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Thermal and Spectroscopic Studies of Transition Metal Complexes with Dihydro*bis*(2-Mercaptobenzothiazolyl)borate

Naushad Ahmad[1,*], Manawwer Alam[1], Parveen Kumar[2], Athar Adil Hashmi[2] and Rizwan Wahab[3]

[1]Department of Chemistry, College of Science King Saud University, Riyadh 11451, Kingdom of Saudi Arabia
[2]Department of Chemistry, Jamia Millia Islamia, New Delhi-110 025, India
[3]Department of Zoology, College of Science, King Saud University, Riyadh 11451, Kingdom of Saudi Arabia

*Corresponding author: E-mail: naushaddrnaima@gmail.com

The complexing behaviour of dihydro*bis*(2-mercaptobenzothiazolyl)borate towards the transition metal ions namely, Co(II), Ni(II) and Cu(II) have been examined by elemental analysis, magnetic susceptibility, thermal, conductivity and spectral studies *viz*. FT-IR, NMR, UV-VIS and ESI-MS. Spectroscopic results support a square planar geometry in Cu(II) complex, while an octahedral geometry is suggested in case of Co(II) and Ni(II) complexes. Thermal behaviour and kinetics of all compounds are investigated by thermogravimetric analysis. The TGA profile of borate anion and Cu(II) complex shows a single stage unlike that of two stage decomposition plot of the Co(II) and Ni(II) complexes. The evaluation of kinetic parameters (E, ln A, ΔH, ΔS and ΔG) of all thermal decomposition stages have been evaluated by graphical method using the equation of Coats-Redfern equation. The activation energy of Co(II), Ni(II) and Cu(II) complexes expected to increase in relation with decreasing in their radius. The molar conductance of these complexes shows a non-electrolyte behaviour.

Key Words: Dihydro*bis*(2-mercaptobenzothiazolyl)borate, Metal complexes, Thermal analysis, Energy of activation.

## INTRODUCTION

Nitrogen containing borate, such as triazolyl[1], pyrazolyl[2] indazolylm[3], poly(indazolyl) and poly(2-mercaptothiazolyl) borate[4] occupy a unique place in coordination chemistry because having outstanding biological and thermal properties towards with transition metals. This family of N-donors is not able only to control the steric and electronic environment about a metal center by modification of the pyrazolyl substituents but also to give multimetallic transition metal complexes maintaining the metal centers in close proximity. This is a very interesting feature because of the potential role of this kind of derivative in multimetal-centered catalysis in both biological and industrial thermal reactions. Tripodal borate S, N ligands such as hydrotris(thioxoimidazolyl)borate and hydrotris(2-mercaptothiazolyl)borate[5] are softer than the pyrazolyl analogues and as such are more useful to be used as supporting ligands with transition metals. Although these ligands are closely related to the *bis*(pyrazolyl)borate ligands, they exhibit a number of characteristics that set them apart. The combination of boron, sulfur and nitrogen containing ligands led to work in coordination chemistry of transition metal complexes.

In present work, we reports the synthesis, spectral and thermogravimetric (TGA) studies of dihydro*bis*(2-mercapto-benzothiazolyl)borate and its transition metal complexes (**Scheme-I**). The thermal degradation kinetic parameters such as energy of activation (E) and the pre-exponential factor (ln A) by employing Coats-Redfern method and thermodynamic parameters like entropy (ΔS), enthalpy (ΔH) and activation energy (ΔG) for each step of degradation have been evaluated.

EXPERIMENTAL

All chemicals were used of Analytical grade and purchased from Sigma Aldrich. Elemental analyses were performed on a Perkin-Elmer 2400 Series II, CHNS/O Analyzer. The metal contents were determined by EDTA titration after decomposition with mixture of HCl and $HClO_4$. The molar conductances of the complexes were measured using a Consort type C-533 conductivity instrument at room temperature in 10^{-3} M DMSO solvent. FT-IR spectra were recorded on Perkin-Elmer system 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX200 spectrometer operating using tetramethylsilane(TMS) as an internal standard. ^{11}B NMR spectrum was recorded on a Bruker Avance DPX400 spectrometer using BF_3. Et_2O as an internal reference. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 UV-Vis spectrometer using water as solvent. The magnetic susceptibility measurement at room temperature was carried

Where M= Co(II) or Ni(II)
X = H$_2$O
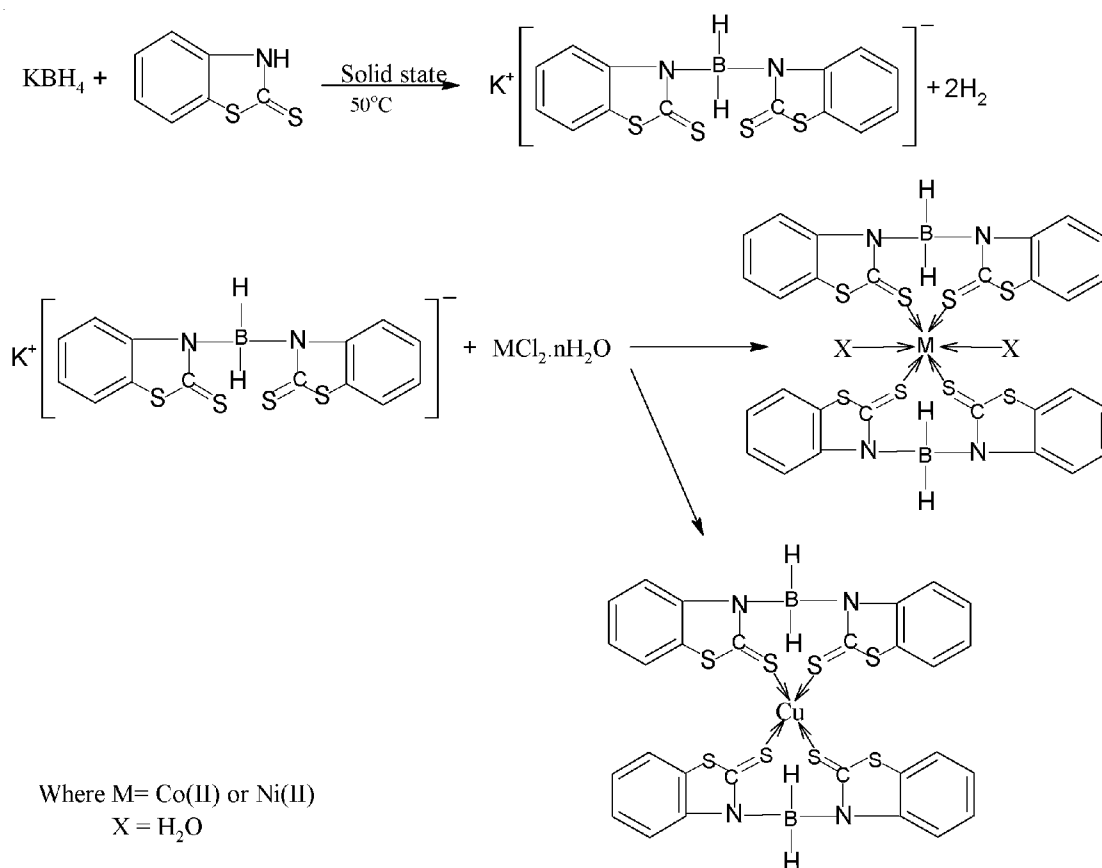
Scheme-I

out by Gouy's method using mercury(II) tetraisothiocyanato-cabaltate(II), as reference. Diamagnetic susceptibility corrections for ligand susceptibility were made using Pascal's constants 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. The thermal analysis was performed using TA instruments, SDT Q-600. All TGA experiments were conducted in a helium environment with a purge flow rate of 100 mL min^{-1}. For each experiment, 8 to 10 mg of the sample was loaded into alumina crucibles (Al$_2$O$_3$) in the heating zone of the TGA. An empty pan was used as reference and samples were runs from room temperature to 800 °C at heating rates 20 °C min^{-1}. Positive and negative mode ESI mass spectra were recorded on a MICRO MASS QUATTRO (II), triplet quadruple mass spectrometer using CH$_3$OH as 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.

Synthesis of potassium dihydro*bis*(2-mercaptobenzothiazolyl)borate ligand (KL): Fine powder of 2-mercaptobenzothiazole (10.03 g, 60 mmol) and potassium borohydride (1.08 g, 20 mmol) were placed in a 250 mL round bottom flask connected with a gas collecting device through a condenser containing magnetic stirring bar. This assembly placed in an oil bath and mixture was heated at 50 °C until 530.05 mL (20 mmol) hydrogen gas had been evolved. It was allowed to cool at room temperature and 20 mL methanol was added and mixture was stirred for 0.5 h. Ligand separated and washed several times with hexane, THF and diethyl ether. The solid residue was dried in vacuum desiccator to constant weight

under reduced pressure to leave the desired compound as a yellowish power. It was re-crystallized from methanol. Yield (%): 70.39; m.p. 275 °C; MS (ESI+): 384 [M]$^+$, 318 [KBC$_{14}$H$_8$N$_2$S$_4$], 288 [BC$_8$H$_8$ON$_2$S$_4$]; Elemental analysis (%) found (calcd. for KBC$_{14}$H$_{10}$N$_2$S$_4$): C 43.68 (43.74), H 2.59 (2.61), N 7.26 (7.29), S 33.34 (33.37); IR (KBr, ν_{max}, cm^{-1}): 1425 (B-N), 2327 (B-H), 990 (C=S).

Synthesis of metal(II) complexes: A methanolic solution (15 mL) of corresponding metal salt (1 mmol) was added to methanolic solution (15 mL) of ligand (0.769 g, 2 mmol). The resulting mixture was heated under reflux with stirring for 4-5 h. On cooling coloured complex precipitated out, which was filtered washed with several times with cold methanol and diethyl ether and dried *in vacuo* over anhydrous CaCl$_2$. The compound was recovered in solid state and was re-crystallized from methanol. Yields, elemental analysis results and characteristic FT-IR bands are given in Tables 1 and 2.

RESULTS AND DISCUSSION

Ligand is hygroscopic yellow solids, soluble in polar organic solvents and water and relatively resistant towards aerobic oxidation and hydrolysis. The ligand is expected to act as monoanionic bidentate ligand towards the divalent metal ions. All the isolated complexes were insoluble in most common organic solvent but soluble in polar solvents with meting point above 300 °C. The results of the elemental analyses (Table-1) and spectral studies are consistent with proposed composition of the ligand and its corresponding metal complexes. The molar conductance measurements at room temperature show a non-electrolytic nature of metal complexes[6]. Molecules of water

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE BORATE LIGAND AND ITS Co(II), Ni(II) AND Cu(II) METAL COMPLEXES

Compounds	f.w.	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Yield (%)	Colour	Elemental analysis[a]				
					C	H	N	S	M
Ligand, KLKBC$_{14}$H$_{10}$N$_2$S$_4$	384.5	–	79.39	Yellow	43.68 (43.74)	2.59 (2.61)	7.26 (7.28)	32.34 (33.37)	–
[Co(L)$_2$(H$_2$O)$_2$] B$_2$C$_{28}$H$_{24}$N$_4$S$_8$O$_2$Co	785.5	15.29	73.05	Blue	42.72 (42.81)	3.05 (3.08)	7.09 (7.13)	32.62 (32.65)	7.48 (7.50)
[Ni(L)$_2$(H$_2$O)$_2$] B$_2$C$_{28}$H$_{24}$N$_4$S$_8$ O$_2$Ni	785.3	12.09	70.12	Green	42.79 (42.82)	3.06 (3.08)	7.09 (7.13)	33.61 (33.66)	7.41 (7.47)
[Cu(L)$_2$] B$_2$C$_{28}$H$_{20}$N$_4$S$_8$ Cu	754.2	16.49	68.09	Brown	45.29 (45.31)	2.63 (2.67)	7.42 (7.43)	34.13 (34.01)	8.41 (8.43)

[39a] Observed (calculated) values. [40]L = BC$_{14}$H$_{10}$N$_2$S$_4$.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF THE BORATE LIGAND AND ITS METAL COMPLEXES

Compound	ν(B-N)	ν(B-H)	ν(C=S)	ν(C-H)	ν(M-S)	ν(M-O)
Ligand, KL	1425	2327	990	2926	–	–
[Co(L)$_2$(H$_2$O)$_2$]	1429	2343	1023	2939	343	551
[Ni(L)$_2$(H$_2$O)$_2$]	1431	2354	1029	2921	354	582
[Cu(L)$_2$]	1434	2339	1036	2928	364	–

in Co(II) and Ni(II) complexes are supported by elemental analysis and spectral data. The ligand and its metal complexes were formed according to the **Scheme-I**.

Infrared spectral: A stretching vibration of medium intensity at 1425 cm^{-1} due to the B-N, strongly favours formation of ligand[7]. The ligand showed a strong B-H stretch[8] at 2327 cm^{-1} and medium vibration of C=S group[9] at 990 cm^{-1} confirmed attachment of 2-mercaptobenzothiazoline moiety with boron through sulfur atom (Table-2). In addition, several other bands in the broad region of 1563-700 cm^{-1} can be attributed to vibrations involving interaction between C=S and C-N. The infrared spectra of the metal complexes confirmed that after coordination to transition metal(II) ions, all the above stretching bands of ligand were insignificantly shifted except the C=S peak which is significantly shifted to higher wavenumber confirmed the formation of a coordinate bond between C=S and metal(II) ions. These shifts are consistent with a decrease in the order of the C=S bonds upon coordination and a shift of electron density, producing a partial double-bond character in the C-N bond. The low frequency vibrations due to M-O and M-S stretching provide direct evidence for the complexation. Presence of stretching vibration at 551 and 582 cm^{-1} in Co(II) and Ni(II) complexes, respectively shows the linkage between M-O bonds[15]. The presence of coordinated water molecules in the metal 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[11,12]. Another signal in the region 364-343 cm^{-1} shows the presence of M-S bond in all metal complexes[13].

NMR spectra: In ^{1}H NMR spectrum of the ligand, the absence of N-H or S-H proton signal 12-15 ppm and presence of a broad singlet of B-H protons at 4.52 ppm confirmed formation of the ligand[14]. The two doublets between 7.6-8.2 ppm show the aromatic ring protons of 2-mercaptobenza-thiazoline[15]. In ^{13}C NMR spectrum of ligand, the signals of >C-N and >C-S appear at 155 and 135 ppm, respectively while other benzene ring carbons of 2-mercaptobenzathiazoline are at 122-131 ppm. The chemical shift at 190.83 ppm indicates the presence of C=S group[16]. ^{11}B NMR has show a signal at 4.21 ppm for the B-H[4]. FT IR spectra also confirmed the characteristics band at 2317 cm^{-1} for B-H.

Electronic spectra and magnetic moments: The electronic spectra of metal complexes were measured and their spectral data are listed in the Table-3, which include the absorption regions, band assignments, ligand field parameters and the proposed geometry of the complexes. The electronic spectrum of Cu(II) complex (Fig. 1a) showed two characteristic bands at 14010 and 19596 cm^{-1}. These bands may be assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow 2E_g$ transitions, respectively[17], which indicate square-planar geometry. In the present study the magnetic moment value of Cu(II) complex was found to be 1.79 BM, which is in accordance with square planar geometry[18].

The Co(II) complex had a magnetic moment of 4.83 BM, corresponding to four unpaired electrons. This value was consistent with the high spin octahedral geometry. This higher μ_{eff} value of the Co(II) complex was attributed to the orbital contribution[19]. Electronic spectrum of the Co(II) complex exhibits absorptions in the region 9135, 16285 and 23041 which may

TABLE-3
MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES

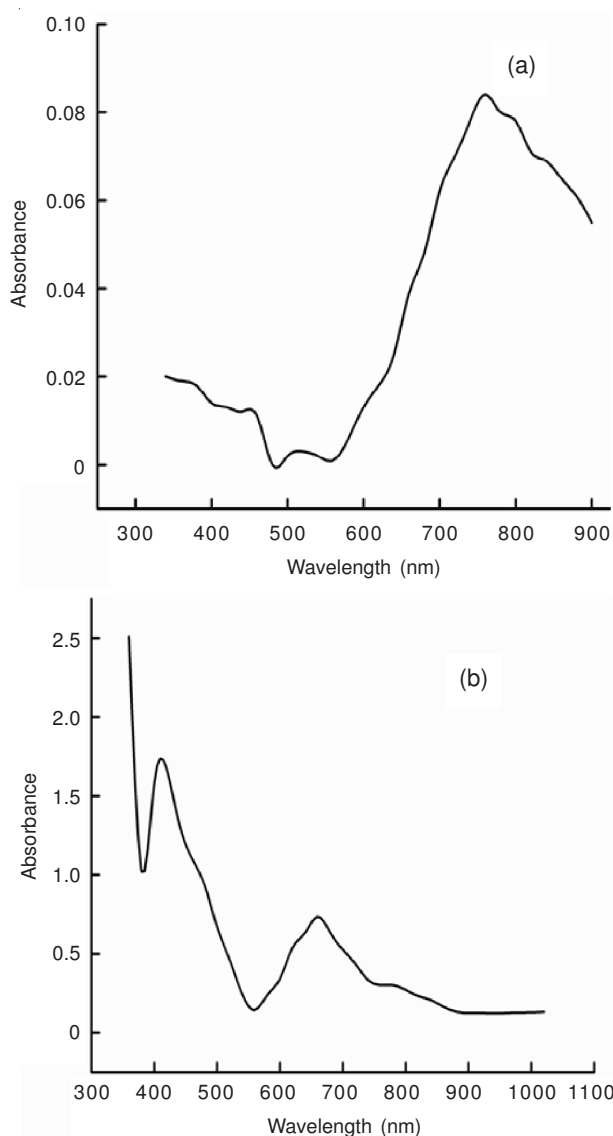| Compounds	Magnetic moment (μ_{eff})	Frequency (cm^{-1})	Assignments	Δ_o (cm^{-1})	B (cm^{-1})	β	Geometry
[Co(L)$_2$(H$_2$O)$_2$]	4.83	9135, 16285, 23041	$^4T_{1g\,(F)} \rightarrow ^4T_{2g\,(F)}$, $^4T_{1g\,(F)} \rightarrow ^4A_{2g\,(F)}$, $^4T_{1g\,(F)} \rightarrow ^4T_{1g\,(P)}$	10375	415	0.370	Octahedral
[Ni(L)$_2$(H$_2$O)$_2$]	2.90	9810, 15384, 23520	$^3A_{2g\,(F)} \rightarrow ^3T_{2g\,(F)}$, $^3A_{2g\,(F)} \rightarrow ^3T_{1g\,(F)}$, $^3A_{2g\,(F)} \rightarrow ^3T_{1g\,(P)}$	11118	654	0.605	Octahedral
[Cu(L)$_2$]	1.79	14010, 19596	$B_{1g\,(F)} \rightarrow ^2A_{1g\,(F)}$, charge transfer				Square planar

Fig. 1. Electronic spectra of Cu(II) and Ni(II) complexes

be assigned to the $^4T_{1g\,(F)} \rightarrow ^4T_{2g\,(F)\,(v1)}$, $^4T_{1g\,(F)} \rightarrow ^4A_{2g\,(F)\,(v2)}$ and $^4T_{1g\,(F)} \rightarrow ^4T_{1g\,(P)\,(v3)}$, respectively[20] suggesting an octahedral environment around the Co(II) ion in the complex. On the basis of these assignments the ligand field parameters calculated for Co(II) complex are $\Delta_o = 10375$ cm^{-1}; B = 415; β = 0.370. Similarly Ni(II) complex (Fig. 1 b) exhibits absorption bands in the region around 9810, 15384 and 23520 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 which display the characteristic pattern for octahedral Ni(II) complex[21]. On the basis of these assignments the ligand field parameters calculated for Ni(II) complex are $\Delta_o = 11118$ cm^{-1}; B = 654; β = 0.605. 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 octahedral Ni(II) complex was expected to be paramagnetic owing to the two unpaired *d*-electrons and the experimental magnetic moment was found to be 2.90 BM[22]. The above discussion is strongly indicates octahedral geometry around the central metal ion in the Co(II) and Ni(II) complexes, requiring occupation of two coordination by H_2O.

Thermogravimetric analysis: Thermogravimetric and differential DTG were carried out for ligand and its complexes under helium flow. The TGA exhibited one and two-stage decomposition patterns. Typical TGA and DTG curves are presented in Fig. 2 and the temperature ranges with percentage weight losses of the decomposition process are given in Table-4, together with the temperature of greatest rate of decomposition (DTG$_{max}$). Ligand was stable up to 250 ºC, leaving more than 5 % residue of B-N moiety. The first stage of degradation at 239.83 and 288.95 ºC in Co(II) and Ni(II) complexes which is accompanied by a weight loss of 52.56 and 34.74 %, respectively corresponding to the loss chemically bound water (coordinated water) and metals with organic parts. The second decomposition stage occurs at a maxima temperature of 482.04 and 643.80 ºC for Co(II) and Ni(II) complexes, respectively. The weight loss associated with this step is 36.69 % for Co(II) and 32.55 % for Ni(II) due to the loss of the organic compounds. 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 the anhydrous nature of the Cu(II) complex. The complex is stable up to 205 ºC and decomposition begins beyond this temperature. The complex shows a major step of weight loss between 220-400 ºC corresponds to the loss of organic moiety followed by CO_2 and leaves bluish black CuS as residue.

Thermal kinetics investigation: Non-isothermal methods have been extensively used for the evaluation of kinetic parameters of solid-state decomposition reactions by analysis of TGA curves. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion[23], using

$$\nu = \left(\frac{d\alpha}{dt}\right) = k(T)f(\alpha) \qquad (1)$$

where α is the fraction decomposed at time t, k(T) the temperature dependent function and f(α) is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function k(T) is of the Arrhenius type and can be considered as the rate constant k:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where A is the frequency factor, is a measure of the probability that a molecule having activation energy E will participate in a reaction. R is gas constant (8.314 J mol^{-1} K^{-1}). In non-isothermal conditions with a linear heating rate of β = dT/dt, eqn. 2 can be written as

$$\left(\frac{d\alpha}{dt}\right) = \left(\frac{A}{\beta}\right)f(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (3)$$

On integration and approximation, this equation can be obtained in the following form:

$$g(\alpha) = -\frac{E}{RT} + \ln\left[\frac{AR}{\beta E}\right] \qquad (4)$$

where g(α) is a function of α dependent on the mechanism of the reaction. The integral on the right-hand side is known as temperature integral and has no closed for solution. So several techniques have been used for the evaluation of temperature
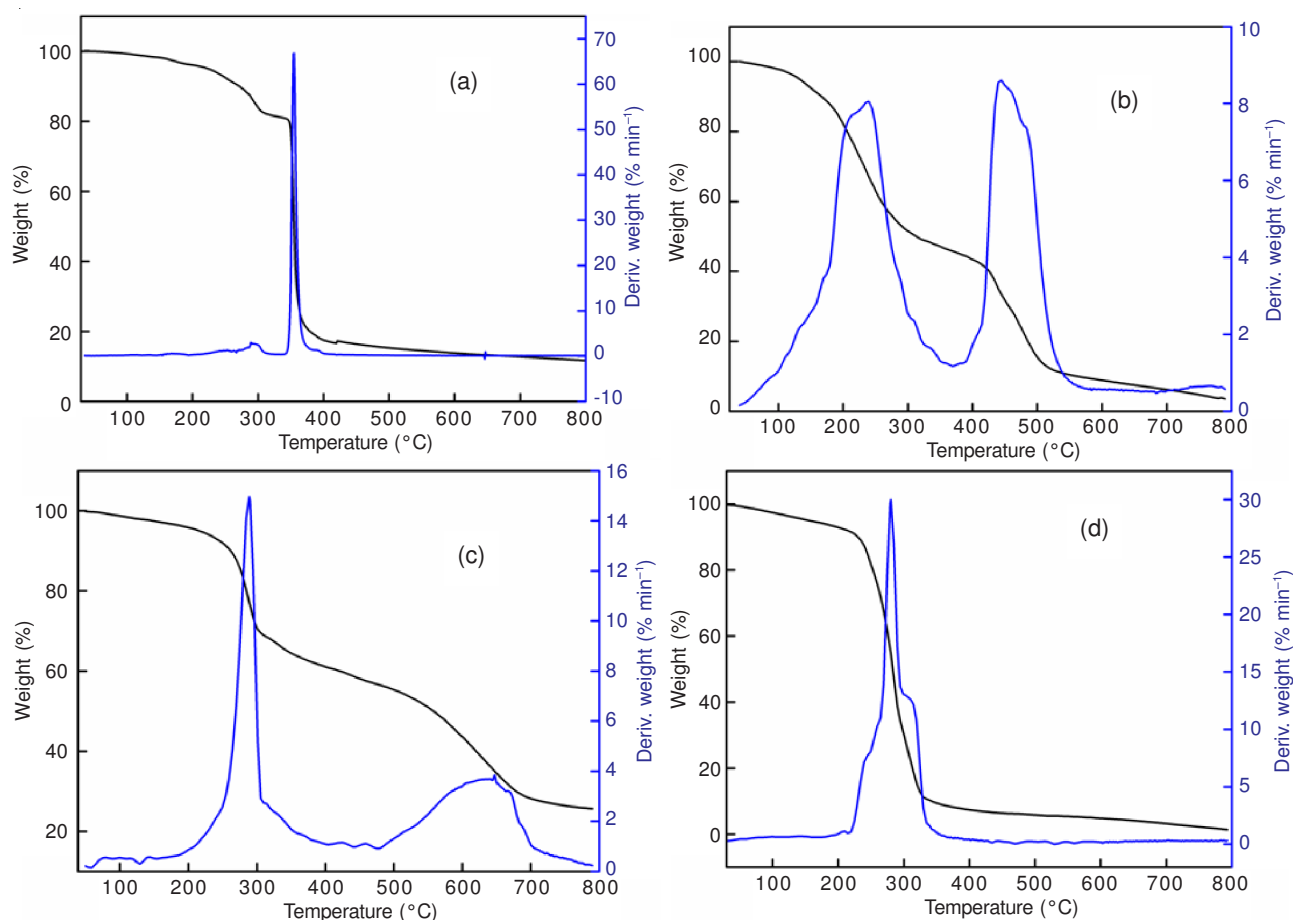
Fig. 2. TG-DTG curves of: (a) KL (b) Co(II) (c) Ni(II) and (d) Cu(II) complexes

Compound	Stage	Temperature range (ºC)	DTG$_{max}$	Weight loss (%)	Residue
Ligand, KL	I	250-400	355.78	74.87	5.81
[Co(L)$_2$(H$_2$O)$_2$]	I, II	50-350, 350-550	239.83, 482.04	52.56, 36.69	6.87
[Ni(L)$_2$(H$_2$O)$_2$]	I, II	200-400, 400-700	288.95, 643.80	34.74, 32.55	2.83
[Cu(L)$_2$]	I	220-400	280.48	80.01	12.65

TABLE-4
THERMO ANALYTICAL RESULTS OF LIGAND AND ITS METAL COMPLEXES

integral. In the present investigation integral method of Coats-Redfern[24] has been used to evaluate kinetic parameters because it is superior to other methods and shows the best linearity of the data.

The Coats-Redfern eqn. 5 can be represented as

$$g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \left(\frac{A}{\beta}\right)\int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT \qquad (5)$$

where T_0 is the temperature at the onset of the reaction. No conversion occurs before T_0; therefore, T_0 can bet set equal to zero for convenience. This equation on integration gives

$$\ln-\frac{\ln(1-\alpha)}{T^2} = -\frac{E}{RT} + \ln\frac{AR}{\beta E} \qquad (6)$$

A plot of left-hand side against 1000/T was drawn. E (kJ mol^{-1}) and calculated from the slop and A (s^{-1}) from the intercept value. The other kinetic parameters, ΔH, ΔS and ΔG were computed using the relationships; ΔH = E-RT, ΔS = R[ln(Ah/kT)] and $\Delta G = \Delta H$-TΔS, where k is the Boltzmann's constant, h is the Planck's constant and T is the DTG peak temperature. The kinetic parameters are listed in Table-5 and Fig. 3.

From the results obtained, the following remarks can be pointed out: All decomposition stages show a best fit for (n = 1) indicating a first order decomposition in all cases. Taking the first and second decomposition stages as a criterion, the data show that activation energy (E), enthalpy (ΔH), activation entropy (ΔS) and Gibbs free energy (ΔG), for metal complexes.

TABLE-5
KINETIC PARAMETERS DETERMINED USING THE COATS-REDFERN (CR)

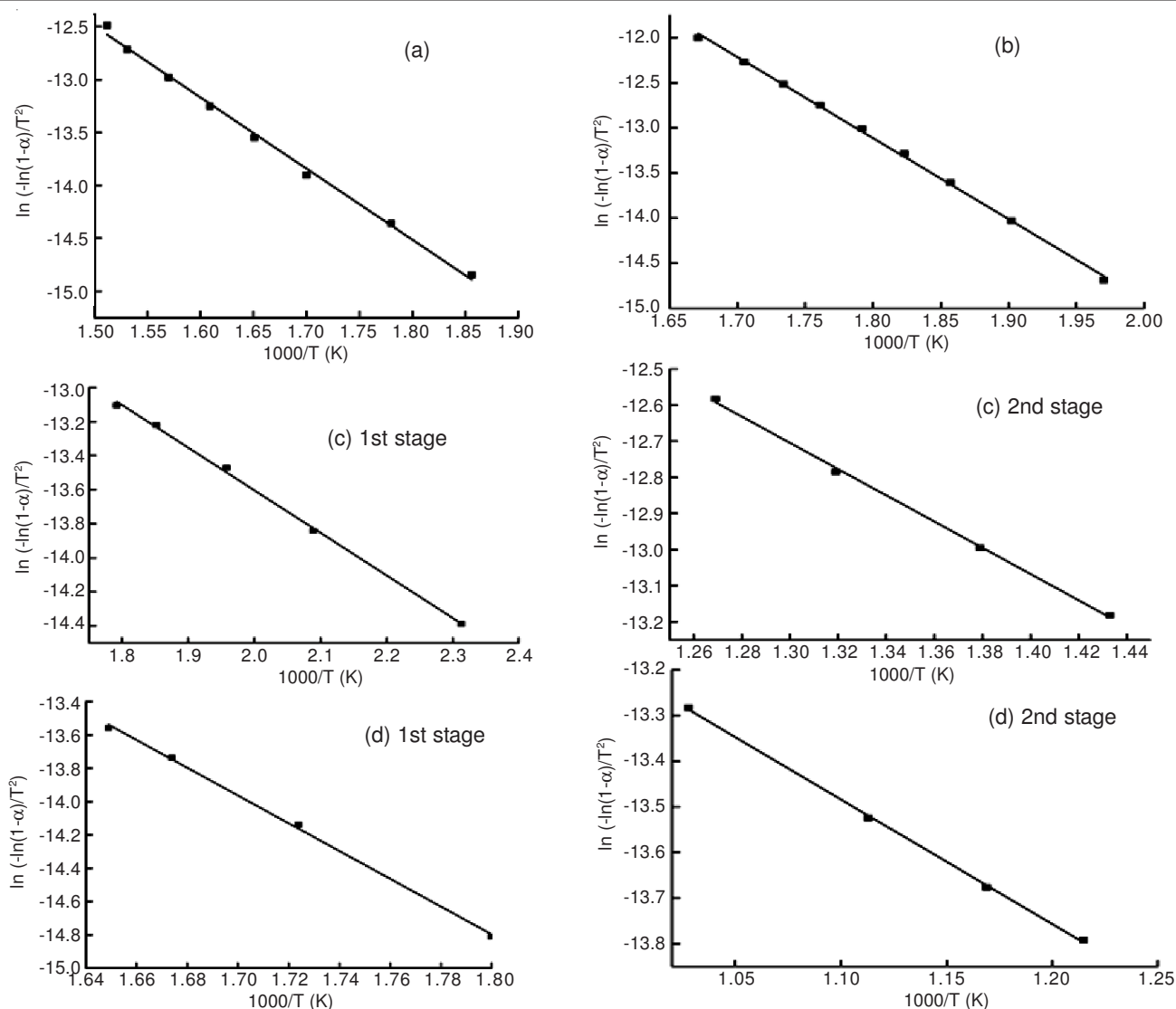| Compound	Stage	E (kJ mol^{-1})	ln A	ΔH	ΔS	ΔG	r^2
Ligand, KL	I	55.98	9.50	53.30	-0.167	112.12	0.998
[Co(L)$_2$(H$_2$O)$_2$]	I, II	20.80, 30.20	2.23, 3.21	18.81, 26.19	-0.225, -0.222	72.67, 133.29	0.998, 0.998
[Ni(L)$_2$(H$_2$O)$_2$]	I, II	69.28, 22.73	12.23, 0.439	66.88, 17.38	-0.143, -0.248	108.2, 176.84	0.997, 0.998
[Cu(L)$_2$]	I	74.76	15.17	72.43	-0.118	105.61	0.998

Fig. 3. Coats-Redfern (CR) plots for: (a) KL (b) Cu(II) (c) first stage and second stage of Co(II) and (d) first stage and second stage of Ni(II) complexes

All the complexes are higher values than those for ligand, this shows that the thermal stability for ligand is lower than that for metal complexes. The activation energy values increases on going from one decomposition stage to another for a Co(II) complex, indicating that the rate of decomposition decreases in the same order. This may be attributed to the structural rigidity of the remaining metal complex which requires more energy for its rearrangement before undergoing any compositional change. In case of Ni(II) complex the activation energy of second stage is lower than the first stage indicating that faster than first stage. The activation energy of Co(II), Ni(II) and Cu(II) complexes is expected to increase with decreasing in their radius[25-27], the smaller size of Cu(II) permits a closer approach to the ligand as compared to Co(II), Ni(II). Hence activation energy value for the Cu(II) complex higher than that of others that is thermal stability of Cu(II) complex is higher than Co(II), Ni(II). The positive values of enthalpy (ΔH) mean that the decomposition processes are endothermic. The negative values of activation entropies ΔS indicate a more ordered activated complex than the reactants and/or the reactions are slow[28]. The value of ΔG increases significantly for the subsequently decomposition stages of a given complex. This is due

to increasing values of TΔS significantly from one stage to another which over rides the values of ΔH. Increasing the values of ΔG of a given complex as going from one decomposition step subsequently to another reflects that the rate of removal of the subsequent ligand will be lower than the precedent ligand[29,30].

Electron-spray ionization mass spectra (ESI-MS): The positive and negative electron spray ionization mass spectra of the compounds were recorded in methanol (Table-6). The ESI-MS spectra of the compounds have differences of 1, 3 and 4 amu their calculated and observed mass fragmentations due to the isotopic nature of boron ([10]B and [11]B), carbon (^{12}C and ^{13}C) and sulfur ([32]S, [34]S). In some cases, the molecular ion peak was also associated with solvent, water molecules and some adduct ions from the mobile phase solution[31]. In positive ion ESI-mass spectrum of the ligand (Fig. 4), the molecular ion peak was observed at *m/z* 384, which is in agreement with the molecular weight (384) of the proposed structure and other fragmentation peaks at *m/z* 317, 288, 229 and 207 are ascribed to the cleavage of $[KBC_{14}H_8N_2S_2]^+$, $[KBC_8N_2S_4]^+$, $[KBC_8H_6NS_2]^+$ and $[C_{10}H_3NS_2]^+$, respectively.

Positive ion ESI-MS spectra of metal complexes confirm the presence of dipositive mononuclear core structure. Positive

TABLE-6
ESI-MS MASS SPECTRAL ANALYSIS OF THE
LIGAND AND ITS METAL COMPLEXES

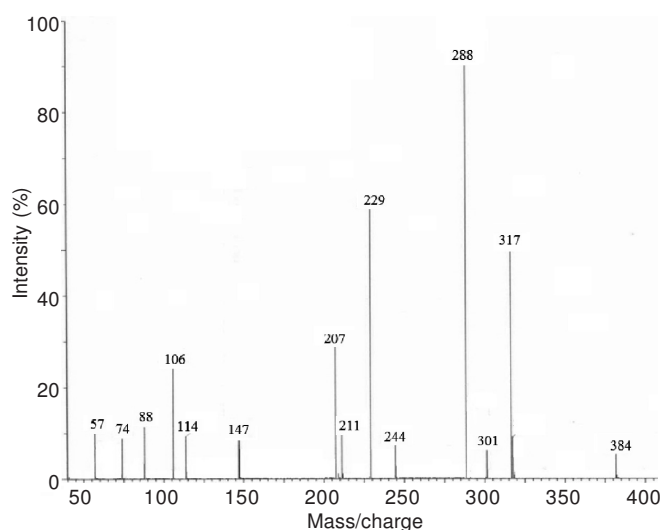| Compound	m/z	Peak assignment	Relative abundance (%)
Ligand, KL	384	$[KBC_{14}H_{10}N_2S_4]^+$	12
	317	$[KBC_{14}H_8N_2S_2]^+$	50
	288	$[BC_8H_8ON_2S_4]^+$	95
	229	$[KBC_8H_6NS_2]^+$	60
	207	$[C_{10}H_3NS_2]^+$	35
$[Co(L)_2(H_2O)_2]$	816	$[M + CH_3OH]^+$	19
	787	$[M + 2]^+$	38
	751	$[M - 2H_2O]^+$	65
	548	$[BC_{21}H_{18}N_3S_6O_2]^+$	53
	359	$[B_2C_{14}H_{12}N_2S_4]^+$	32
$[Ni(L)_2(H_2O)_2]$	786	$[M+2]^+$	45
	747	$[B_2C_{28}H_{18}N_4S_8Ni]^+$	19
	337	$[BC_{14}N_2S_4]^+$	33
$[Cu(L)_2]$	753	$[M - 1]^+$	76
	524	$[B_2C_{21}H_{16}N_3S_6]+$	64
	347	$[C_{14}H_{12}N_2S_4]+$	17

Fig. 4. ESI-Mass spectrum of ligand

ion spectra of the Co(II) and Ni(II) complexes show $[M + 2]^+$ peaks at *m/z* 787 and 786, respectively, which supports the presence of coordinated water molecules. Copper(II) complex show $[M-1]^+$ peak at *m/z* 753. The most relevant fragmentations of ligand and its metal complexes with their assignments are shown in Table-6.

Conclusion

The results of this study clearly indicate that ligand is coordinated to metal ions *via* >C=S group. The magnetic and electronic spectral studies of transition metal complexes suggest a square-planar geometry for the Cu(II) complex and octahedral configurations for Ni(II) and Co(II) ions. The stability of ligand and its metal complexes was explained and kinetic parameters

of all thermal decomposition stages have been evaluated using Coats-Redfern method. These studies show that there is a relationship between the ionic radius of metal and thermal stability of their complexes.

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