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SYNTHESIS OF TRANSITION METAL COMLEXES OF POTASSIUM DIHYDROBIS(4-AMINO-1,2,4-TRIAZOLYL)BORATE

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ABSTRACT

Novel potassium dihydridobis(4-amino-1,2,4-triazolyl)borate ligands and their Mn(II), Ni(II), and Cu(II) complexes were synthesized via controlled reflux reactions and characterized by elemental analysis, IR, magnetic susceptibility, and electronic spectroscopy. Analytical data confirmed 1:2 metal–ligand stoichiometry with coordination through triazolyl nitrogen. IR spectra evidenced B–N bond formation, while magnetic and spectral studies revealed tetrahedral geometry for Mn(II) and square planar arrangements for Ni(II) and Cu(II). These findings highlight the structural versatility of triazolylborate ligands in stabilizing diverse transition metal geometries.

KEYWORDS: Triazolylborate Ligands, Transition Metal Complexes, Characterization

Azoles are a class of five-membered nitrogen heterocyclic ring compounds containing at least one other noncarbon atom, nitrogen, sulfur or oxygen. The parent compounds are aromatic and have two double bonds, there are successively reduced analoges (azolines and azolidines) with less number of double bonds. Azoles maintain the prefix upon reduction such as pyrazoline, pyrazolidine, except for pyrrole, which has no azole suffix and is reduced to pyrroline and pyrrolidine. The azoles include pyrazoles, imidazoles, triazoles and tetrazoles. It is well-known that azole derivatives block ergosterol biosynthesis, causing its depletion and accumulation of lanosterol and some other 14-methylsterols (Siemer *et al.*, 2001; Rheingold *et al.*, 2000; Han *et al.*, 1989). Such sterols alter membrane fluidity with concomitant reduction in the activity of membrane-associated enzymes, increased permeability, and inhibition of cell growth and replication. Polynuclear co-ordination compounds containing derivatives of 1,2,4-triazole have been of great interest during last decade. Several studies have dealt with search for magneto-structural correlations for transition metal (II) compounds containing N^1, N^2-1,2,4-triazole bridges. On the other hand polynuclear iron(II) 1,2,4-triazole compounds have been found to yield spin-crossover materials exhibiting co-operative behavior. In order to acquire a more detailed understanding about the propagation of the magnetic super exchange via diatomic N-N bridges, the structure and magnetic properties of doubly N^1, N^2-1,2,4-triazole bridged binuclear Cu (II) compounds have been investigated (Janiak, 1994; Edelmann, 2001; Hanson, 1999). These compounds contain polyfunctional 1,2,4-triazole derivatives with N- donating substituents forming five membered chelate rings (Navon *et al.*, 2000; Fujita *et al.*, 1994). The Cu(II) ions are linked in equatorial co-ordination plane by two N^1, N^2 bridging 1,2,4 triazole ligands. For the class of compounds the magneto-structural co-relations could be established for the first time. In the compounds the magnetic exchange is propagated via the $d_{(x^2-y^2)}$ orbitals on Cu(II) ions which interact with the orbitals of the nitrogen atoms of the bridging ligand. It has been experimentally found that the maximal value for the isotopic interaction J is attained, when the 1,2,4-triazole ligands like the Cu(II) ions in most symmetrical way allowing the N-Cu-N angles to be close to 90° (Ibrahim and Soliman, 1994; Santini *et al.*, 1998; Santini *et al.*, 1998). An increase in these N-Cu-N angles, which in most cases is accompanied by asymmetric bridging of μ- N^1,N^2-1,2,4-triazole ligands leads to a decrease in value of J. Therefore, the dependence of the J-value on structural parameters has a certain relation found by not filled and nodgson for planar dihydroxo-bridged Cu(II) compounds (Santini *et al.*, 1998; Effendy *et al.*, 2000; Effendy *et al.*, 2001; Pellei *et al.*, 2000; Lobbia *et al.*, 2004). Considering the pharmacological importance of azole family and importence of 1,2,4-triazoles as being widely used in pharmaceuticals and agriculture chemicals, which may be connected to their similarity in geometry as well as coordinating properties. We have synthesized three different boron-triazole compounds and incorporated metal in them.

EXPERIMENTAL

4-Amino-1,2,4-triazole (Merck), N,N-dimethylactamide (Merck), potassium tetrahydridoborate,

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and transition metal chlorides (all BDH) were commercially obtained.

Synthesis of The Ligands

Synthesis of Potassium Dihydridobis(4-amino-1,2,4-triazolyl)borate

The ligand, potassium dihydridobis(4-amino-1,2,4-triazolyl) borate, was prepared according to the following method. 4-Amino-1,2,4-triazole (1 g, 11.09 mmol) and potassium tetrahydridoborate (0.321 g, 18.44 mmol) were mixed and dissolved in 20 mL N,N-dimethylacetamide and refluxed for 1.5 h till the calculated quantity of hydrogen gas was evolved. The evolution of hydrogen gas was brisk at the beginning but subsided as the reaction reached completion. The reaction mixture was allowed to cool to room temperature. It yielded a light cream solid, which was filtered off several times with N,N- dimethylactamide, washed and finally dried *in vacuo*.

Synthesis of Potassium Hydridotris(4-amino-1,2,4-triazolyl)borate

The ligand, potassium hydridotris(4-amino-1,2,4-triazolyl)borate was prepared by refluxing a mixture of potassium tetrahydridoborate (0.21g, 3.96 mmol) and 4-amino-1,2,4-triazole (1.00 g, 11.5 mmol) in N,N-dimethylacetamide for a period of ½ h. The reaction was stopped when the thereotical amount of hydrogen gas was evolved. The reaction mixture was allowed to cool to room temperature and the resulting colourless solid was filtered off off, washed several times with N,N-dimethylactamide and finally dried *in vacuo*.

Synthesis of Potassium Tetrakis(4-amino-1,2,4-triazolyl)borate

The ligand potassium tetrakis(4-amino-1,2,4-triazolyl)borate was synthesized by reacting 4-amino-1,2,4-triazole (1.00 g, 2.56 mmol) with potassium tetrahydrido-borate (0.55 g, 10.24 mmol) in N,N-dimethylacetamide under reflux for about ½ h. The reaction was stopped when the theoretical amount of hydrogen gas was evolved. The reaction mixture was allowed to cool to room temperature and the resulting colourless solid was filtered off, washed several times with N,N- dimethylactamide and finally dried *in vacuo*.

SYNTHESIS OF THE TRANSITION METAL COMPLEXES

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

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

A mixture of manganese(II) chloride (0.44 g, 2.20 mmol) and potassium diydridobis(4-amino-1,2,4-triazolylborate) (1.00 g, 4.50 mmol) in methanol was refluxed for about 2 h. The reaction mixture was allowed to cool to room temperature, resulting black solid product was filtered off off, washed with methanol and finally dried *in vacuo*.

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

The potassium dihydridobis(4-amino-1,2,4-triazolylborate) (1.00 g, 3.49 mmol) suspension and nickel(II) chloride (0.41 g, 1.74 mmole) were mixed togather and the content refluxed for about 2 h. The resulting light blue product, which separated out after cooling to room temperature was filtered off off, washed repeatedly with methanol and dried *in vacuo*.

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

To a hot suspension of potassium dihydridobis(4-amino-1,2,4-triazolyl)borate (1.00 g, 3.49 mmol) was added a copper(II) chloride (0.29 g, 1.74 mmol) solution in methanol. The reaction run at reflux for about 2 h. The reaction mixture was cooled to room temperature. The resulting green solid product, was filtered off, washed with methanol and dried *in vacuo*.

RESULTS AND DISCUSSION

Analysis and Physical Measurements:

The results of the analysis of carbon, hydrogen and nitrogen were performed by Central Drug Research Institute, Lucknow, using Heraeus Vario EL III analyzer. India and the results were within 0.4% of the theortical values. Analysis for metals was carried out chrlometric titration with standard EDTA solution. Prior to titration the metal was liberated from the complex by the addition of a few drops of mixture of nitric acid and perchloric acid to an accurately weighed 0.1g sample. IR spectra on KBr disk of the ligands and their metal complexs were run 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 recorded at SAIF, IIT

Madras, using VU-VIS-NIR CARYSE (185-3150 nm) spectrophotometer.

Characterization

The Transition Metal Complexes of Dihydridobis (4-amino-1,2,4-triazolyl)-Borate Anion.

The color, melting point and analytical data of the potassium dihydridobis (4-amino-1,2,4-triazolyl)borate and its transition metal complexes are listed in Table 1. The analytical results of ligand and the complexes are in conformity with their proposed compositions. In the formation of ligand, the imino-hydrogen atom of 4-amino-1,2,4-triazole molecule is removed together with two hydrogen atoms from potassium tetrahydridoborate according to following reaction:

$KBH_4 + 2\ C_2N_4H_6 \rightarrow K\ [\ H_2B(C_2N_4H_5)_2] + 2H_2$

The IR spectra of the ligand as well as its complexes along with their possible assignments are listed in Table 2. The IR spectrum of dihydridobis(4-amino-1,2,4,-triazolyl)borate anion displays a strong absorption band (absent in free 4-amino-1,2,4-triazole) at 1331 cm^{-1} attributed to B-N stretching frequency (Davidson, 2002). The formation of B-N bond is further supported by disappearance of the infrared N-H stretching frequency (1383 cm^{-1}, and a broad singlet at 3230 cm^{-1}). However, a doublet at 3419 cm^{-1} shows the presence of NH_2 group of the triazole ring. The presence of a broad doublet band at 2470-2435 cm^{-1} and 2413-2295 cm^{-1} in the spectrum of ligand and its metal complexes indicates the presence of B-H linkage (Price, 1949). The IR frequencies characteristic of 1,2,4-triazole ring system such as C=N, N-N also appear in the spectrum. The structure as given in Fig. 1 may be proposed for this ligand.

Analytical results indicate that metal complexes are formed in 1:2 metal : ligand ratios for Mn(II), Ni(II) and Cu(II). The formation of the complexes with bivalent metal ions may be depicted by the following equation:

$2K^+ + 2(C_2H_5N_4)^- + MCl_2 \rightarrow [M(C_{12}H_5N_4B)_2] + 2KCl$

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

The IR spectra of the complexes exhibit the B-N and B-H stretching frequencies slightly lower than that observed in the free ligand. A decrease in the $\nu_{C=N}$ in these complexes is noticed, suggesting the coordination through the N-2 of the triazolyl group. The proposed coordination site is further supported by the decrease in stretching vibrations of ν_{N-N} band. The appearance of the stretching frequencies of NH_2 group at their orginal position shows that the amino-nitrogen of 1,2,4-triazolyl ring does not take part in the coordination linkage. The non-ligand band observed in the range 450-425cm^{-1} may reasonably be assigned to M-N stretching frequencies.

Table 1: Colour, melting point and analytical calculations

Complex (% Yield)	Colour	M. P. (^oC)	Analysis							
			Calculated				Found			
			C	H	N	M	C	H	N	M
$K(C_4H_{12}N_8B)$ (73)	Colourless	>300	21.54	5.38	50.26		21.16	5.46	50.3	
$[Mn\ (C_4N_8H_{12}B)_2]$ (56)	Black	>300	23.86	5.96	55.68	11.04	23.50	5.85	55.94	11.37
$[Ni\ (C_4N_8H_{12}B)_2]$ (48)	Light Blue	>300	23.71	5.93	55.34	10.99	24.09	5.99	55.50	11.43
$[Cu(C_4N_8H_{12}B)_2]$ (69)	Green	>300	22.36	5.59	52.19	12.79	22.64	5.73	52.40	12.52

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}
$K(C_4H_{12}N_8B)$	2470, 2413	1331	1652	3365	1128	433
$[Mn\ (C_4N_8H_{12}B)_2]$	2435, 2310	1310	1618	3339	1060	427
$[Ni\ (C_4N_8H_{12}B)_2]$	2452, 2365	1316	1616	3417	1064	448
$[Cu(C_4N_8H_{12}B)_2]$	2455, 2295	1295	1604	3364	1053	439

In the IR spectra of complexes B-H and B-N stretching frequencies are observed at almost the same positions or slightly lower than that observed in the free ligand.

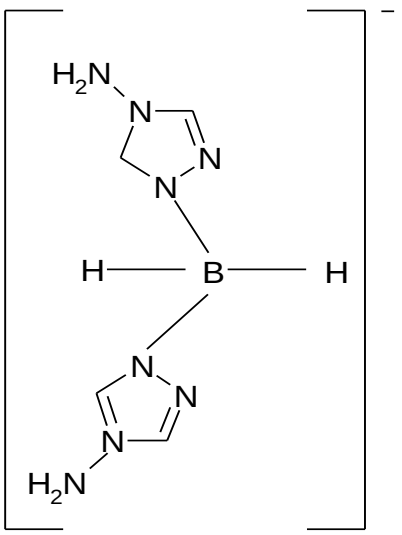
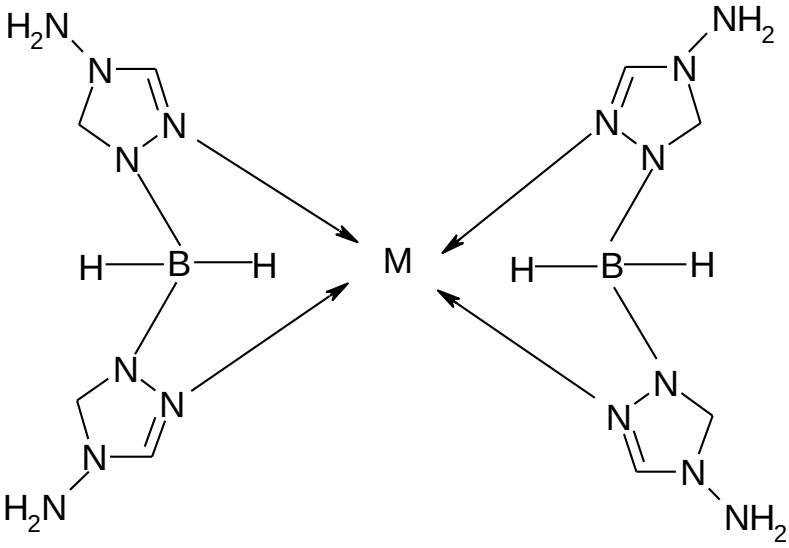


Figure 1: Proposed structure of Dihydridobis(4-amino-1,2,4-triazolyl)borate anion



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

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

The Magnetic Moment and Electronic Spectral Data

The magnetic moment values and the electronic spectral data of bis[dihydridobis(4-amino-1,2,4-triazolyl)borato]metal(II) complexes are given in Table 3:

The observed magnetic moment value for Mn(II) complex is 5.49 BM, indicating a tetrahedral structure. The electronic spectra of $C_{12}H_{36}N_{24}B_3Mn$ exhibit three bands at 20,000, 18,181, 12,500 cm^{-1} assigned to $^6A_1 \rightarrow {}^4E_g$, $^6A_1$ (G),$\rightarrow {}^4T_2$, $^6A_1 \rightarrow {}^4T_1$ respectively indicative of tetrahedral coordination of ligands around the Mn(II) ion. The μ_{eff} value for Cu(II) complex is 1.41 BM, which favours a square planar arrangement (ref). The electronic spectrum of Cu(II) complex exhibit two d-d transition bands at 17,543 and 11,764 cm^{-1} assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively (Jorgenson, 1962; Bertrand and Eller, 1974; Nakamoto, 1978).

The magnetic moment value for Ni is 2.45 BM favours a square planar structure for the complex. The electronic spectrum of Ni(II) shows three bands at 23,255, 15,384, 11,111 cm^{-1} assigned to $^3A_{2g}(g) \rightarrow {}^3T_{1g}$ (P), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions. On the basis of magnetic moments and the electronic spectral data a tetrahaedral structure may be suggested for the Mn(II) complex. The Ni(II) and Cu(II) complexes are, however, proposed to be square planar in geometry (Fig 2).

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

Complex	Magnetic Moment (MB)	Spectral Bands (cm^{-1})	Assignments
$[Mn(C_4N_8H_{12}B)_2]$	5.47	20,000 18,181 12,500	$^6A_{1g} \rightarrow {}^4E_g$ $^6A_{1g}(G), \rightarrow {}^4T_{2g}$ $^6A_{1g} \rightarrow {}^4T_{1g}$
$[Ni(C_4N_8H_{12}B)_2]$	2.51	23,255 15,384 11,111	$^3A_{2g}(g) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{2g}$
$[Cu(C_4N_8H_{12}B)_2]$	1.414	17543 11764	$^2B_{1g} \rightarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2B_{2g}$

REFERENCES

Bertrand J.A. and Eller P.G., 1974. Spectral and structural studies of iron (III) salicylaldimine complexes. Six-coordinate dinuclear complex. Inorganic Chemistry, **13(4)**: 927-934.

Davidson G., 2002. Vibrational spectra of some coordinated ligands. Spectroscopic Properties of Inorganic and Organometallic Compounds, **35**: 282-338.

Effendy, Lobbia G.G., Pellei M., Pettinari C., Santini C., Skelton B.W. and White A.H., 2000. Solution and solid-state structural properties of silver (I) dihydrobis (pyrazolyl) borate compounds with tertiary mono (phosphine) ligands. Journal of the Chemical Society, Dalton Transactions, **29(13)**: 2123-2129.

Effendy, Lobbia G.G., Pellei M., Pettinari C., Santini C., Skelton B.W. and White A.H., 2001. Bridged poly (1-imidazolyl) borate silver (i) complexes containing tertiary mono (phosphine) ligands. The first structurally authenticated bis (imidazolyl) borate metal complex. Journal of the Chemical Society, Dalton Transactions, **30(5)**: 528-534.

Edelmann F.T., 2001. Versatile Scorpionates—New Developments in the Coordination Chemistry of Pyrazolylborate Ligands. Angewandte Chemie International Edition, **40(9)**: 1656-1660.

Fujita M., Kwon Y.J., Washizu S. and Ogura K., 1994. Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium (II) and 4, 4'-bipyridine. Journal of the American Chemical Society, **116(3)**: 1151-1152.

Han R., Looney A. and Parkin G., 1989. Tris (pyrazolyl) hydroboratomagnesium and aluminum alkyl derivatives: alkyl exchange with methyl iodide and enolate formation with acetone. Journal of the American Chemical Society, **111(18)**: 7276-7278.

Hanson B.E., 1999. New directions in water soluble homogeneous catalysis. Coordination chemistry reviews, **185**: 795-807.

Ibrahim A.M. and Soliman T.M., 1994. Safaa El-din H. Etaiw and RD Fischer. J. Organometal. Chem, **468**: 93.

Janiak C., 1994. Clathrates and coordination polymers: new dimensions in poly (azolyl) borate chemistry with poly-(triazolyl)-and-(tetrazolyl)-borate ligands. Journal of the Chemical Society, Chemical Communications, **4**: 545-547.

Jorgenson C.K., 1962. Absorption Spectra and Chemical Bonding in Complexes (Pergamon Press, New York) pp.292.

Lobbia G.G., Hanna J.V., Pellei M., Pettinari C., Santini C., Skelton B.W. and White A.H., 2004. Gold derivatives of scorpionates: comparison with the other coinage metal poly (pyrazolyl) borate analogues. Dalton Transactions, **6**: 951-958.

Nakamoto K., 1978. Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York.

Navon N., Cohen H., Paoletti P., Valtancoli B., Bencini A. and Meyerstein D., 2000. Design of ligands which improve Cu (I) catalysis. Industrial & Engineering Chemistry Research, **39(10)**: 3536-3540.

Pellei M., Pettinari C., Santini C., Skelton B.W., Somers N. and White A.H., 2000. Synthesis, spectroscopic characterization, and structural systematics of new triorganophosphinecopper (I) poly (pyrazol-1-yl) borate complexes. Journal of

the Chemical Society, Dalton Transactions, **19**: 3416-3424.

Price W.C., 1949. The Infra-Red Absorption Spectra of Some Metal Borohydrides. The Journal of Chemical Physics, **17(11)**: 1044-1052.

Rheingold A.L., Incarvito C.D. and Trofimenko S., 2000. Dihydrobis (4-cyanopyrazol-1-yl) borate, [Bp4CN], a functionalized heteroscorpionate ligand with cross-linking potential. Inorganic Chemistry, **39(24)**: 5569-5571.

Santini C., Gioia Lobbia G., Pettinari C., Pellei M., Valle G. and Calogero S., 1998. Syntheses and Spectroscopic and Structural Characterization of Silver (I) Complexes Containing Tertiary Phosphines and Hydrotris (pyrazol-1-yl)-, Hydrotris (4-bromopyrazol-1-yl)-, Hydrotris (3, 5-dimethypyrazol-1-yl)-, and Hydrotris (3-methyl-2-thioxo-1-imidazolyl)borates. Inorganic Chemistry, **37(5)**: 890-900.

Santini C., Lobbia G.G., Pellei M., Pettinari C., Valle G. and Calogero S., 1998. Coordination chemistry of the sterically hindered N3-donor hydrotris (3, 5-diphenylpyrazol-1-yl) borate toward silver (I) triorganophosphino compounds. Synthesis, structural and spectroscopic characterization. Inorganica Chimica Acta., **282(1)**: 1-9.

Santini C., Pettinari C., Lobbia G.G., Leonesi D., Valle G. and Calogero S., 1998. Silver (I) and gold (I) complexes of hydrotris (3, 5-dimethylpyrazol-1-yl) borate: synthesis, spectroscopic and structural characterization, and reactivity toward C-, N-and S-donor ligands. Polyhedron, **17(18)**: 3201-3210.

Siemer C.J., Goswami N., Kahol P.K., Van Stipdonk M.J. and Eichhorn D.M., 2001. Dihydrobis (4-cyano-3-phenylpyrazol-1-yl) borate: Homoleptic mononuclear Cobalt (II) and Copper (II) complexes with a cyano-substituted scorpionate ligand. Inorganic Chemistry, **40(16)**: 4081-4084.