

SYNTHESIS OF TRIPODAL BORATE LIGAND WITH NI(II) AND CU(II) COMPLEXES

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Abstract

New tripodal ligand sodium[2,2',2''-(λ 4-boranetriyl)tris(1 H-indole-1,3-diyl)tri acetic acid]hydrate (BIAA) was synthesized by the reaction of heteroauxin (indole -3- acetic acid) with sodium tetrahydroborate in 3:1 mole ratio. The ligand was characterized by elemental analysis, spectral studies such as FTIR, UV-Vis., ¹HNMR and thermal analysis spectra, the results were agreement with the proposed structure. The coordination property of the ligand was studied through preparation of two metal complexes with Ni(II) and Cu(II) in 2:1 (L:M) mole ratio. Depending on elemental analysis, FTIR , UV-Vis. spectra, magnetic susceptibility measurements , atomic absorption and molar conductivity of metal complexes ,the suggested geometry of nickel and copper complexes were octahedral structures.

Keywords: Tripodal ligands , borate ligands.

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Introduction

Borate-based ligands were used in coordination chemistry and have gained significant attention such as scorpionate ligands. The substituted polypyrazolyl borates have been excellent used for the biomimetic modelling of nitrogen-rich active sites, as a facial coordination and allow mimicking of a tetrahedral geometry [1].

Tripodal ligands (as tri- and tetra dentate [ligands](#)) used in the areas of [coordination chemistry](#) and [homogeneous catalysis](#). Various studies shown that the tripodal ligands can be classified into two main groups: flexible and rigid tripodal ligands. The donor groups in the tripodal ligands lead to complexation with a good formation constant. The donor groups in tripodal ligands are usually donor soft groups that are connected to nitrogen atoms and the molecule resemble a flexible tripod [2].

The tripodal ligands can act as receptors for different chemical species: anions, or cations and anions in the same time, transition metal ions, lanthanide and actinide ions. The thermodynamic stability of the host-guest complexes makes from the tripodal ligands good candidates for biomedical applications as sequestering agents for iron, aluminium or actinide ions [3].

Tris (2 pyridyl) methylamine (tpm) ionophore as a basic part for the potential response of ion selective electrodes (ISEs) and has been used to prepare the membrane [2]

The tripodal *tris* (2-mercapto-1-R-imidazolyl) hydroborato ligand [Tm^R] (Figure 1) and its selenium complex [Tse^R], supply useful rostrum for organometallic and bioinorganic aspects of the chemistry of zinc, cadmium and mercury in (sulfur and selenium)-rich coordination environments. The tridentate [Tm^R] ligand supply [S₃] donor configuration that is use for mimicking aspects of zinc-enzymes and proteins that have sulfur-rich active sites [4]. The S-donor methimazolyl borates Tm, analogous to the pyrazole borates, also show some differences in their behaviour, the S-donor atom is exo- to the heterocycle ring, the methimazolylborates take eight-membered chelates, whereas the pyrazole borates take six-membered chelates. [5]

N-donor ligands, hydrido *tris*(pyrazolyl) borate (Tp) (Figure 1) and hydrido *tris*(3,5-dimethylpyrazolyl)borate (Tp*) are the basis for an extensive chemistry with metallic elements [5]. Several cobalt complexes with tripodal chelating ligands Tp and Tp* were synthesized as the homo scorpionates under different conditions such as isolation the product after stirring or after stored in the air and from crystallization of mother liquid [5,6].

The oxygen derivatives of [Tp^{iPr2}]Cu and [Tp^{tBu}]Cu were dimeric with a μ - η^2 : η^2 -peroxo bridge, the 3-*tert*-butyl pyrazole substituents in the latter perform a monomer, with side-on superoxide ligation. These ligands with strong field donors such as *tris*(phosphino) borates (PhBP₃) and *tris*(carbene) borates with hybrid ligands containing two or three different heteroatom donors. Less common tripodal ligands with sulfur heteroatom donors contain the poly(thioether) borates (Tt) (Figure 1) [7]

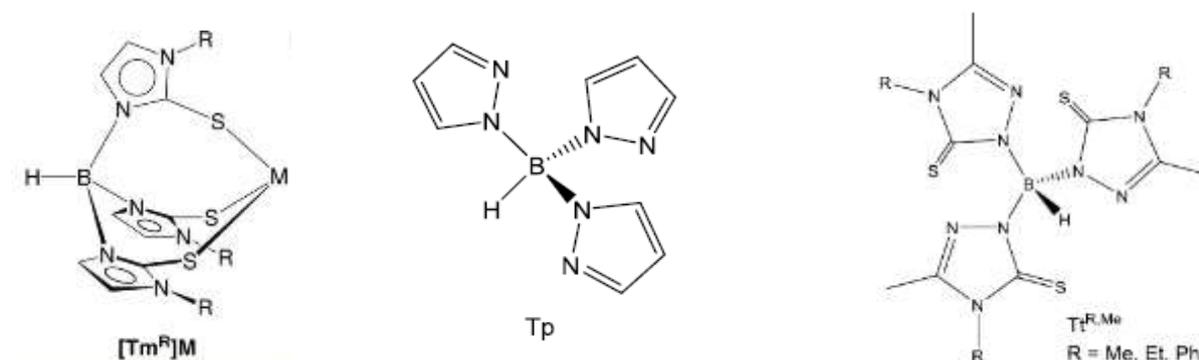


Figure 1: Examples of Scorpionate Ligands

The indole-3-acetic acid (IAA) (auxin) is a plant hormone for regulates plant growth and development, also plays plays arole in plant microbe interactions [8].. It has been found the different fungi,bacteria, and algae are capable of producing physiologically active amounts of IAA [9]. The interaction of IAA with cobalt (II), copper (II) and nic kel (II) in ethanol and in solid state were studied [10]. Also the complexes with Fe(III) and Zn(II), Al(III), Bi(III), Sb(III), Sn(II) and Pb(II) were synthesized [11,12, 13]

In the present work, new tripodal borate ligand (BIAA) was synthesized with Nickel and Copper metals to form the new complexes. All synthesized compounds were characterized using physicochemical and spectral methods. Thermal stability of the ligand and coordination properties of complexes were also studied.

Experimental Part

All chemicals were used as received without further purification.

Synthesis of the tripodal ligand (BIAA) $\text{Na}[\text{BH}(\text{IAA})_3] \cdot 3.5\text{H}_2\text{O}$

Synthesis of the ligand carried out depending on the literature [14,15]with modified from NaBH_4 and indole acetic acid (IAA) in 1:3 mole ratio. The solution of NaBH_4 (0.05 g, 1.321 mmol) in 6ml toluene was added to a hot solution of IAA (0.6946 g, 3.965 mmol) in 8ml toluene, the mixture was heated under reflux for 15 hour with vigorous stirrer, the crystal product washed with hot toluene, recrystallization from the mixture (acetone: H_2O 5:1) and washed with petroleum ether, the final product was greenish gray crystals.

Synthesis of Nickel (II) and Copper (II) Complexes

The ethanolic solution of ligand and metal salt in 2:1 mole ratio was stirred at room temperature for 6 hours and the color changed from green to brown Part of solvent was evaporated ,the brown product appeared after adding acetone, standing overnight and finally isolated the product.

(Ligand (0.20g, 0.318mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0378g, 0.159mmol), CuCl_2 (0.0213g, 0.159mmol) in 9ml ethanol).

Results and Desiccation

The molecular formulae, physical properties, elemental analysis and metal content data illustrated in (Table 1)

Table 1: Analysis data of the tripodal ligand and its metal complexes

Comp.	molecular formulae	M.wt g.mol ⁻¹	m.p (°C)	% Yield	Color	Elementa Analysis Found (Calc.)			Micro Metal conten t
						C%	H%	N%	
Ligand (BIAA)	Na[BC ₃₀ H ₂₅ N ₃ O ₆]3.5H ₂ O	619.8	140- 142	73.93	Greenish gray	57.46 (58.08)	5.29 (5.16)	6.14 (6.77)	-
C₁ Ni(II)	[B ₂ C ₆₀ H ₆₂ N ₆ O ₁₈ Ni ₃ Cl ₄]6H ₂ O	1601.6 7	> 280	44.68	Light brown	44.51 (44.95)	4.36 (4.62)	4.53 (5.24)	(10.15) (10.99)
C₂ Cu(II)	[B ₂ C ₆₀ H ₆₂ N ₆ O ₁₈ Cu ₃ Cl ₄]9H ₂ O	1670.2 2	> 280	31.51	Dark brown	42.26 (43.10)	4.18 (4.78)	4.34 (5.02)	10.32 (11.41)

Infrared spectroscopy

The spectrum of ligand showed band at 3549 cm⁻¹ which assigned to stretching vibration of lattice water, in complexes this band appeared at 3600 and 3614 cm⁻¹ (Table 2) in Ni and Cu complexes respectively [16]. Broad band appeared at 2966-3124 cm⁻¹ due to stretching vibration of OH group [17] this band appeared at higher frequency in complexes as a result of coordination to metal ions through OH group. The stretching vibration of carboxylic carbonyl group (νC=O) appeared at 1701 cm⁻¹ [10,11] and νB-N appeared at (1458-1463 cm⁻¹) [18], these bands not changed in complexes while the stretching vibration of B-H (νB-H) appeared at (2335-2360 cm⁻¹) [18] and changed in complexes as a result of a gostic interaction. The spectra of complexes showed low frequency bands which assigned to νM-O and νM-Cl (Table 2) [19, 20].

Table 2 |: The FT-IR data of the BIAA ligand and its metal complexes

Compounds	νH ₂ O Lattice (coord.)	νOH	νB-H	νC=O	νB-N	νM-O	νM-Cl
BIAA Ligand	3549	2966-3124	2360	1701	1458	-	-
C ₁ (Ni (II))	3600 (740 , 800)	3190-3481	2335	1703	1463	500	273
C ₂ (Cu(II))	3614 750 , 810) (3352-3442	2350	1705	1460	480	223

Thermal Analysis (TGA & DTG)

The thermal study of the BIAA ligand was carried out by TGA and DTG analysis (Figure 2) using Helium as inert gas in rate 20ml /min . The suggested structure of the ligand has confirmed by obtaining a good agreement between practical and theoretical percentage of

mass loss (Table 3) . The results showed that percentage of residue was 21.76% at 850°C and this indicates the stability of BIAA ligand[16].

Table 3: Thermal decomposition of the BIAA ligand

compound	Steps	DTG of the Decomposition °C	Suggested formula of loss	Mass loss% Cal. (Found.)
BIAA Ligand Na[BC ₃₀ H ₃₂ N ₃ O _{9.5}] 619.8 g/mol	1	93.11	0.6H ₂ O	(0.65) 1.74
	2	227.31	2.9H ₂ O	8.42(7.53)
	3	344.73	Na , C ₁₀ H ₈ NO ₂ , C ₃ H ₃ O ₂ , C ₆ H ₄ , CH	57.59(57.48)
	4	653.39	C ₂ H ₃ O ₂ , BH, H	11.58(12.55)
	Residue	850	C ₈ H ₄ N ₂	20.65(21.76)

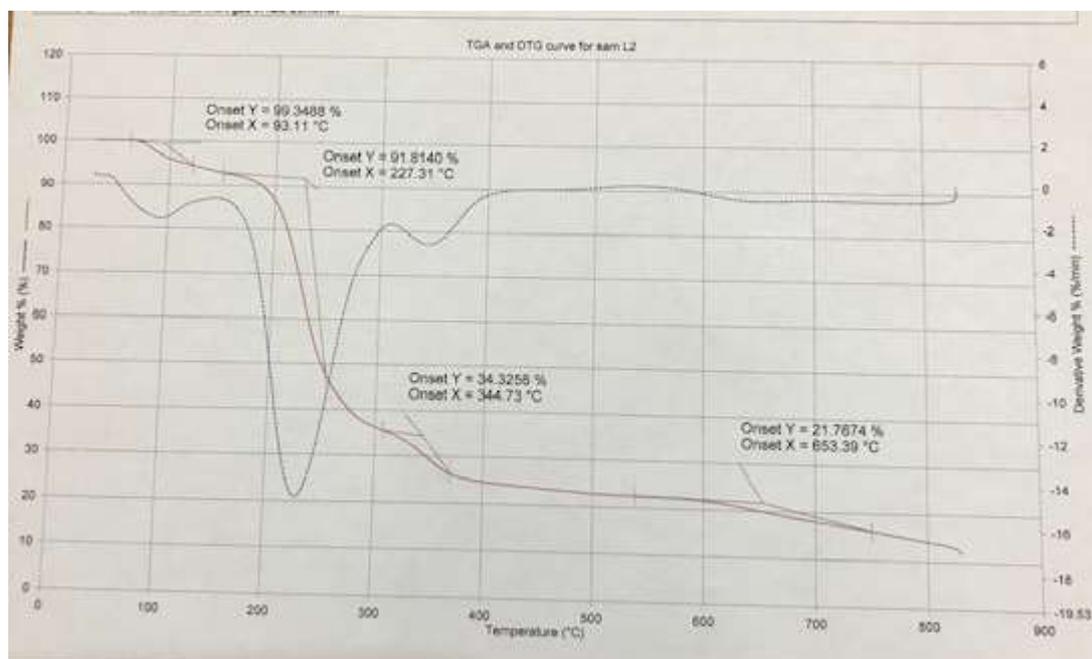


Figure 2: The thermogram of the BIAA ligand

¹H NMR spectrum

The ¹H NMR spectra of the ligand (Figure 3) was recorded in DMSO .The chemical shifts and peak assignments are given in (Table 4) .The peak appeared at δ = 10.88 ppm due to

for octahedral geometry of Ni(II) complexes [22,23]. The spectrum of copper complex (Figure 4B) showed the following bands: 284 nm (35211 cm^{-1}), 350 nm (28571 cm^{-1}), 400 nm (25000 cm^{-1}), 670 nm (14925 cm^{-1}), 990 nm (10101 cm^{-1}) which assigned to

$\pi \longrightarrow \pi^*$, $n \longrightarrow \pi^*$, $(L \longrightarrow M)$ charge transfer C.T, $(\nu_2) {}^2B_{1g} \longrightarrow {}^2B_{2g}$ and $(\nu_1) {}^2B_{1g} \longrightarrow {}^2A_{1g}$ respectively for octahedral geometry of Cu(II) complexes [16, 23].

The molar conductivities of nickel and copper complexes were 0.124 and $0.064\text{ S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$ and this assigned to nonelectrolyte behavior of complexes. The magnetic moment of Ni(II) and Cu(II) as polynuclear complexes were $\mu_{\text{eff}} = 5.75$ and 2.462 M.B for Ni and Cu complexes respectively for octahedral geometries and these results assigned to noninteracting metal centers of polynuclear complexes [24]

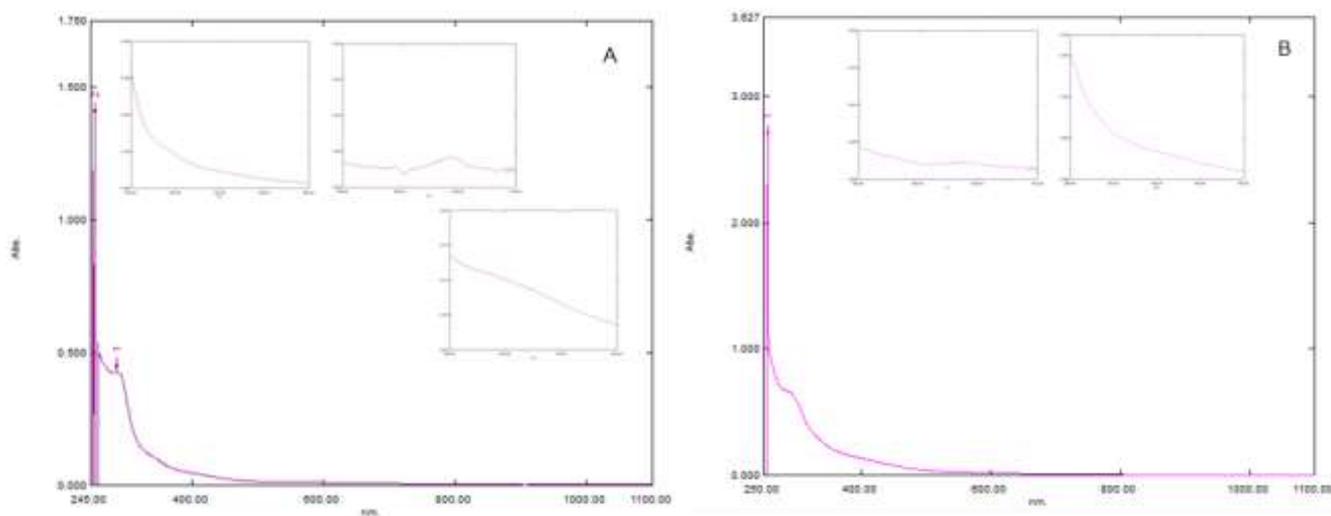


Figure 4: A-Electronic spectrum of Ni(II) complex , B- Electronic spectrum of Cu(II) complex

Conclusion

In this work, the new ligand (Figure 5) and its complexes with Ni(II) and Cu(II) metal ions (Figure 6) were synthesized and characterized by spectral and chemo physics methods. Based on the results of these techniques, the structures of new compounds was suggested and the complexes were octahedral geometry. Thermal stability Study of the ligand showed that 21.76 % from the ligand was stable up to $850\text{ }^{\circ}\text{C}$. The coordination properties study of metal complexes showed coordination of metal ions with H_2O , OH (acetic acid), Cl and $\text{M}\dots\text{H}$ as agostic interactions. This multiple coordination due to formation of polynuclear complexes.

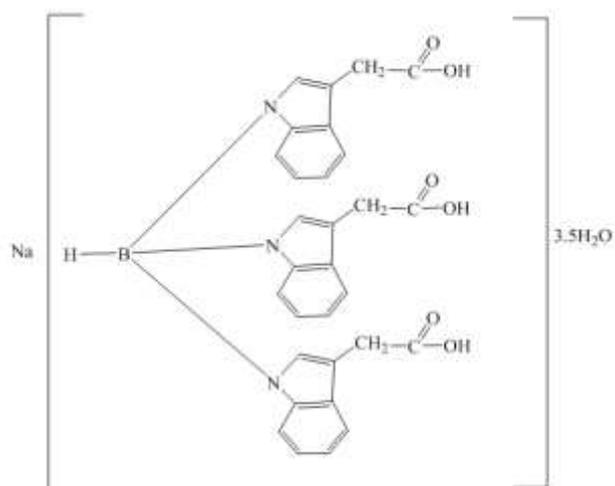


Figure 5: The suggested structure of BIAA ligand

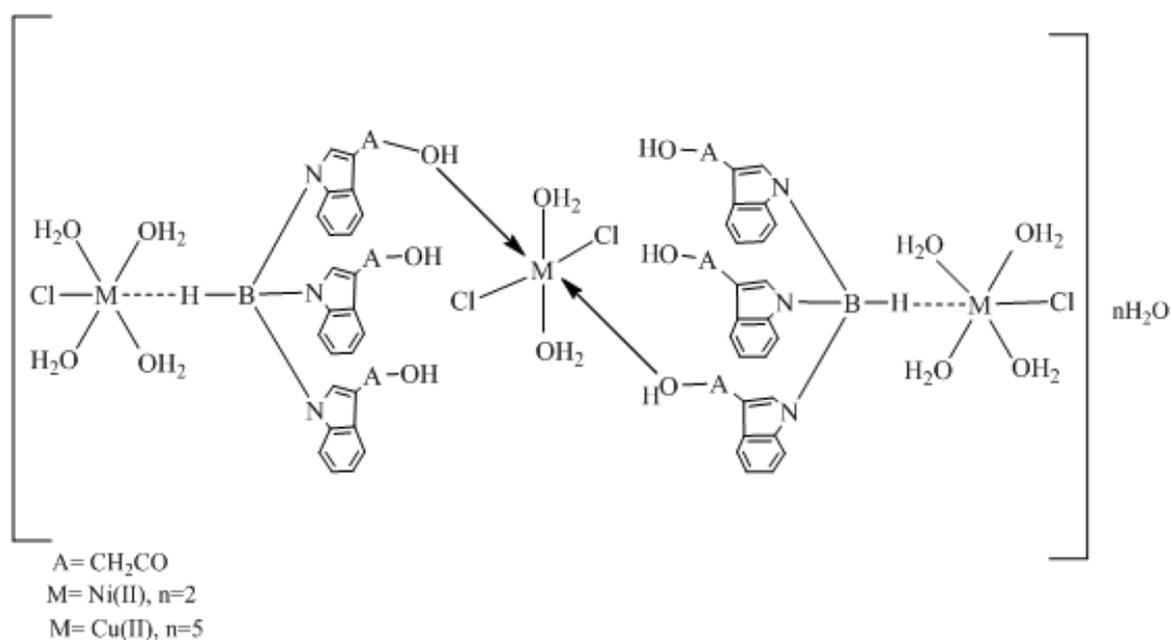


Figure 6: The suggested structures of Ni(II) and Cu(II) complexes

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