydridotris(4amino-1,2,4-triazolyl)borate (1.27 g, 3.26 mmol) and ferric chloride (0.27 g, 1.63 mmol) in methanol for about 2 h. The wine-red solid product appeared on cooling the reaction mixture to room temperature was isolated, washed with methanol and dried *in vacuo*.

Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]manganese(II)

To a suspension of manganese(II) chloride (0.16 g, 0.81 mmol) in methanol 20 mL was added a solution of potassium hydridotris(4-amino-1,2,4-triazolylborate) (0.95 g, 2.45 mmol) in methanol 20 mL. The mixture was refluxed for about 2 h. The brown colored solid product, which separated out after cooling to room temperature was filtered off, washed thoroughly with methanol and dried *in vacuo*.

The complexes of Potassium hydridotris(4-amino-1,2,4-triazolyl)borate with some Transition metal ions.

Potassium hydridotris(4-amino-1,2,4-triazolyl)borate has been synthesized by the reaction of potassium tetrahydridoborate and 4-amino-1,2,4-triazole in a 1:3 stichiometric ratio as depicted by following reaction:

$$KBH_4 + 3C_2H_6N_4 \rightarrow K[HB(C_2H_5N_4)_3] + 3H_2$$

The ligand potassium hydridotris(4-amino-1,2,4-triazolyl)borate and its complexes are listed in Table 1 along with their color, melting point, percentage yield and analytical results. The results of the elemental analysis are in good agreement with the proposed stoichiometries of the ligand and the metal complexes. The evolution of three moles of hydrogen during the synthesis of potassium hydridotris (4-amino-1,2,4-triazolyl)borate also lends support to the proposed stoichiometry.

The complexes were prepared by the reaction of respective metal chlorides with $K(C_6H_{16}N_{12}B)$ according to the following reactions:

$$MCl_2 + 2K(C_6H_{16}N_{12}B) \rightarrow [M(C_6H_{16}N_{12}B)_2] + 2KCl$$

Where M= Mn(II), Ni(II), and Cu(II)

$$MCl_3 + 2K(C_6H_{16}N_{12}B) \rightarrow [M(C_6H_{16}N_{12}B)_2]Cl + 2KCl$$

Where M= Fe(III)

RESULTS AND DISCUSSIONS

Elemental analysis for carbon, hydrogen, and nitrogen was performed at the Central Drug Research Institute, Lucknow, using a Heraeus Vario EL III analyzer. The results were found to be within ±0.4% of the theoretical values, confirming the accuracy of the proposed stoichiometries. Metal content was determined by complexometric titration with standard EDTA solution. Prior to titration, the metal ions were liberated from the complexes by treating an accurately weighed 0.1 g sample with a few drops of a nitric acid–perchloric acid mixture. Infrared spectra of the ligands and their metal complexes were recorded as KBr pellets on a Perkin Elmer Model 1620 FT-IR spectrophotometer. Magnetic susceptibility measurements were carried out at IIT Roorkee using a Vibrating Sample Magnetometer (EG & G Model 150) at room temperature. Diffuse reflectance spectra were obtained at SAIF, IIT Madras, using a UV–VIS–NIR Cary SE spectrophotometer (185–3150 nm range).

The important IR spectral bands and their tentative assignments are given in Table 2. The IR spectrum of ligand $KC_6H_{16}N_{12}B$ does not show any singlet band in the region 3000-3400 cm^{-1} indicating the absence of N-H bond. However, a doublet in the same region corresponds to the presence of NH_2 group of the triazolyl ring. The appearance of a new band at 1425 cm^{-1} suggests the formation of a B-N bond. A singlet at 2413 cm^{-1} attributed to B-H stretching frequency (Davidson, 2002; Price, 1949) indicates the presence of only one hydrogen atom attached to boron. The proposed structure

of the ligand and complexes are shown in Fig. 1 and Fig.2.

A comparison of the infrared spectral bands of the free and complexed ligand indicate that $\nu_{C=N}$ stretching frequency observed at 1635 cm^{-1} in free ligand is shifted to 1617-1522 cm^{-1} in the complexes. This indicates the bonding of N-2 nitrogen of triazole ring to the metal. The stretching frequencies of ν_{B-N} and ν_{B-H} are unperturbed and are observed at about the same positions as in the uncoordinated ligands. However, the ν_{H-N-H} and ν_{N-N} bands shows bathochromic shift in the metal complexes which also supports the coordination occurs through the N-2 nitrogen of the triazolyl ring. The presence of a doublet band assigned to ν_{H-N-H} at almost the same positions in both free ligand and the metal complexes indicate the non-involvement of the NH_2 group in the metal-ligand bond formation. Thus $K(C_6H_{16}N_{12}B)$ behaves as a tridentate ligand coordinating through nitrogen atom (N-2) of the three 4-amino-1,2,4-triazolyl groups attached to boron atom. The far-IR spectra of the complexes exhibit absorption bands in the region of 435-415 cm^{-1} assigned to the M-N stretching vibration. (Table 1 & 2)

Table 1: Colour, Melting Point and Analytical Calculations

Complex % Yield	Colour	M. P. (°C)	Analysis							
			Calculated				Found			
			C	H	N	M	C	H	N	M
$K(C_6H_{16}N_{12})$ 68	Colourless	>180	24.32	5.40	56.75		24.06	5.25	56.96	
$[Co(C_6N_{12}H_{16}B)_2]$ 32	Orange	>300	24.30	5.40	56.70	8.39	24.45	5.83	56.55	8.73
$[Fe(C_6N_{12}H_{16}B)_2]Cl$ 53	Wine red	>300	19.55	4.34	45.63	8.80	20.23	4.86	45.12	9.07
$[Cu(C_6N_{12}H_{16}B)_2]$ 48	Green	>300	24.11	5.35	56.26	9.32	24.52	5.64	56.52	9.68
$[Ni(C_6N_{12}H_{16}B)_2]$ 44	Blue	>300	24.31	5.40	56.72	8.27	24.15	5.15	56.89	8.56
$[Mn(C_6N_{12}H_{16}B)_2]$ 45	Brown	>300	24.46	5.43	57.08	8.30	24.83	5.68	57.46	8.63

Table 2: Important IR bands (cm^{-1}) and their possible assignments

Complex	ν_{B-H}	ν_{B-N}	$\nu_{C=N}$	ν_{H-N-H}	ν_{N-N}	ν_{M-N}
$K(C_6H_{16}N_{12})$	2413	1425	1635	3296	1137	----
$[Co(C_6N_{12}H_{16}B)_2]$	2395	1392	1617	3277	1048	426
$[Fe(C_6N_{12}H_{16}B)_2]Cl$	2398	1368	1596	3288	1050	415
$[Cu(C_6N_{12}H_{16}B)_2]$	2433	1324	1560	3258	1122	423
$[Ni(C_6N_{12}H_{16}B)_2]$	2411	1405	1522	3242	1049	435
$[Mn(C_6N_{12}H_{16}B)_2]$	2390	1373	1618	3267	1050	429

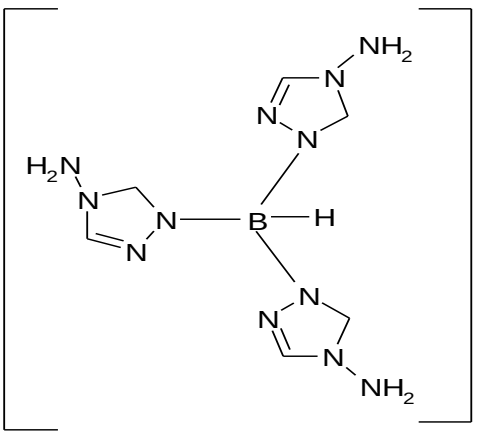
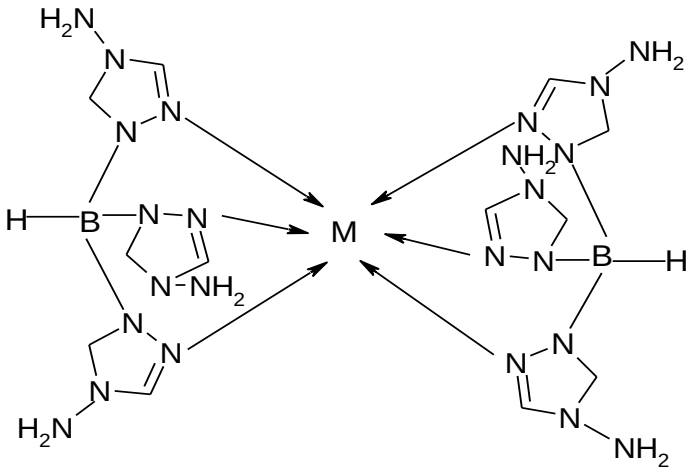


Figure 1: Suggested structure of Hydridotris(4-amino-1,2,4-triazolyl)borate anion



Metal = Co(II), Ni(II), Mn(II)

Figure 2: Proposed structure of Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]metal(II)

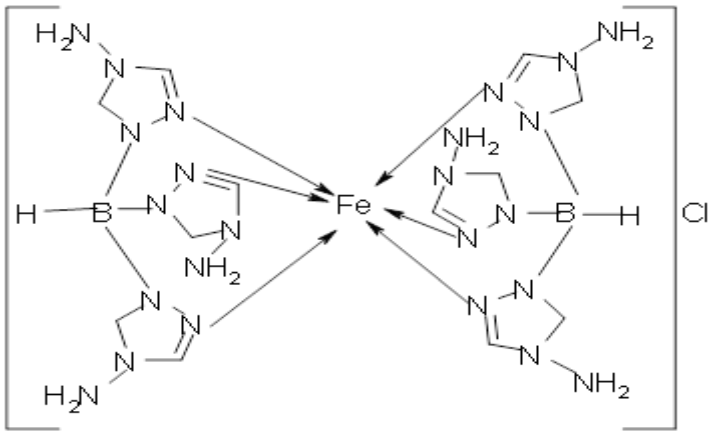


Figure 3: Proposed structure of Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]iron(III)

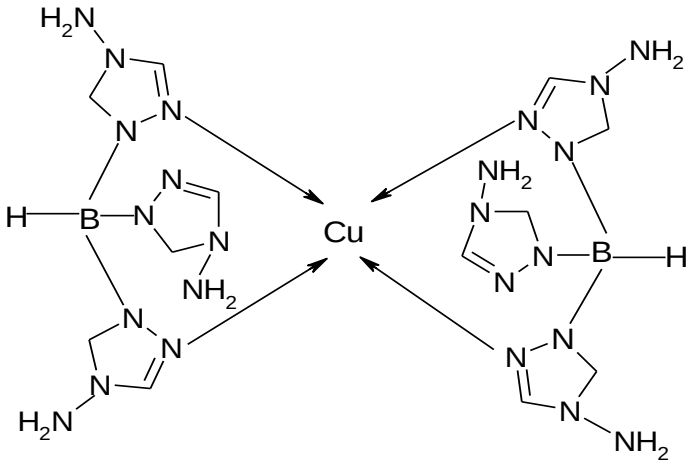


Figure 4: Suggested structure of Bis[hydridotris(4-amino-1,2,4-triazolyl)borato]copper(II)

The magnetic moment and reflectance spectral data

The magnetic moment values and electronic spectral data along with their possible assignments of the complexes are presented in Table 3:

The room temperature magnetic moment value (5.15 MB) of Co(II) complex are in the range expected for an octahedral stereochemistry. The $[Co(C_6N_{12}H_{16}B)_2]$ complex displays three absorption bands. The first band observed at 10,520 cm^{-1} is attributed to $^4T_{1g}$ (F) →

$^4T_{2g}$(F), second band at 16,950 cm^{-1} is attributed to $4T_{1g}$ (F) → $4A_{2g}$(F) and third band at 23,255 cm^{-1} is assigned to $4T_{1g}$ (F) → 4 T_{1g} (P) transition. The room temperature magnetic moment of Fe(III) complex (5.90 BM) is consistent with an octahedral geometry around the metal ion. Three electronic transitions are observed at 24,218, 12195, 16666 cm^{-1} ($^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and $^6A_{1g} \rightarrow {}^4E_g$) for this complex, which are in good agreement with the reported values [251] for octahedral Fe(III) complexes. On the basis of magnetic moment and spectral studies an octahedral structure as given in Fig (3) may be proposed for the Fe(III) complex. The magnetic moment of the Cu(II) complex is 1.99 BM at room temperature. Its reflectance spectrum displays two bands at 15,300 and 24,991 cm^{-1} which can be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. The position of these bands indicate that the complex has a square planar stereochemistry as proposed in Fig.4.

The magnetic moment of Ni complex (3.54 BM) is in the range required for six coordinated Ni(II) complexes (fig 5). The electronic spectrum shows a band at 10200 cm^{-1} attributed to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), a band at 17857 cm^{-1} attributed to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transition and a band at 21749 cm^{-1} assigned $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition. The magnetic moment of 5.97 BM of Mn(II) complex corresponds to a high spin configuration. The electronic spectral bands are observed at 19348 cm^{-1} assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) transition at 25530 cm^{-1} assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) transition and at 30126 cm^{-1} assigned to $^6A_{1g} \rightarrow {}^4E_g$ transition (Jorgenson, 1962; Bertrand and Eller, 1974; Nakamoto K., 1963). (Table 3)

Table 3: Magnetic Moment, Reflectance Spectral Data and Their Possible Assignments

Complex	Magnetic Moment (BM)	Spectral Bands (cm^{-1})	Assignments
$[Co(C_6N_{12}H_{16}B)_2]$	5.15	10520 16950 23255	$4T_{2g}$ (F) → $4T_{1g}$ (F) $4A_{2g}$(F) → $4T_{1g}$ (F) $4T_{1g}$ (F) → 4 T_{1g} (P)
$[Fe(C_6N_{12}H_{16}B)_2]Cl$	5.90	12195 16666	$5T_{2g} \rightarrow 5E_g$ $5T_{2g} \rightarrow 5E_g$
$[Cu(C_6N_{12}H_{16}B)_2]$	1.99	15300 24991	$2B_{1g} \rightarrow 2B_{2g}$ $2B_{1g} \rightarrow 2E_g$
$[Ni(C_6N_{12}H_{16}B)_2]$	3.54	10200 17857 21739	$3A_{2g} \rightarrow 3T_{2g}$ (F) $3A_{2g} \rightarrow$ $3T_{1g}$ (F) $3A_{2g} \rightarrow 3T_{1g}$ (P)
$[Mn(C_6N_{12}H_{16}B)_2]$	5.97	20050 25530 30126	$6A_{1g} \rightarrow 4T_{1g}$ (G) $6A_{1g}$ → $4T_{2g}$ (G) $6A_{1g} \rightarrow 4E_g$

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