

## Synthesis, Structural and Magnetic Studies of Dinuclear Complexes with Oxo-Homoscorpionate Borate Ligand

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**Abstract:** Oxo-homoscorpionate borate ligand, potassium *bis*(phthalato)borate (KL) has been synthesized as its potassium salt. It was converted into its Co(II), Ni(II) and Cu(II) dinuclear complexes by mixing and stirring with methanol solution of metal chloride. The compositions of ligand and its metal complexes were investigated by elemental analysis in order to ensure their purity and the structural elucidations were based on conductivity measurements, room temperature magnetic susceptibility, thermal and spectral studies (IR, <sup>1</sup>H NMR, UV-Vis and MS-ESI mass spectra). Spectroscopic results support a square planar (SP) geometry in the Cu(II) complex while an octahedral ( $O_h$ ) geometry is suggested in the Ni(II) and Co(II) complexes. Magnetic susceptibility measurements of complexes reveal that these complexes exhibit antiferromagnetic coupling behavior due to the presence of two metal ions in close proximity. The molar conductance measurement in water shows 1:1 electrolyte natures. The thermal behaviour of compounds was investigated by thermal gravimetrical analysis (TGA), in order to determine their mode of decomposition and thermal stability. All these complexes and ligand show three step loss upon dynamic heating to 1000°C, with simultaneous loss of both of inorganic and organic fragments exhibiting almost the same mode of decomposition pattern. The residue after heating above 500°C corresponded to metal chlorides, confirmed by microanalysis and IR spectroscopy. It is observed from the results that the thermal stability of the complexes increases in the following sequence:



**Key words:** Borate • Metal complexes • Magnetic moments • Thermal behavior

### INTRODUCTION

The aromatic carboxylic acid complexes provide interesting coordination compounds because the phenoxy carboxylate ions adopt various coordination modes [1], usually monodentate, bridging bidentate or chelating bidentate. An absence of the inter-metal magnetic interaction (paramagnetism) and its presence (ferromagnetism, antiferromagnetism) is largely related to the coordination mode of the compounds with focus on the magnetic path between the adjacent metal ions. The magnetostructural characterization of dinuclear metal(II) complexes has played a key role in the development of magnetochemistry [2, 3]. The possibility of achieving strong magnetic interactions between magnetic centers which are linked through more and more

extended bridges actually appears as a very active area of molecular magnetism. Coordination chemistry of metal-carboxylato species is an attractive subject from the magneto-structural standpoint because the carboxylate group mediates magnetic exchanges by bridging paramagnetic first-row transition metal cores.

The organoborate chemistry has been extensively explored in the past three decades [4]. Interactions of  $\text{KBH}_4$  with pyrazole, indazole, imidazole and indol [5] have been shown to yield a variety of ligands which have exploited mainly in the synthesis of transition metal complexes. Scorpionate-type poly (pyrazole) borate and poly (pyrazole) alkane ligands have found wide applications in coordination, organometallic and bioinorganic chemistry [6]. The increasing robust nature and ease with which their steric and electronic properties

can be modified via simple synthetic protocols, thereby allowing a fine-tuning of ligand properties [7]. Oxo-Homoscorpionate borate anions ligands containing two or more substituted pyrazol-1-yl moieties provide a unique opportunity to construct transition metal complexes of low symmetry. Keeping the above facts in mind of an unprecedented interest in the boron compounds and carboxylic acid Joshi *et al.* [8] reported that potassium bis(phthalato)borate and its organotin complexes, which can be considered as a module system for metal ligand interaction in biological system. With the aim of elucidating the coordination chemistry of this biological active ligand, we synthesized potassium bis(phthalato)borate with minor modification and its dinuclear complexes of Co(II), Ni(II) and Cu(II). So here we are reporting the synthesis, spectroscopic characterization, thermal and magnetic studies.

## MATERIALS AND METHODS

All chemicals and reagent were of analytical grade obtained from commercial sources and were used as received (Sigma-Aldrich and Merck). All synthesis were carried out under nitrogen atmosphere using standard Schlenk techniques and sample for microanalysis were dried in vacuum to constant weight. The solubility of the ligand and its metal complexes in various solvent was checked at room temperature. Melting point was recorded on a matrix melting point apparatus. The composition of ligand and its complexes was established based on the analysis of content of metals, carbon, hydrogen, oxygen and chlorine. Metals and chlorides were measured volumetrically and gravimetrically [9]. Elemental microanalyses of solid samples were performed by Perkin-Elemer-Model-2400 CHONS elemental analyzer. The molar conductance measurement was carried out using a TACUSSEL, CD 810 conductivity meter at room temperature (25°C) in water ( $10^{-3}$  M). IR spectra were recorded on KBr pellets using a Perkin-Elemer-Model 1620 FTIR spectrophotometer. Far infrared spectra were recorded CsI pellets using JASCO FTIR 550 spectrophotometer.  $^1\text{H}$  NMR was recorded using Brucker DPX300 MHz Spectrometer operating at room temperature using with DMSO-d<sub>6</sub> solvent. The chemical shifts ( $\delta$ ) are reported in part per million using tetramethyl silane (TMS) as internal standard. Electronic spectra were taken on a Shimadzu UV-Vis-NIR 3600 spectrophotometer in H<sub>2</sub>O solvent in the range of 200-1100 nm. The magnetic susceptibility measurement of powdered samples at room

temperature was carried out by vacuum-mounted Gouy balance at 5 KOe, using Hg[Co(NCS)<sub>4</sub>] as the reference. Diamagnetic susceptibility corrections for ligand susceptibility were made using Pascal's constants [10] and effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ , where  $\chi_M$  is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms. TGA Data was obtained from TA-2000 DuPont apparatus in air atmosphere at heating rate of 20°C/min over the 20-900°C. About 2-4 mg of samples was placed in Pt crucible and  $\alpha\text{-Al}_2\text{O}_3$  was used as the reference material. Positive and negative mode ESI mass spectra were recorded on a MICRO MASS QUATTRO (II), triplet quadrupole mass spectrometer using CH<sub>3</sub>OH as solvent. The sample was introduced into the ESI source through a syringe pump at the rate of 5  $\mu\text{L}$  per min. The ESI capillary was set at 3.5 kV and voltage 40 V. The spectrum was obtained in 6 s scans and the print outs were averaged spectra of 6-8 scans.

**Synthesis of the Ligand (Potassium Bis(phthalato) Borate) (KL):** Potassium borohydride (100 mmole) and phthalic acid (300 mmole) were dissolve with 20 mL ethanol in Schlenk flask containing magnetic stirring bar. The flask was connected to a condenser and placed in oil bath; the other opening of the condenser was fitted with gas collecting device. The content of the flask was carefully heated on controlled temperature oil bath until 9260 mL (400 mmole) of hydrogen gas evolved. The melt was cooled at room temperature, when it become viscous then poured into 500 mL of hot toluene. It was stirred for one hour. The mixture was filtered and a white solid obtained which was washed with successive portions of hot toluene, benzene, diethyl ether and finally dried in vacuo over fused CaCl<sub>2</sub>.

**Synthesis of Dinuclear Complex:** Complexes of Co(II), Ni(II) and Cu(II) were prepared by adding hot methanolic solution(20 mL) of corresponding metal salts (2 mmole) to hot methanolic solution borate ligand (1mmole, 20 mL). The resulting solution was reflux with stirring for 6 hours and the solution was concentrated to 30 mL. It was then allowed to stand overnight in a refrigerator. Colored complexes separate out, which was isolated by filtration under vacuum. The isolated metal complexes were washed several times with hot methanol and diethyl ether and finally dried in vacuo over fused CaCl<sub>2</sub>. The compound was recovered in solid state and was recrystallized from methanol.

Table 1: Analytical and physical data of the ligand and its dinuclear complexes

Compounds	Atomic mass	$\Lambda_m(\Omega^{-1}cm^2mol^{-1})$	M.P.		Yield (%)	Found (Calc.) (%)			
			State	(°C)		M	C	H	O
Ligand, KL	378		Solid	265	Colorless	75	49.19	2.27	32.84
KBC <sub>16</sub> H <sub>8</sub> O <sub>8</sub>							(50.79)	(2.11)	(33.86)
K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	709	109.52	Soli	>300	Pink	65	16.32	26.11	2.53
KBC <sub>16</sub> H <sub>16</sub> O <sub>12</sub> Co <sub>2</sub> Cl <sub>4</sub>							(16.62)	(27.09)	(2.25)
K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	709	93.86	Solid	>300	Green	62	16.48	26.12	2.44
KBC <sub>16</sub> H <sub>16</sub> O <sub>12</sub> Ni <sub>2</sub> Cl <sub>4</sub>							(16.55)	(27.09)	(2.25)
K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ]	647	88.98	Solid	>300	Blue	67	19.98	29.68	1.90
KBC <sub>16</sub> H <sub>8</sub> O <sub>8</sub> Cu <sub>2</sub> Cl <sub>4</sub>							(19.64)	(30.10)	(1.25)
									(20.02) (21.94)

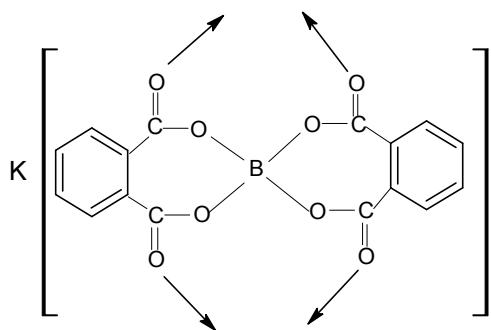


Fig. 1: Structure of the multidentate ligand showing the possible coordination sites.

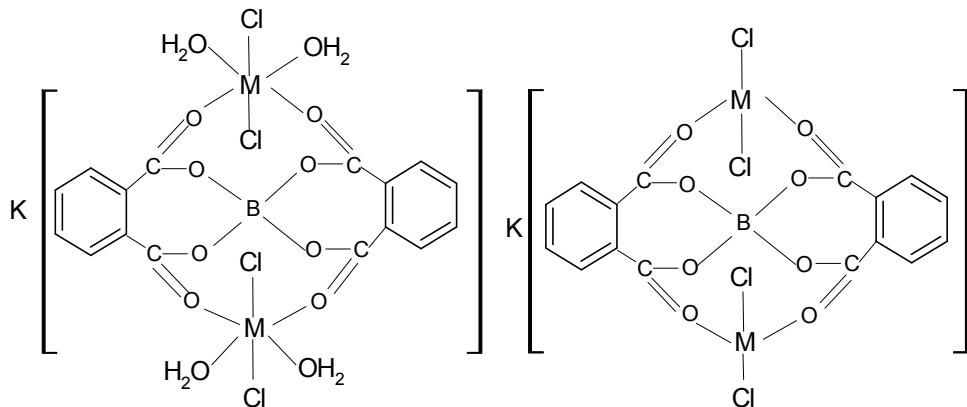


Fig. 2: Structure of dinuclear bimetallic complexes.

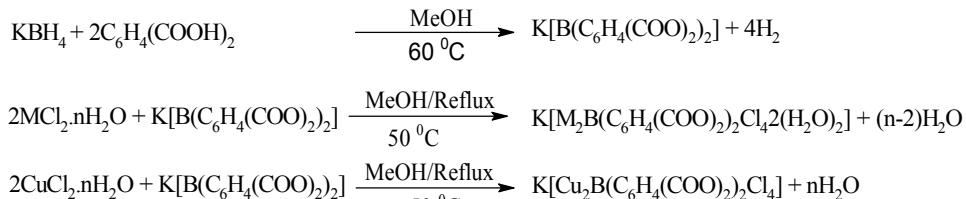
## RESULTS AND DISCUSSION

The ligand and its corresponding dinuclear complexes were obtained as solid, air stable, sparingly soluble in common organic solvents but soluble in H<sub>2</sub>O, DMSO, CH<sub>3</sub>OH and acetonitrile. The stoichiometry of the complexes was established on the basis of their elemental analysis. The results of elemental analysis are

presented in Table 1. The structure pattern and geometry (Figures 1 and 2) of the complexes were assigned on the basis of the physico-chemical parameters. The molar conductance measurements of complexes in water ( $10^{-3}$ M) correspond to be electrolytic nature for Co(II), Ni(II) and Cu(II) complexes. The ligand and its dinuclear complexes were formed according to the following equations:

Table 2: IR spectral data of the ligand and its dinuclear complexes ( $\text{cm}^{-1}$ )

Compound	$\nu(\text{Ar}-\text{CH})$	$\nu(\text{B} - \text{O})$	$\nu(\text{C} = \text{O})$	$\nu(\text{M} - \text{O})$	$\nu(\text{M} - \text{Cl})$
Ligand,	KL	3075	1381	1673	..... .....
K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3091	1401	1584	556	340
K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3098	1405	1562	557	336
K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ]	3084	1398	1527	530	310



M= Co(II) and Ni(II)

**Infra Red Spectra:** The IR spectra provide some information regarding the mode of coordination in the complexes and were analyzed by a careful comparison with that of the free ligand (Table 2). The spectrum of ligand showed the absence of O-H absorption band at 2500-3100  $\text{cm}^{-1}$  indicating deportation of phthalic acid. Similarly, absence of B-H band absorption in the 2200-2400  $\text{cm}^{-1}$  region indicates formation of desired ligand [11]. The weak band at 3075  $\text{cm}^{-1}$  is due to stretching vibrations of aromatic ring. These vibrations were shifted towards the higher frequency region in the complexes. The absorption band observes at 1381  $\text{cm}^{-1}$  may tantavily assigned to  $\nu_{\text{sym}}$  (B-O) bond [12], which is further confirmed by absence of O-H stretching vibration for the formation of desired ligand. After complexation, the B-O stretching vibrations appear at 1398-1405  $\text{cm}^{-1}$  negligible shift indicates non-involvement of esteric oxygen (B-O) in coordination. The ligand shows an expected absorption at 1673  $\text{cm}^{-1}$  [13], assigned as  $>\text{C}=\text{O}$  stretching vibration. The characteristic  $>\text{C}=\text{O}$  stretching vibrations in the complexes is at 1527-1584  $\text{cm}^{-1}$  have significant shifts from the ligand and clearly indicate that the free ligand is coordinated to metal (II) ion through this group. The coordination of oxygen to metal atom would be expected to reduce the electron density on the carbonyl oxygen and thus cause a shift in  $\text{C}=\text{O}$  band. Medium to weak absorption bands at 1300-1315  $\text{cm}^{-1}$  found in all the metal complexes and ligand due to C-O stretching. The low frequency skeletal vibrations due to M-O and M-Cl stretching provide direct evidence for the complexation. In the present investigation, the bands in the region 530-557  $\text{cm}^{-1}$  region have been assigned to M-O bond [14,15] and the bands observed in the 310-340  $\text{cm}^{-1}$  region for M-Cl bond [16] respectively in all the metal complexes.

The IR spectra Nickel and Cobalt complexes exhibit a broad stretching vibration in the 3444-3420  $\text{cm}^{-1}$  region can be attributed to coordinate the water molecules [17]. The presence of broad band at 800-900  $\text{cm}^{-1}$  further confirms the coordination of water molecule in the complexes [18]. Thus the IR spectral result provides strong evidences for the complexation of borate ligand with metal ions in the bidentate mode.

**<sup>1</sup>HNMR:** Proton spectra support and provide additional information about the formation a of ligand and its metal complexes in their usual region. In the <sup>1</sup>HNMR spectra of ligand the absences of broad signal at 9-12 indicate removal of acidic protons of phthalic acid [19]. The absence of another signal 3.4-5 ppm was due to deprotonation of B-H protons which let the formation of ligand [20]. The multiplets at 7.56-7.84 ppm show the presence of aromatic protons of both rings [21]. After complexation, in all cases the resonances of the ligand protons are deshielded upon coordination. The shift in the position of resonance signal of complexes to ligand due to change in the electronic environment as a result of coordination of ligands to the metal. The NMR spectra of these three are consistent with their structures and revealed that both metal ions are attached through ketonic oxygen. Thus the NMR results further support the IR inferences.

**Electronic Spectra:** In order to obtain further structural information, the electronic reflection spectra of these binuclear complexes were measured and the spectral data are given in the Table 3, which includes the absorption regions, band assignments and ligand field parameters, calculated by using the Tanabe-Sugano diagram. The Nephelauxetic parameter  $\beta$  was readily obtained by using the relation:

Table 3: Magnetic moment and electronic spectral data of dinuclear complexes

Compound	Frequency (cm <sup>-1</sup> )	$\epsilon$ (l mol <sup>-1</sup> cm <sup>-1</sup> )	$\Delta_0$ (cm <sup>-1</sup> )	Assignments	B (cm <sup>-1</sup> )	$\beta$	$\mu_{\text{eff}}$ (B.M.)
K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	11,904	30	<sup>4</sup> T <sub>1g(F)</sub> → <sup>4</sup> T <sub>2g(F)</sub>	11348	793.6	0.708	5.16
	15,037	68	<sup>4</sup> T <sub>1g(F)</sub> → <sup>4</sup> A <sub>2g(F)</sub>				
	20,202	81	<sup>4</sup> T <sub>1g(F)</sub> → <sup>4</sup> T <sub>1g(P)</sub>				
	26,315	122	Charge Transfer				
K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	13,984	39	<sup>3</sup> A <sub>2g(F)</sub> → <sup>3</sup> T <sub>2g(F)</sub>	15492	847.5	0.784	4.45
	15,873	57	<sup>3</sup> A <sub>2g(F)</sub> → <sup>3</sup> T <sub>1g(F)</sub>				
	25,641	88	<sup>3</sup> A <sub>2g(F)</sub> → <sup>3</sup> T <sub>1g(P)</sub>				
K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ]	15,625	76	<sup>2</sup> B <sub>1g(F)</sub> → <sup>2</sup> A <sub>1g(F)</sub>	2.47			
	25,000	162	Charge Transfer				

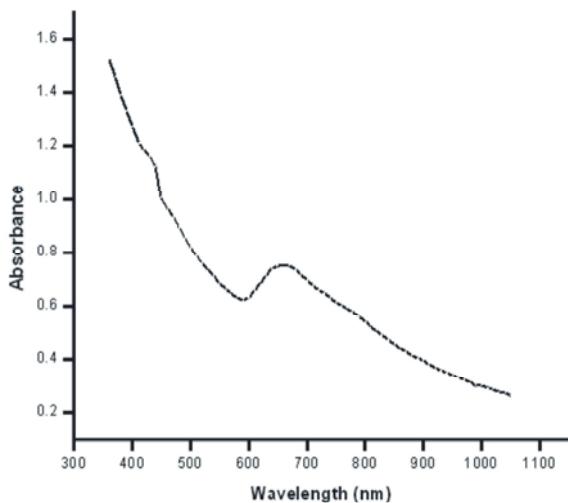


Fig. 3: Electronic spectrum of copper (II) complex.

$$\beta = \frac{B(\text{complex})}{B(\text{freeion})}$$

Where B is the free ion for Co(II) is 1120, for Ni(II) is 1080 cm<sup>-1</sup> [22].

The electronic spectrum of Co(II) complex exhibit absorption bands in the region around 11,904, 15,037, 20,202 and 26,315 cm<sup>-1</sup>. These bands may be assigned to the transitions: <sup>4</sup>T<sub>1g(F)</sub> → <sup>4</sup>T<sub>2g(F)</sub> (v<sub>1</sub>), <sup>4</sup>T<sub>1g(F)</sub> → <sup>4</sup>A<sub>2g(F)</sub> (v<sub>2</sub>) and <sup>4</sup>T<sub>1g(F)</sub> → <sup>4</sup>T<sub>1g(P)</sub> (v<sub>3</sub>), respectively and forth band may be due to charge transfer. The position of bands indicates that complex have octahedral geometry [23]. On the basis of these assignments the ligand field parameters calculated for Co(II) complex are  $\Delta_0$  = 11348 cm<sup>-1</sup>; B = 796.6;  $\beta$  = 0.708. Similarly Ni(II) complex exhibit three absorption bands in the region around 13,984, 15,873 and 25,641 cm<sup>-1</sup>. These bands may be assigned to the spin allowed transitions: <sup>3</sup>A<sub>2g(F)</sub> → <sup>3</sup>T<sub>2g(F)</sub> (v<sub>1</sub>), <sup>3</sup>A<sub>2g(F)</sub> → <sup>3</sup>T<sub>1g(F)</sub> (v<sub>2</sub>) and <sup>3</sup>A<sub>2g(F)</sub> → <sup>3</sup>T<sub>1g(P)</sub> (v<sub>3</sub>), respectively. The position of bands indicates that the complex have six-coordinated octahedral geometry [24]. On the basis of these assignments the ligand field

parameters calculated for Ni(II) complex are  $\Delta_0$  = 15492 cm<sup>-1</sup>; B = 847.5;  $\beta$  = 0.784. Thus the reduction of the Racah parameter from the free ion values and values of  $\beta$  indicate covalent character of the metal ligand ‘o’ bond. The above discussion very strongly indicates octahedral geometry around the central metal ion in these two complexes, requiring occupation of two coordination sites by H<sub>2</sub>O.

The electronic spectrum of Cu (II) complex exhibit absorption in the region around 15,625 and 25,000 cm<sup>-1</sup> (Figure 3). These bands may be assigned to the transition: <sup>2</sup>B<sub>1g(F)</sub> → <sup>2</sup>A<sub>1g(F)</sub> and second band may be due to charge transfer. An examination of these bands indicates that the complexe have square planer geometry [14, 25].

**Magnetic Susceptibility Measurement:** The geometry assessment of the complexes around the Cu(II), Co(II) and Ni(II) ions were supported further from the results magnetic moments (Table 3). The observed magnetic moment per dinuclear complex at room temperature is considerably less than the spin only values. This suggests the operation of antiferromagnetic spin-exchange interaction in these complexes, brought about by the bridging of paramagnetic centers through the oxygen atoms and aromatic rings. This bridging often leads to change in reduction of paramagnetic partially or completely of the metal atoms bridge. The reduction in electron density on the bridged group weakens the electron-electron repulsion and lowers the bridged magnetic orbital levels. This in turn will lead to larger energy gap between the metal and the bridged orbitals. Hence, the subnormal magnetic moments observed for the present dinuclear metal complexes. The observed magnetic moment value of Cu(II) was found to be 2.47 BM. This value is lower than the expected value for two Cu(II) ions involved, most possible because of antiferromagnetic interactions between the adjacent Cu(II) ions in the complex. The square-planar geometry is achieved by the coordination of two Cu(II) ions with

Table 4: ESI-MS mass spectral analysis (positive mode) of the ligand and its dinuclear complexes.

Compound	m/z	Peak assignments	Relative% abundance
Ligand, KL	379	[M+1] <sup>+</sup>	33
	214	[K[B(C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup>	45
	175	[B(C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup>	64
	74	[BO <sub>4</sub> ] <sup>+</sup>	35
K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	710	[M+1] <sup>+</sup>	77
	653	[M+1-(Co)] <sup>+</sup>	20
	589	[M+1-(CoCl <sub>2</sub> )] <sup>+</sup>	40
	485	[M-BCoCl <sub>2</sub> CO <sub>2</sub> ] <sup>+</sup>	25
	372	[M+1-(CoCl <sub>2</sub> + BC <sub>8</sub> H <sub>8</sub> O <sub>6</sub> )] <sup>+</sup>	55
K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	709	[M] <sup>+</sup>	20
	670	[M-K] <sup>+</sup>	45
	655	[M-3H <sub>2</sub> O] <sup>+</sup>	65
	639	[M-Cl <sub>2</sub> ] <sup>+</sup>	55
	445	[M-(NiCl <sub>2</sub> +C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> )] <sup>+</sup>	
	329	[M-Ni <sub>2</sub> Cl <sub>2</sub> (C <sub>8</sub> H <sub>8</sub> O <sub>6</sub> )] <sup>+</sup>	50
K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ]	649	[M+2] <sup>+</sup>	40
	414	[M-(CuCl <sub>2</sub> 2CO <sub>2</sub> B)] <sup>+</sup>	15
	318	[M-(KCu <sub>2</sub> C <sub>8</sub> H <sub>4</sub> O <sub>6</sub> )] <sup>+</sup>	50
	229	[M+2-(Cu <sub>2</sub> Cl <sub>2</sub> B(C <sub>9</sub> H <sub>8</sub> O <sub>6</sub> ))] <sup>+</sup>	65
	207	[M-Cu <sub>2</sub> Cl <sub>2</sub> +2CO <sub>2</sub> +B+C <sub>6</sub> H <sub>4</sub> ] <sup>+</sup>	30

single ligand molecule, each through (OC)<sub>2</sub> coordination sites and chloride ions [26]. This fact suggests the dinuclear nature of the Cu(II) complex. On the other hand, Co(II) and Ni(II) complexes have shown magnetic moments values 5.16 and 4.45 BM respectively which are lower than the calculated values for two Co(II) and Ni(II) ions in a octahedral geometry, indicating the possible antiferromagnetic interactions between the adjacent metal ions in the complexes which further confirm the dinuclear nature of the complexes. Thus low magnetic moment values and IR data indicate the presence of oxygen bridged structure, in which metal ions exhibits coordination number four or six.

**Electron Spray Ionization Mass Spectra (ESI-MS):** The most relevant fragmentations of ligand and its metal complexes with their assignments are shown in Table 4. The fragmentation pattern confirms the dinuclear nature of metal complex. The ESI-MS spectra of the compounds have differences of 1, 2 or 3 amu in their calculated and observed mass fragmentations due to the isotopic nature of chlorine (<sup>35</sup>Cl, <sup>37</sup>Cl), boron (<sup>10</sup>B and <sup>11</sup>B) and carbon (<sup>12</sup>C and <sup>13</sup>C). In some cases, the molecular ion peak was also associated with solvent, water molecules and some adduct ions from the mobile phase solution [27]. Positive ion mass spectra gave better data than negative ion mass spectra. The positive ion ESI spectrum of the metal free ligand confirms the proposed formula by showing a peak at m/z 379 corresponding to the moiety K[B(C<sub>6</sub>H<sub>4</sub>(COO)<sub>2</sub>]<sup>+</sup> (calculated atomic mass m/z 378). The fragmentation peaks, at m/z 214,175 and 74 are

ascribed to the cleavage of [KB(C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>O<sub>4</sub>)]<sup>+</sup>, [B(C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>O<sub>4</sub>)]<sup>+</sup> and [BO<sub>4</sub>]<sup>+</sup>, are well observed in mass spectrum. Their intensity gives an idea of stability of the fragments. Similarly positive ion spectra ESI- MS of the copper complex (Figure 4) show [M+2]<sup>+</sup> peaks at m/z 649 and nickel and cobalt complexes show peak at 709 and 710 corresponding to the m/z [M]<sup>+</sup> and [M+1]<sup>+</sup> respectively.

**Thermal Studies (TGA):** Table 5 summarizes some results of thermal analysis of ligand and its metal complexes. It shows that they are thermally stable to a varying temperature. Thermogravimetric (TG) analysis of the ligand shows three distinct losses of weight. The low temperature losses at between 175-230°C are commonly assumed to correspond to the loss of non-combustible CO<sub>2</sub> gas from ligand. The second weight loss occurring between 230 and 350°C likely corresponds to the loss half moiety of ligand. Similarly third weight loss at between 350-540°C is due to loss of potassium, leaving more than 30% residue.

The proposed decomposition of the complexes occurred by fragmentation and thermal degradation of organic part in metal complexes, resulting in the corresponding metal chlorides as residue, identified by microanalysis and IR spectroscopy. Thermal degradation of complexes under study takes place according to mechanisms involving dehydration and decomposition process of organic ligand followed by inorganic ligand. Both the number of steps and temperature ranges corresponding to release of water molecules are markedly dependent on the nature of the metal ions. On this basis

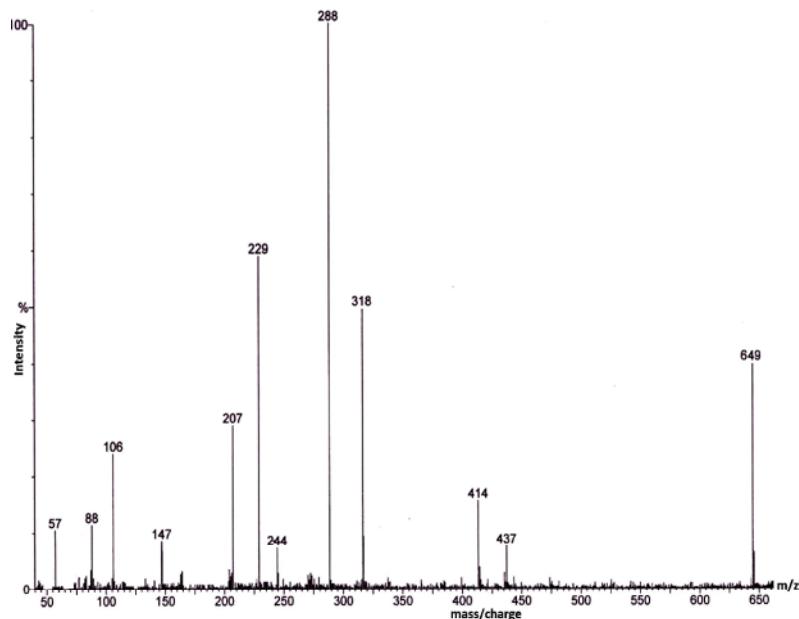


Fig. 4: ES - mass spectrum of copper(II) complex.

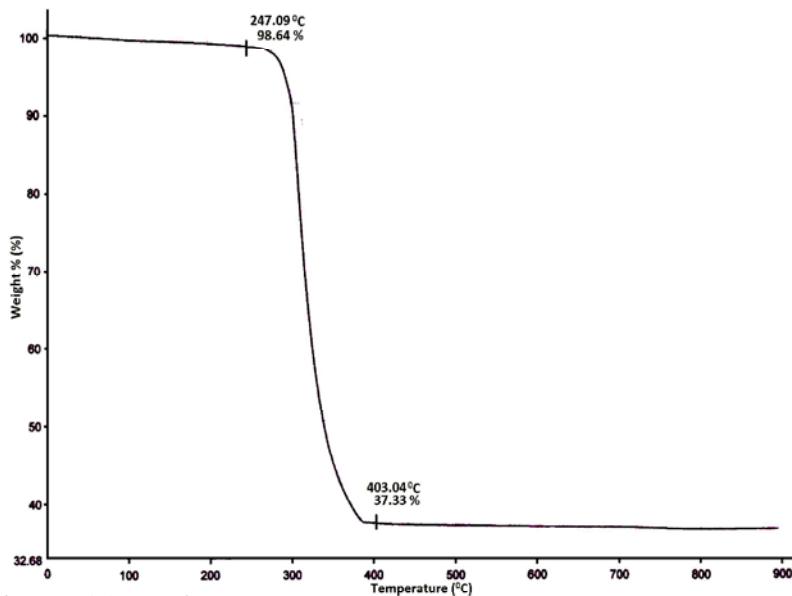


Fig. 5: TG curve of copper(II) complex.

thermal stability order Co<Ni<Cu obtained. The TGA curve Co(II) complex show three stages of decomposition. The first stage show the loss of chemically bound water molecules between 110 and 205°C, show the presence of water molecules in the coordination sphere. The second stage of decomposition in the range 205-350°C in due to loss of organic moiety while the third stage of decomposition occurs in the range 350-480°C, indicating the loss of oxyborate and leaves  $\text{CoCl}_2$  as residue. Similarly the TGA curve of Ni (II) complex show three

significant temperature transition of mass loss, take place according to mechanisms of involving dehydration and decomposition process of ligand and leave  $\text{NiCl}_2$  as residue.

The TGA curve of Cu (II) complex is interestingly different than other two complexes showing a stable plateau up to 175°C indicating that the complex is stable up to this temperature and confirms the absence of water molecules either in or out of the coordination sphere (Figure 5). Onset of decomposition (2% weight loss)

Table 5: TGA data of the borate ligand and its dinuclear complexes.

Compound	Temp.range (°C)	Reaction	Weight lost (%)			Residue (%)	
			Calculated	Found	Moiety lost	Calculated	Found
Ligand, KL	175-230	K(BC <sub>16</sub> H <sub>8</sub> O <sub>8</sub> ) → K(BC <sub>15</sub> H <sub>8</sub> O <sub>6</sub> ) + CO <sub>2</sub>	11.64	11.27	CO <sub>2</sub>	34.65	33.24
	230-350	K(BC <sub>15</sub> H <sub>8</sub> O <sub>6</sub> ) → K(BC <sub>7</sub> H <sub>4</sub> O <sub>2</sub> ) + C <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	44.08	43.29	C <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	(BC <sub>7</sub> H <sub>4</sub> O <sub>2</sub> )	
	350-540	K(BC <sub>7</sub> H <sub>4</sub> O <sub>2</sub> ) → BC <sub>7</sub> H <sub>4</sub> O <sub>2</sub> + K	10.31	11.98	K		
K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	110-205	K[Co <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ] → [Co <sub>2</sub> L(Cl) <sub>4</sub> ] + K + 4H <sub>2</sub> O	15.07	13.39	K + 4H <sub>2</sub> O	36.38	35.54
	205-350	[Co <sub>2</sub> L(Cl) <sub>4</sub> ] → [Co <sub>2</sub> (BC <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )Cl <sub>4</sub> ] + C <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	23.13	24.55	C <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	(2CoCl <sub>2</sub> )	
	350-480	[Co <sub>2</sub> (BC <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )Cl <sub>4</sub> ] → 2CoCl <sub>2</sub> + BC <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	24.54	25.89	BC <sub>8</sub> H <sub>4</sub> O <sub>4</sub>		
K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ]	130-257	K[Ni <sub>2</sub> L(Cl) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ] → K[Ni <sub>2</sub> L(Cl) <sub>4</sub> ] + 4H <sub>2</sub> O	10.14	11.02	4H <sub>2</sub> O	36.02	37.29
	257-450	K[Ni <sub>2</sub> L(Cl) <sub>4</sub> ] → K[Ni <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> )Cl <sub>4</sub> ] + BC <sub>10</sub> H <sub>2</sub> O <sub>8</sub>	37.05	38.84	BC <sub>10</sub> H <sub>2</sub> O <sub>8</sub>	(2NiCl <sub>2</sub> )	
	450-650	K[Ni <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> )Cl <sub>4</sub> ] → 2NiCl <sub>2</sub> + K + C <sub>6</sub> H <sub>6</sub>	16.58	15.99	K + C <sub>6</sub> H <sub>6</sub>		
K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ]	175-257	K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ] → K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ] + 1/2BO	3.20	2.10	1/2BO	38.89	37.33
	257-405	K[Cu <sub>2</sub> L(Cl) <sub>4</sub> ] → (2CuCl <sub>2</sub> ) + K + BC <sub>16</sub> H <sub>8</sub> O <sub>7</sub>	56.65	59.89	K + BC <sub>16</sub> H <sub>8</sub> O <sub>7</sub>	(2CuCl <sub>2</sub> )	

occurs just above 200°C and approximately two-third of mass is gone by 405°C, which corresponds to the loss of ligand moiety. Continued heating eventually leads to stable plateau with a residue of 37.33%. Thus, in the absence crystal data, the TG analysis could be another alternative technique use to support the proposed structure complexes via the formula mass of metal complexes as well as the percentage of metal content, provided the identity of the residue is beyond the doubt.

## CONCLUSION

The results of this study clearly indicate that ligand is coordinated to metal ions via >C=O group. The ligand was so designed that it can secure two metal ions in the close proximity. The magnetic and electronic spectral studies of solid metal complexes suggest a square-planar geometry for the Cu(II) complex and octahedral configurations for the other metal complexes, namely, Ni(II) and Co(II) ions. The magnetic susceptibility measurements of Cu (II), Ni (II) and Co (II) complexes reveal that these complexes exhibit antiferromagnetic coupling behavior due to presence of two metal ions in close proximity.

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