SPECTRAL, THERMAL AND ANTIMICROBIAL STUDIES OF A BORATE LIGAND AND ITS DINUCLEAR COMPLEXES

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Abstract

A new borate ligand potassium bis (succinyl) borate (KL) has been synthesized by reaction of potassium borohydride and succinic acid in methanol solution. It was converted into its Co(II), Ni(II) and Cu(II) dinuclear complexes by mixing and stirring with MeOH solution of metal chloride salts. The compounds have been characterized by elemental analysis, spectral studies (IR, NMR, UV-vis, ESI mass spectra and EPR), magnetic susceptibility and thermogravimetric analysis (TGA). Spectroscopic results supported a square planar geometry in the Cu(II) complex while octahedral geometry in case of the Co(II) and Ni(II) complexes. In the light of these results, it is suggested that ligand acts as monoanionic tetradentate and coordinate to each metal by oxygen atoms of borate and chloride ions. Magnetic susceptibility measurements of dinuclear complexes revealed that these exhibit antiferromagnetic coupling behavior due to the presence of two metal ions in close proximity. The nature of the metal complexes was confirmed by conductometric measurements; indicated that the complexes are 1:1 electrolytes. The antimicrobial activities of the ligand, as growth inhibiting agents, have been screened in vitro against several species of bacteria and plant pathogenic fungi. The antimicrobial data revealed that the metal complexes act more as bactericidal and fungicidal agents as compared to the ligand.

Keywords: Borate; Dinuclear complexes; Thermogravimetric analysis; Antimicrobial activity.

INTRODUCTION

Self-assembly of metal-organic complexes have been attracted due to their fascinating structures and applications as functional materials in catalysis, optics, magnetism and pharmaceutical agents, antibacterial and as corrosion inhibitors [1–3]. The final structures of these complexes can be influenced by multiple factors among which the most important are geometrical and electronic properties of metal ions and ligands [4, 5]. Such complexes containing transition metal ions play fundamental role in many catalytic reactions of metalloenzymes as well as in supporting structures of many proteins [6]. Metal complexes of carboxylic acid continuously provide interesting new types of coordination compounds because of their ability to adopt various coordination modes [7], typically monodentate, bridging bidentate or chelating bidentate. It has been reported that the biological activity of these acids is enhanced by binding with metal [8].

Organoborate compounds have been extensively exploited in inorganic, bioinorganic and coordination chemistry [9] more than 30 years. They display broad-spectrum activity against bacteria, fungi and insects when coupled with some toxic organic and organometallic compounds [10, 11]. Interactions of potassium borohydride with heterocyclic system such as pyrazole, imidazole and indol [12] have been shown to yield a variety of ligands which have exploited largely in the synthesis of transition metal complexes. The increasing robust nature and ease with which their steric and electronic

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properties can be modified via simple synthetic protocols, thereby allowing a fine-tuning of ligand properties [13]. This approach was adopted to take advantage of the intrinsic ability

All the chemicals used were of AnalaR grade and were purchased from Sigma–Aldrich, E-Merck and Fluka. Elemental analyses were performed on a Perkin-Elmer 2400 CHONS

Table 1. Analytical and physical data of the ligand and its dinuclear complexes. L = $BC_8H_8C_8$

Compounds	F.W. (g moL^{-1})	Λ_M ($\Omega^{-1}cm^2moL^{-1}$)	M.P. (°C)	Color	Yield (%)	Metal	C	H	O
Ligand, KL	282	-	245	White	70	-	34.10	2.78	45.28
$KBC_8H_8O_8$							(34.04)	(2.83)	(45.39)
$K[Co_2L(Cl)_4(H_2O)_4]$	613	104.52	>300	Pink	62	19.29	15.56	2.55	31.15
$KBC_8H_{16}O_{12}Co_2Cl_4$						(19.23)	(15.60)	(2.60)	(31.20)
$K[Ni_2L(Cl)_4(H_2O)_4]$	613	95.86	>300	Green	60	19.28	15.63	2.58	31.16
$KBC_8H_{16}O_{12}Ni_2Cl_4$						(19.14)	(15.60)	(2.60)	(31.20)
$K[Cu_2L(Cl)_4]$	551	87.56	>300	Blue	65	23.01	17.53	1.56	23.16
$KBC_8H_8O_8Cu_2Cl_4$						(23.06)	(17.40)	(1.45)	(23.19)

of borates ion to form boroesters with acids, aldehydes and phenols [14]. This ester formation with boron compounds provides a mean of production of interesting magnetic, catalytic and electron transfer properties boron compounds with transition metal ions [15, 16].

elemental analyzer. The metal contents were determined by EDTA titration after decomposition with mixture of HCl and $HClO_4$. The molar conductance measurement was carried out using a TACUSSEL, CD 810 conductivity meter at room temperature (25°C) in 10^{-3} molar solution using water as solvent. IR

Table 2. Magnetic moment and electronic spectral data of dinuclear complexes.

Compound	μ_{eff} (B M.)	Frequency (cm^{-1})	Assignments	(cm^{-1})	Δ_o (cm^{-1})	B β	Geometry
$K[Co_2L(Cl)_4(H_2O)_4]$	5.23	11,895	$^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$	13010	371.7	0.337	Octahedral
		19,602	$^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$				
		25,125	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$				
$K[Ni_2L(Cl)_4(H_2O)_4]$	4.12	8500	$^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$	7083	472.2	0.454	Octahedral
		15,384	$^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$				
		25,000	$^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$				
$K[Cu_2L(Cl)_4]$	2.64	14,285	$^2B_{1g(F)} \rightarrow {}^2A_{1g(F)}$				Square planar
		22,222					Charge Transfer

Keeping the above facts in mind of an unprecedented interest in the boron compounds and carboxylic acid, in this article, we report the synthesis of boroester ligand of potassium bis(succinyl)borate and its dinuclear complexes with the object of gaining information about their nature of coordination and related structure, magnetic thermal, spectral and antimicrobial properties.

MATERIALS AND METHODS

2. Experimental

spectra were recorded on KBr pellets using a Perkin-Elmer 1620 FT-IR spectrophotometer. NMR (^{1}H NMR and ^{13}C NMR) spectra were recorded using Brucker DPX300 MHz Spectrometer operating at room temperature using DMSO solvent. The chemical shifts (δ) are reported in part per million using tetramethylsilane (TMS) as internal standard. Electronic spectra were taken on a Spectronic 20D+ Spectrophotometer in water in the range of 200-1100 nm. The magnetic susceptibility measurement at room temperature was carried out by Gouy's method using $Hg[Co(NCS)_4]$ as the

Table 3. ESI-MS mass spectral analysis of the ligand and its dinuclear complexes.

Compound	m/z	Peak assignments	Relative abundance (%)
Ligand, KL	283	$[K (BC_8H_8O_8)]^+$	15
	351	$[K (BC_8H_8O_8)]^+ +2CH_3OH$	65
	252	$[KB(C_7O_7H_6]^+$	25
	233	$[C_8H_8O_8]^+$	27
	157	$[K(C_4H_6O_4)]^+$	35
$K[Co_2L (Cl)_4(H_2O)_4]$	615	$[M+2]^+$	46
	526	$[M+2 -(2CO_2]^+$	65
	333	$[M+2-(KB(C_8H_8O_8)]^+$	50
	252	$[M+2-(Co +4H_2O+(C_8H_8O_8)]^+$	43
	232	$[M-(CoCl_2+B_2(C_8H_8O_8)]^+$	85
$K[Ni_2 L (Cl)_4(H_2O)_4]$	614	$[M+1]+$	65
	485	$[M+1-(NiCl_2)]^+$	25
	307	$[M-(NiCl_2+B(C_5H_{10}O_6)]^+$	90
	293	$[M+1-(K_2+B(C_8H_8O_8)]^+$	80
	225	$[M-(NiCl_2+KB(C_6H_{10}O_8)]^+$	53
$K[Cu_2L(Cl)_4]$	553	$[M+2]^+$	65
	453	$[M+2-(CuCl)]^+$	90
	397	$[M+2-(B3CO_2CH_2]^+$	75
	316	$[M-(CuCl_2B(C_2O_4)]^+$	70
	261	$[M-CuCl_2BC_4H_4O_4]^+$	65

reference. Diamagnetic susceptibility corrections for ligand susceptibility were made using Pascal's constants [17] and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms. EPR measurement were taken on Varian E-4X band with following settings: TCNE as the g-marker (g

solvent. The sample was introduced into the ESI source through a syringe pump at the rate of 5 μL min^{-1}. The ESI capillary was set at 3.5 kV and voltage 40 V. Thermogravimetric analysis was performed in a TA Instruments model SDT Q-600 in the temperature range from 25 ^{o}C to 800 ^{o}C at a heating rate is 20 ^{o}C min^{-1} in helium atmosphere with a flow rate of 100 mL min^{-1}. Approximately 6-10 mg of sample was used for

Table 4. TGA data of the borate ligand and its dinuclear complexes.

Compound	Temperature range (^{0}C)	Weight lost (%)	Moiety lost	Residue (%)
Ligand, KL	150-300	84.93	$C_4H_4O_3$, BO_2	15.35 (B_2O_3)
$K[Co_2L (Cl)_4(H_2O)_4]$	25-300	48.62	$4H_2O$, $4Cl_2$	6.25 (2CoO)
	300-700	45.13	BC_2O_4, B_2O_3	
$K[Ni_2L(Cl)_4(H_2O)_4]$	25-225	8.52	$4H_2O$, $3Cl_2$	0.42 (2NiO, CO)
	225-400	61.08	$BC_8H_8O_8$	
$K[Cu_2L(Cl)_4]$	205-500	75.36	$BC_8H_8O_8, CO_2$	11.29 (2CuO)

= 2.00277); modulation amplitude, 2G; modulation frequency, 100 kHz; time constant 163.84 ms; scan time, 83.886s; receiver gain, 1.6 × 10^3 unless otherwise noted. Positive and negative mode ESI mass spectra were recorded on a MICRO MASS QUATTRO (II), triplet quadruple mass spectrometer using CH_3OH as

each sample preparation.

2.2. Synthesis of potassium bis(succinyl)borate, KL

Fine powder of succinic acid (5.90 g, 50 mmol) and potassium borohydride (1.08 g, 20 mmol) were dissolved in 20 mL methanol in a

Table 5. Antimicrobial activity data of the ligand and its dinuclear complexes.

Compound	*S.typhi*	*S.subtillis*	*S.aureus*	*C.albicans-*10261	*C.tropicalis-*750	*C.kruesi-*6258
Ligand, KL	08	06	07	08	07	10
K[Co$_2$S(Cl)$_4$(H$_2$O)$_4$]	21	18	14	18	23	18
K[Ni$_2$S(Cl)$_4$(H$_2$O)$_4$]	27	18	20	22	21	29
K[Cu$_2$S (Cl)$_4$]	20	18	25	25	20	17
Kanamycin	18	27	30	--	--	--
Nystatin	--	--	--	30	29	33

Inhibition value 20-35 mm-significant active, 10-20 mm-moderate active, <10 mm-less active

three-necked round-bottom flask equipped with a water-cooled condenser, thermometer and magnetic stirrer. 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 mixture was heated upto 60 ^{o}C, where upon the evaluation of hydrogen gas commences. It was heated until 2054.56 mL (80 mmol) of hydrogen gas had evolved. Then it was allowed to cool at room temperature and the precipitate was filtered, washed several times with hexane, THF and diethyl ether. The solid residue was dried in vacuum desiccator to

warm methanolic solution of potassium bis(succinyl)borate (0.282 g, 1 mmol). The resulting mixture was heated for 4 hours at the 45 ^{o}C temperature and the solution was concentrated to 20 mL. It was then allowed to stand overnight in a refrigerator. Blue colored complex separate out, which was isolated by filtration under vacuum. The isolated metal complex was washed several times with hot methanol and diethyl ether and dried in vacuo over fused CaCl$_2$. The compound was recovered in solid state and was re-crystallized from methanol. Yield (%): 65; m.p. >300 °C; ESI-MS:
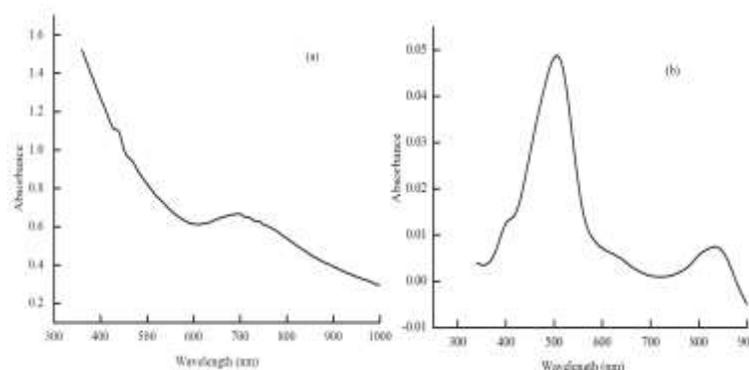
Figure 1. Electronic spectra of (a) Cu(II) and (b) Co(II) complexes.

constant weight under reduced pressure to leave the desired compound as a white powder. It was re-crystallized from methanol. Yield (%): 70; m.p. 245 °C; ESI-MS: m/z = 283 [M+1, 15%] $^+$; Elemental analysis (%) found (calc. for KBC$_8$H$_8$O$_8$): C 34.10 (34.04), H 2.78 (2.83), O 45.28 (45.39); IR (cm^{-1}): 1705 ν(C=O), 1320 ν(B-O), 2962 ν(CH$_2$).

2.3. Synthesis of Cu(II) Complex

Methanolic solution (15 mL) of copper chloride (1.70 g, 2 mmol) was added to 15 mL of

m/z = 553 [M+2, 65%] $^+$; Elemental analysis (%) found (calc. for KBC$_8$H$_8$O$_8$Cu$_2$Cl$_4$): C 17.53 (17.40), H 1.56 (1.45), O 23.16 (23.19); IR (cm^{-1}): 1648 ν(C=O),1330 ν(B-O), 2982 ν(CH$_2$), 578 ν(M-O), 378 ν(M-Cl).

2.4. Synthesis of Co(II) Complex

This compound was synthesized using the above same procedure with cobalt chloride (2.37 g, 2 mmol) and warm methanolic solution of potassium bis(succinyl)borate (0.282 g, 1 mmol). A pink product in solid state was

obtained which was re-crystallized from methanol. Yield (%): 62; m.p. >300 °C; ESI-MS: m/z = 615 [M+2, 46%] $^+$; Elemental analysis (%) found (calc. for $KBC_8H_{16}O_{12}Co_2Cl_4$): C 15.56 (15.60), H 2.55 (2.60), O 31.15 (31.20); IR (cm^{-1}): 1651 v(C=O), 1311v(B-O), 2961v(CH$_2$), 551 v(M-O), 343 v(M-Cl).
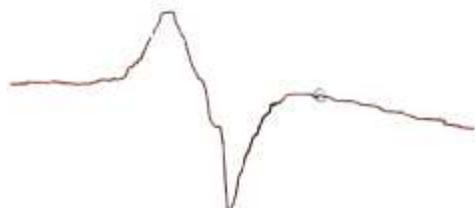
This compound was also synthesized using the above same procedure with NiCl$_2$.6H$_2$O instead of CoCl$_2$.2H$_2$O. A green product in solid state was obtained which was re-crystallized from methanol. Yield(%): 60; m.p. >300 °C; ESI-MS: m/z = 614 [M+1, 65%]$^+$; Elemental analysis

Figure 2. EPR spectrum of Cu(II) complex.

1660 v(C=O), 1310 v(B-O), 2932 v(CH$_2$), 582 v(M-O), 354 v(M-Cl).

2.6. Antimicrobial screening

Disc diffusion method [18] was employed to study the antimicrobial effect against the pathogens. YEPD agar (yeast extract 1%, peptone 2%, D-glucose 2% and agar 2.5%) and Luria agar were used as a nutrient standard medium that allows growth of test microbes. The ligand and its metal complexes were prepared from the given stock solutions in deionized water to examine the variable antimicrobial effects. The sterilized (watt man number-3) filter paper discs of 6 mm diameter were dipped in the solution of ligand and its metal complexes at a single concentration (2000 μg/mL) and after drying placed on the surface of agar plates. For control studies sterilized disc of same diameter were dipped in water and then placed on the surface of same agar plate. The plates were then incubated at 37 °C for 24 hours for bacteria and 72 hours for fungi. After suitable incubation the activities were
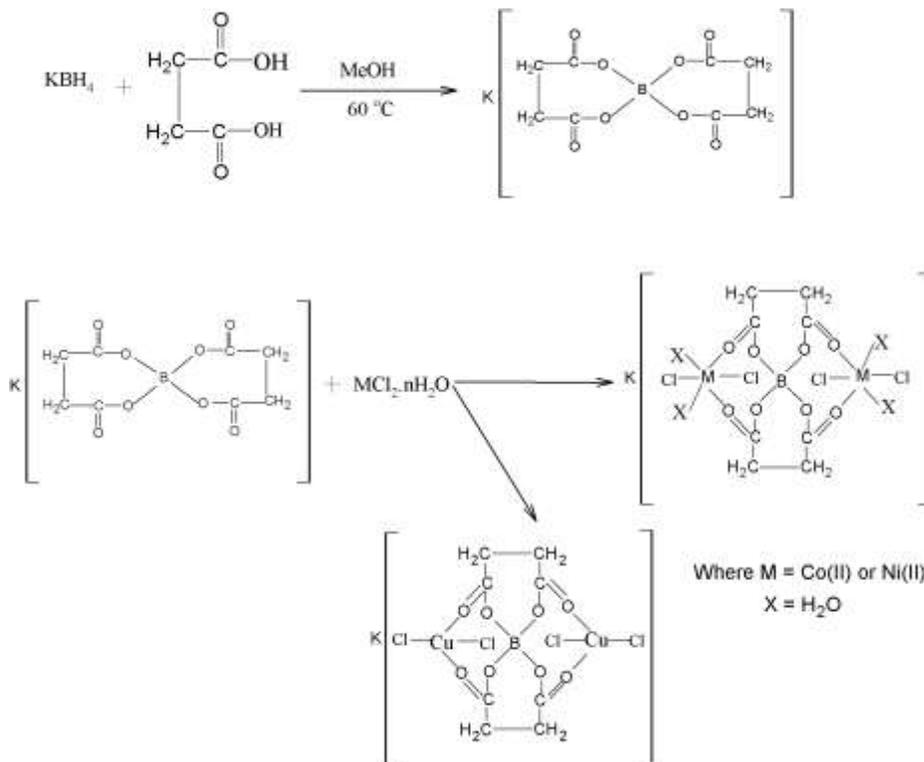
Scheme1. Synthesis of the ligand and its dinuclear metal complexes

(%) found (calc. for $KBC_8H_{16}O_{12}Ni_2Cl_4$): C 15.63 (15.60), H 2.58 (2.60), O 31.16 (31.20); IR (cm^{-1}):

determined by measuring the width of the inhibition zone (mm) around the disc.

Antibacterial activities of the compounds were compared to that the standard Kanamycin,

The ligand and its dinuclear complexes were formed according to the following equations:
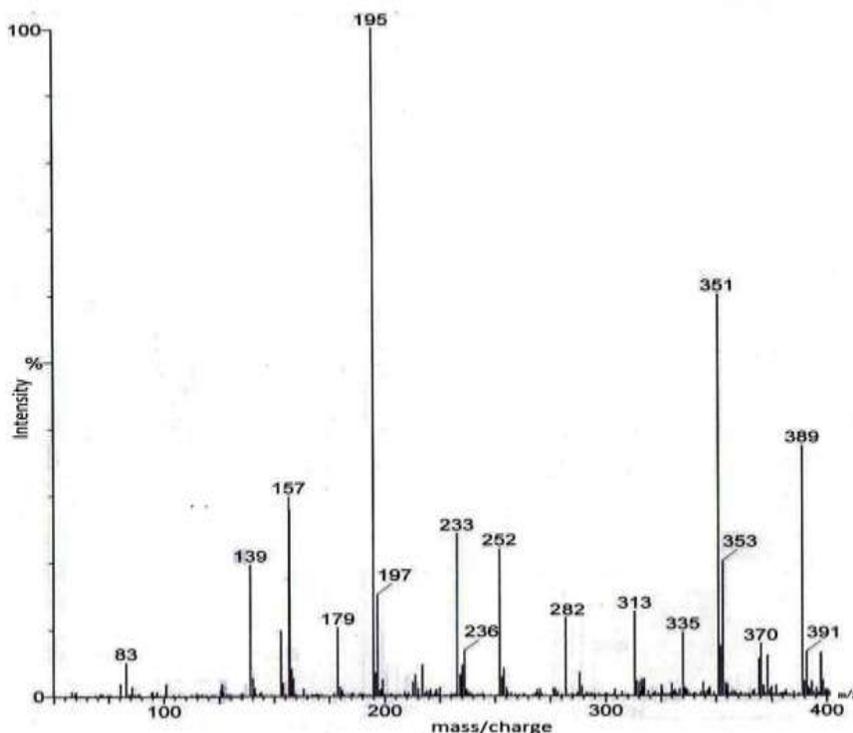

Figure 3.   ESI-MS spectrum of Ligand.

whereas antifungal activities were compared with Nystatin.

RESEULT AND DISCUSSION

3. Results and discussion

The analytical and physical data of the ligand and metal complexes are listed in Table 1.The ligand is expected to act as monoanionic tetradentate ligand towards the divalent metal ion, denoting the formation of bimetallic complexes of ligand. The isolated complexes are sparingly soluble in most common organic solvent like methanol and ethanol but soluble in acetonitrile, dmf, water and dmso with meting point above 300 °C. The molar conductance measurements of complexes in water (10^{-3}M) at room temperature show a 1:1 electrolytic nature of all metal complexes, indicating that the chloride anion is situated within the metal coordination sphere. Molecules of water in Co(II) and Ni(II) complexes are supported by microanalysis and spectral data. All the metal complexes show high thermal stability and good antimicrobial activity compared to free ligand.

3.1. Infra red spectra

A remarkable difference between the IR spectra of the succinic acid and the corresponding ligand is the stretching vibration band of hydroxyl group at 2645 cm^{-1} disappears from the spectrum of the ligand. In addition, the absorption frequency of carbonyl group significant decreases in the complexes. The absorption band observed at 1342 cm^{-1} may assigned to v_{sym} (B–O) bond, confirming the formation of ligand [19]. After comp-lexation the B–O stretching vibrations appear at 1335–1325 cm^{-1} negligible shift, discounting coordination through esteric oxygen (B–O). The spectrum of ligand showed a strong band 1705 cm^{-1} which is stretching vibration of carbonyl group [20], this band occurs in all the complexes at lower frequency (1660–1648 cm^{-1}) as compared to the ligand and clearly indicate that the ligand is coordinated to metal(II) ion through this group. The coordination of oxygen to metal ions would be expected to reduce the electron density on the carbonyl oxygen and thus cause a shift in C=O band. Medium to weak
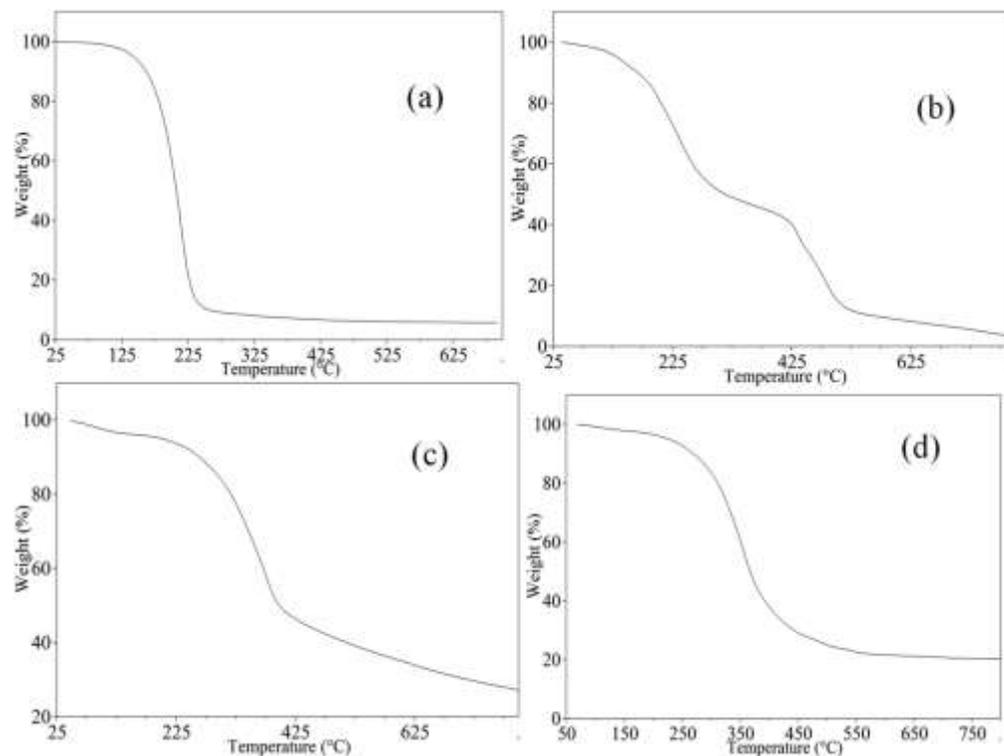
Figure 4. TGA curves of (a) KL, (b) Co(II), (c) Ni(II) and (d) Cu(II) complexes.

absorption bands at 1320-1295 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. Presence of stretching vibration at 582–551 cm^{-1} in all the metal complexes shows the linkage between M–O bonds [21]. Another signal that seen in the region 378–343 cm^{-1} shows the presence of M–Cl bond in all the metal complexes [22].

The IR spectra of Co(II) and Ni(II) complexes exhibit a broad stretching vibration in the 3470–3440 cm^{-1} region can be attributed to coordinate the water molecules [23]. The presence of coordinated water molecules in the Co(II) and Ni(II) complexes was further confirmed by appearance of bands in the region 1600–1540 cm^{-1} for deformation and in 870–840 cm^{-1} for rocking modes of coordinated water [24, 25]. Thus the IR spectral result provides strong evidences for the complexation of ligand with metal(II) ions in tetradentate mode.

3.2. NMR spectral studies

^{1}H NMR spectrum of the symmetrical ligand show the absence of signal at 9.5 ppm indicates

removal of acidic protons of succinic acid [26]. The absence of another characteristic B–H broad signal in the range 5.1–3.4 ppm suggests the deprotanation of succinic acid which let the formation of ligand [27]. In addition, resonance signals corresponding to methylene protons of ligand were found in the region of 2.70 –2.59 ppm as triplet [28].

The ^{13}C NMR spectral data of the ligand confirms the results of the ^{1}H NMR spectra, contains all the desired peaks of carbon skeleton of the ligand. A characteristic signal associated with carbonyl carbon of carboxylic group appeared in the range of 177–170 ppm which showed a significant shift corresponding to the succinic acid. The other methylene carbon signal appeared in the range of 30–20 ppm. The conclusions drawn from the IR and ^{1}HNMR spectra are consistent with ^{13}C spectral data regarding the authenticity of the ligand and confirmed the tetradentate nature of borate ligand

3. 3. Electronic spectra

In order to obtain further structural information, the solution spectra of complexes

were measured and the spectral data are given in Table 2, which include the absorption regions, band assignments, ligand field parameters and the proposed geometry of the complexes. The Nephelauxetic parameter β was readily obtained by using the relation:

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

The electronic spectrum of Cu(II) complex exhibit two prominent absorption bands (Figure 1a). A low intensity broad around 14285 cm^{-1} is assignable to $^2B_{1g (F)} \rightarrow {}^2A_{1g (F)}$, transition. Another high intensity band at 22222 cm^{-1} due to symmetry forbidden ligand →metal charge transfer. The position of bands indicates that complex have square planer geometry [29].

The electronic spectrum of Co(II) complex

octahedral geometry [31]. On the basis of these assignments the ligand field parameters calculated for Ni(II) complex are Δ_o = 7083 cm^{-1}; B=472.2; β= 0.454. Thus the reduction of the Racah parameter from the free ion values and values of β indicate covalent character of the metal ligand 'σ' bond. The above discussion very strongly indicates octahedral around the central metal ion in the Co(II) and Ni(II) complexes, requiring occupation of two coordination by water molecules.

3.4. Magnetic susceptibility measurement

The observed magnetic moment of dinuclear complexes at room temperature is considerably less than the spin only values (Table 2). This suggests the operation of antiferromagnetic spin-exchange interaction in these complexes [32], brought about by the bridging of paramagnetic centers through the oxygen atoms. This oxygen bridging often leads to
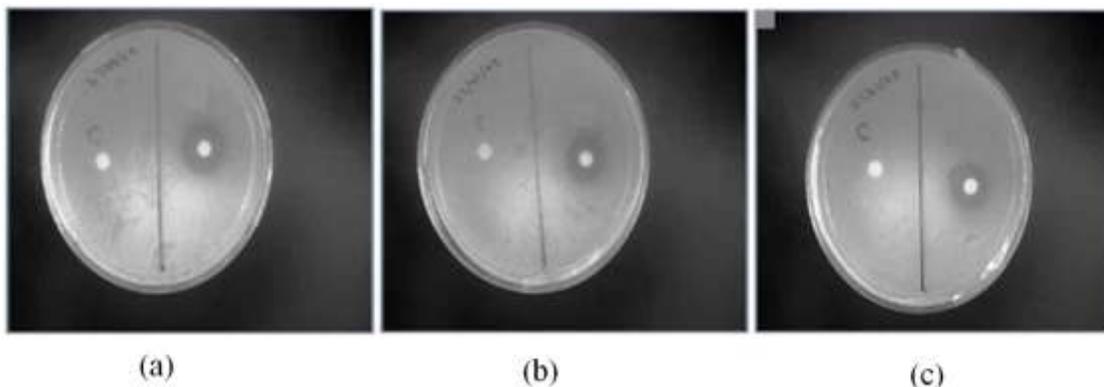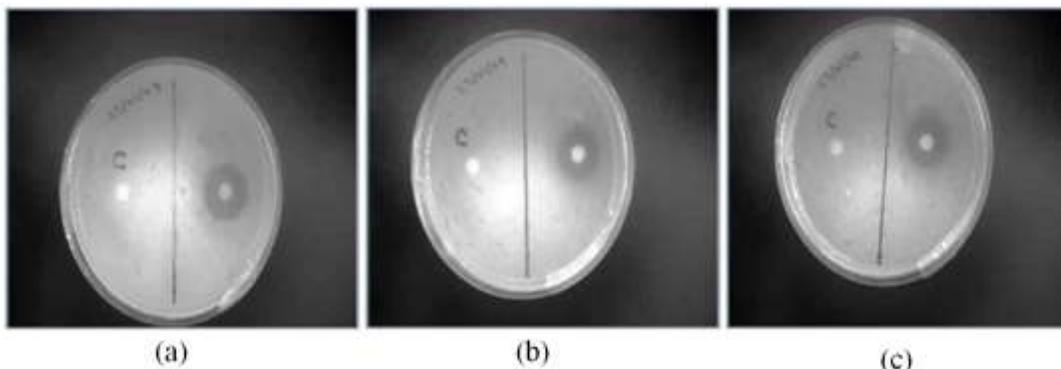
Figure 5.Antibacterial activity of (a) Ni(II) (b) Cu(II) and (c) Co(II) complexes against various bacterial species [(a) *S.typhi,* (b) *S.aureus and* (c) *S.typhi*; C-Control]

exhibit absorption in the region around 11895, 19602 and 25125. These bands may be assigned to the spin allowed transition: $^4T_{1g (F)} \rightarrow {}^4T_{2g (F) (v1)}$, $^4T_{1g (F)} \rightarrow {}^4A_{2g (F) (v2)}$ and $^4T_{1g (F)} \rightarrow {}^4T_{1g (P) (v3)}$, respectively. The position of bands strongly favor the Co(II) complex have six coordinated octahedral geometry [30] (Figure 1 b). On the basis of these assignments the ligand field parameters calculated for Co(II) complex are Δ_o = 13010 cm^{-1}; B=371.7; β= 0.337. Similarly Ni(II) complex exhibit absorption bands in the region around 8500, 15384 and 25000 cm^{-1}. These bands may be assigned to the spin allowed transition: $^3A_{2g (F)} \rightarrow {}^3T_{2g (F) (v1)}$, $^3A_{2g (F)} \rightarrow {}^3T_{1g (F) (v2)}$ and $^3A_{2g (F)} \rightarrow {}^3T_{1g (P) (v3)}$, respectively. The position of bands indicates that the complex have

change in reduction of paramagnetic partially or completely of the metal atoms bridge. Hence, the subnormal magnetic moments observed for the metal complexes. The observed magnetic moment value of Cu(II) was found to be 2.64 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 single ligand molecule, each through (OC)$_2$ coordination sites and chloride ions [33, 34]. 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 5.23 and 4.12

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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 [35] 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

unpaired electron is in the $d_{x^2-y^2}$ orbital of Cu(II) ion with the $3d^9$ configuration, that is, $(e_g)^4$ $(a_1g)^2$ $(b_2g)^2$ $(b_1g)^1$. The $g_{\parallel}/A_{\parallel}$ value of the complex is 116 cm suggesting the square planar geometry of the Cu(II) complex and system is axially symmetric [36]. In the present case the value of 'G' was found to be 2.31. According to Hathaway [38], if G value is greater than 4, the exchange interaction is negligible whereas G

Figure 6. Antifungal activity of (a) Ni(II), (b) Cu(II) and (c) Co(II) complexes against various fungal strains [(a) *C.kruesi*-6258, (b) *C.albicans*-10261 and (c) *C.tropicalis*-750 C-Control].

coordination number four or six.

3.5. EPR spectra

In order to obtain more information about the magnetic environment of metal complexes, polycrystalline samples and in the solution of DMSO were used to record X-band EPR spectra at the room temperature. No X-band EPR signal was observed for all polycrystalline samples at room temperature indicating the presence of strong antiferromagnetic interaction in solid state supports the dinuclear nature of complexes. The solution EPR spectrum of Cu(II) complex at room temperature was found to be anisotropic with two types of g values, $g_{\parallel}$ and $g\perp$, these have been used to distinguish [36] unbiguously between $d_{x^2-y^2}$ (or d_{xy}) ground state on one hand and ground state on the other hand. For example, in ground state EPR spectrum indicates $g_{\parallel} > g\perp > 2.02$ in most cases while a dz^2 ground term usually gives a spectrum with $g\perp > g_{\parallel} \sim 2.00$. In present case the spectrum of Cu(II) complex appeared to slightly broadened with $g_{\parallel} = 2.1841$ and $g\perp = 2.0795$ (Figure 2). The $g_{\parallel}$ value less than 2.3 and α^2 value of the 0.772 suggest the covalent character of the metal ligand bond [37]. The trend $g_{\parallel} > g\perp$ for the complex shows that the

value less than 4 indicates considerable exchange interaction between metal ions in the complex. In present case G value indicate considerable exchange interaction between the Cu(II) ions in the complex which further support the dinuclear nature of the complex.

3.6. Electron- spray ionization mass spectra (ESI-MS)

Simple fragmentations of the ligand and its metal complexes dissolves in methanol were detected at 40 V in positive and negative electron spray ionization mass spectra. Positive ion mass spectra gave better data than negative ion mass spectra. The ESI-MS spectra of the compounds have differences of 1, 3, or 4 amu in their calculated and observed mass fragmentations due to the isotopic nature of chlorine (^{35}Cl, ^{37}Cl), boron (^{10}B, ^{11}B) and carbon (^{12}C, ^{13}C). In some cases, the molecular ion peak was also associated with solvent, water molecules and some adduct ions from the mobile phase solution [39]. The positive ion ESI spectrum of the metal free ligand shows a molecular ion peak at desired position m/z = 283, corresponding to the moiety [K (BC$_8$H$_8$O$_8$)]$^+$ (formula atomic mass m/z 282), which is equivalent to its molecular mass. Another major

fragment of the ligand associated with two molecules of methanol from mobile phase solution appeared at m/z 351 [K $(BC_8H_8O_8)]^+$ $+2CH_3OH$]. The fragmentation peaks, at m/z 252, 233 and 157 are ascribed to the cleavage of [KB $(C_7O_7H_6]^+$, $[C_8H_8O_8]^+$ and [K $(C_4H_6O_4)]^+$ respectively, are well observed in the mass spectrum (Figure 3). Their intensity gives an idea of stability of the fragments.

Positive ion ESI-MS spectra of complexes confirm the presence of dipositive dinuclear core structure. Positive ion spectra of the Cu(II) and Co(II) complexes show $[M+2]^+$ peaks at m/z 553 and 615 (formula atomic mass m/z 551, 613) respectively, which are consistent with the molecular ion fragments and it supports the proposed structure of the complexes. Ni(II) complex show $[M+1]^+$ peak at m/z 614. The most relevant fragmentations of ligand and its metal complexes with their assignments are shown in Table 3.

3.7. Thermogravimetric analysis

To make sure about the proposed formula and presence of water molecules in compounds thermal analysis were carried out in helium atmosphere. Thermal data showed that the crystal water molecules are volatilized within the 75–125 ^{o}C temperature range, while coordinated water molecules are removed in the 120–200 ^{o}C temperature range. The TGA curves of ligand and its metal complexes are presented in Figure 4.The characteristic data and stages of pyrolysis regarding the thermal behavior of these compounds are listed in Table 4. It shows that they are thermally stable to a varying temperature and the obtained data strongly support the structure proposed for the complexes.

The TG curve of the ligand show a stable plateau up to 150 ^{0}C indicating that the ligand is stable up to this temperature and show the absence of water molecules (Figure 4 a). The ligand shows one decomposition stage at temperature between 150-300 ^{o}C which is accompanied by the weight loss of 84.93 % corresponding to weight loss $C_4H_4O_3$ and BO_2 moiety, leaving more than 15 % residue.

The thermal stability and nature of degradation of the complexes are affected by the structure, electronegativity and atomic radius of the central metal atom and basic character of ligand. The TGA curves showed that the thermal decomposition of the metal complexes proceeds approximately with one or two main degradation steps. The proposed decomposition of the complexes occurred by fragmentation and thermal degradation of organic part in metal complexes, resulting in the corresponding metal oxides as residue.TGA curve of Co(II) complex shows two distinct stage of decomposition at temperatures between 25-300 and 300-700 ^{o}C respectively, which is accompanied by a weight loss of 48.62 and 45.13 % (Figure4 b). The first weight loss due to coordinated water and chlorine molecules indicating the complex is hygroscopic in nature. The second decomposition corresponds to loss of organic borate moieties of ligand and leaves CoO as residue. Similarly thermal decomposition of the Ni(II) complex (Figure 4 c) under study take place according to mechanisms of involving dehydration and decomposition process of ligand leaving NiO, CO as residue. The two weight loss is associated with weight losses of 8.52, 61.08 % respectively which is occurred at temperature between 25-225 and 225-700 ^{o}C.

The TGA of Cu(II) complex is interestingly different from that of the other two complexes showing no sign of coordinated water molecule in the complex, which confirms that complex, is anhydrous. The complex is stable up to 210 ^{o}C and decomposition begins beyond this temperature (Figure 4 d). The complex shows a major step of weight loss between 205-500 ^{o}C corresponds to the loss of total organic moiety fallowed by CO_2 . No weight loss was observed beyond 550 ^{o}C, possibly due to the formation of the stable metal oxide. It fallows from the results that the thermal decomposition pattern confirms the proposed formulation of the ligand and its dinuclear complexes.

4. Antimicrobial activity

The results of antimicrobial activity (*in vitro*) suggest that ligand is less active against the tested pathogens but its dinuclear complexes show significantly higher antimicrobial activity. For antibacterial activity the highest zone of inhibition *i.e.* 27, 25 and 21 mm were measured in *S.typhi, S. aureus* and again in *S.typhi* when treated with Ni(II), Cu(II) and Co(II) complexes respectively (Table 5, Figure5). For antifungal

activity the highest inhibitory zone *i.e.* 29, 25 and 23 mm were measured in *C. kruesi* ATCC-6258*, C.albicans* ATCC-10261 and *C.tropicalis* ATCC-750 when treated with Ni(II), Co(II) and Cu(II) complexes respectively. (Table5, Figure6.). Here in case of fungi the highest zone of inhibition was shown by Ni(II) complex when treated against *C. kruesi* ATCC-6258, which proves that Ni(II) complex is having the highest antimicrobial activity both in case of tested bacteria (S.*typhi*), as well as in case of tested fungi (*C.kruesi*). The result showed that, in case of control disc no zone of inhibition was observed so as for as our study is concerned distilled water, as a solvent is having no effect on the tested organisms. The most important thing that was noticed in this study was that the complexes were much effective against fungus than in case of bacteria. Such increased activity of the metal complexes may be due to chelation of the metal ion in the complex [40], which enhances the lipophyllic character of the central atom and favored its permeation through the lipid layer of cell membrane. Other factors *viz*. stability constant, molar conductivity, solubility and magnetic moment are also responsible for increasing the antimicrobial activity of the complexes [41].

5. CONCLUSIONS

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, EPR and electronic spectral studies of dinuclear 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 promising results antibacterial activity of the ligand and its metal complexes showed that the metal complexes, specially the Ni(II) have higher antimicrobial activity as compared to that of the metal free ligand. As for as our results are concerned, these metal complexes can thus be explored in future as an option for decreasing pathogenic potential of infecting bacterial and fungal species.

ACKNOWLEDGMENT

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