



## SYNTHESIS, CHARACTERIZATION, THERMAL AND NON-ISOTHERMAL DEGRADATION STUDIES OF TWO MONONUCLEAR NICKEL AND COPPER COMPLEXES CONTAINING SCHIFF BASE MOIETY

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### ARTICLE INFO

#### Article History:

Received 18<sup>th</sup> January, 2018

Received in revised form 13<sup>th</sup>

February, 2018 Accepted 15<sup>th</sup> March, 2018

Published online 28<sup>th</sup> April, 2018

#### Key words:

Schiff base; Nickel and Copper complexes, Thermal analysis, Non-isothermal kinetics, Coats-Redfern methods.

### ABSTRACT

Herein we report two mononuclear Nickel and Copper complexes of a tridentate 2, 4-dichloro-6-[[5-chloro-2-hydroxyphenyl)imino] methyl} phenol ligand (*dcp*) derived from 3,5-dichlorosalicylaldehyde and 2-amino-4-chlorophenol [general formula:  $ML \cdot xH_2O$  { $L = dcp$ ;  $M = Ni^{II}$  &  $Cu^{II}$  }]. The synthesized compounds have been characterized by elemental; FT-IR, UV-Vis, molar conductance and thermal analysis studies. TGA analysis was performed to determine the thermal stability of synthesized compounds under nitrogen atmosphere up to 800 °C K at 10 °C min<sup>-1</sup> heating rate. Thermal studies show the degradation pattern of complexes. Non-isothermal kinetic parameters, such as activation energy ( $E^*$ ), entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ), frequency factor ( $Z$ ) and free energy change ( $\Delta G$ ) have been calculated using Coats-Redfern (C-R), Piloyan-Novikova (P-N) and Horowitz-Metzger (H-M) methods.

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### INTRODUCTION

In coordination chemistry, ligand properties of Schiff bases are fabulous; hence a large number of complexes are reported with several metal ions. The presence of O, N and S donor groups at suitable (neighbor) position make Schiff bases as an excellent ligand. This may be due to the formation of more stable five or six membered cyclic structure when metal ion is coordinated with Schiff base ligand [1].

In modern age, introduction of sophisticated techniques of better accuracy and potential has significantly deepened our understanding to the metal-ligand bond nature, the structural arrangement, stabilities and other properties of metal complexes. The well-established thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques have been reliably widely used over many decades in studying the thermal behaviour and properties of various types of materials [2]. In association with other spectral techniques like IR, PXRD, Mass etc. thermal studies provide valuable structural information. Kinetic parameters of non-isothermal degradation steps may be evaluated by several methods [3, 4]. Thermal and thermo-oxidative degradation of polymers or polymeric materials, metal complexes, medicinal plants, leaves and thermoplastics obtained by thermoanalytical methods (TG, DTG, DTA, DSC) have been reported [5-7].

There are different methods to study the kinetics of non-isothermal processes.

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These include statistical methods [8-9], predictions of activated complex theory for the value of the pre-exponential factor [10], methods for different reaction models, Coats-Redfern (C-R) [11], Piloyan-Novikova (P-N) [12], Horowitz-Metzger (H-M) [13], Freeman-Carroll (F-C) [14], Sharp-Wentworth (S-W) and iso-conversional model free methods [15].

In this paper we synthesized a new ligand 2,4-dichloro-6-[[5-chloro-2-hydroxyphenyl)imino]methyl}phenol (*dcp*) and studied its ligand properties towards Nickel(II) and Copper(II) metal ions. The thermal degradation pattern of Ni(II) and Cu(II) complexes have been investigated at a specific condition of 10 °C min<sup>-1</sup> heating rate under nitrogen and air in 6:4 ratio and the thermodynamic parameters viz. activation energy ( $E^*$ ), entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ), frequency factor ( $Z$ ) and free energy change ( $\Delta G$ ) are evaluated using Coats-Redfern (C-R), Piloyan-Novikova (P-N) and Horowitz-Metzger (H-M) integral methods for the successive steps in the decomposition sequence.

#### Experimental

All chemicals and solvents were of A.R. grade. 3,5-dichlorosalicylaldehyde (Mol.Wt. 192.01 g/mol) and 2-amino-4-chlorophenol (Mol.Wt. 143.57 g/mol) obtained from Sigma-Aldrich, Metal salts obtained from Merck were used without further purification (Nickel chloride hexahydrate  $NiCl_2 \cdot 6H_2O$ , Mol.Wt. 237.69 g/mol; Copper chloride dihydrate,  $CuCl_2 \cdot 2H_2O$ , Mol.Wt. 170.48 g/mol). Microanalysis (C, H and N) were performed in Thermo Scientific (FLASH 2000) CHN Elemental Analyser at Sophisticated Analytical Instrument

Facility (SAIF), Panjab University, Chandigarh, India. Molar conductance in DMF ( $10^{-3}$  M) at room temperature was measured using Systronic model-304 digital conductivity meter. The FTIR spectra of the ligand and its complexes were obtained as KBr discs in the range  $4000-400\text{ cm}^{-1}$  on a Shimadzu FT IR-8400S instrument. Thermal data were collected on a NETZSCH STA 449F instrument under nitrogen atmosphere (nitrogen and air in 6:4 ratio) at the heating rates of  $10\text{ }^{\circ}\text{C min}^{-1}$  from the room temperature to  $800\text{ }^{\circ}\text{C}$  at Department of Physics, Dr. H.S. Gour University, Sagar (M.P.).

### Synthesis of 2,4-dichloro-6-((5-chloro-2-hydroxyphenyl)imino)methylphenol Ligand (dcp)

To a methanolic solution of 3,5-dichlorosalicylaldehyde (10 mmol); 2-amino-4-chlorophenol (10 mmol) was added dropwise. The reaction mixture has been refluxed for 4 hours and the mixture was allowed to stand overnight. The obtained orange precipitate was filtered off, washed, recrystallized and dried under reduced pressure over anhydrous  $\text{CaCl}_2$ .

Schiff bases (yield 79%) as crystalline orange solid and melting point is  $>500\text{K}$  (Table.1); FT-IR ( $\text{cm}^{-1}$ ): 1476 (C=C skeletal), 3426 (phenolic O-H str.), 1371(phenolic O-H deformation), 1606 (CH=N str.), 1276 (C-O str.) (Table. 2).

### Synthesis of metal complex

A methanolic solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (5 mmol) has been added dropwise into methanolic solution of ligand (5 mmol) in 1:1 molar ratio. The mixture has been continuously stirred and refluxed for 6 hrs. The colored precipitate of metal complexes formed were filtered, washed, recrystallized and dried under reduced pressure over anhydrous  $\text{CaCl}_2$ .

Metal complexes yield were found to 68 and 71 % respectively; decomposition temperature range 385-392K (Table. 1); FT-IR ( $\text{cm}^{-1}$ ): 1473-1474 (C=C skeletal), absent (phenolic O-H str.), absent (phenolic O-H deformation), 3352-3373 (water O-H str.), 822-826 ( $\text{H}_2\text{O}$  rocking), 1592-1597 (CH=N str.), 1243-1271 (C-O str.), 490-497(M-N str.) and 529-530(M-O str.) (Table. 2)

## RESULTS AND DISCUSSION

The synthesized ligand and its Ni(II) and Cu(II) complexes were colored, solid and stable towards air and moisture at room temperature. The complexes decompose on heating at high temperature and insoluble in common organic solvents except DMF and DMSO. The composition was found in good agreement with elemental analyses. Analytical and physical data of the compounds are given in the Table.1. It has been observed that metal(II) complexes have 1:1 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature indicates their non-electrolytic nature. The proposed tentative molecular structures of ligand and its complexes studied in present work are shown in fig. 1.

### FT-IR spectral studies

The FT-IR spectrum of the ligand exhibited some characteristic bands at 3426 (phenolic O-H str.), 1371(phenolic O-H deformation), 1606 (-HC=N-str.), 1276 (C-O str.). Ligand behaves as binategative tridentate in Ni-and Cu-complex coordinating through deprotonated enolic oxygen atom (C-O-),

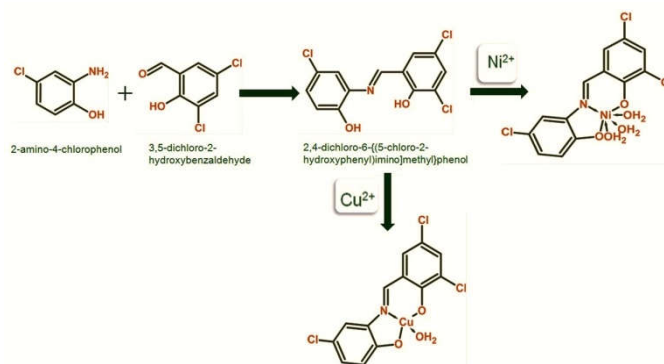
and azomethine nitrogen atom (C=N). This behavior is revealed by: (i) The disappearance of phenolic  $\nu(\text{O-H})$  (ii) Shift the position of  $\nu(\text{C-O})$  in all complexes downwards ( $1276\text{ cm}^{-1}$  to  $1243-1271\text{ cm}^{-1}$ ). (iii) Shift of  $\nu(\text{-HC=N-})$  to lower wavenumber ( $1606\text{ cm}^{-1}$  to  $1592-1597\text{ cm}^{-1}$ ). (iv) Appearance of two new bands of weak intensity corresponding to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibration in the range of  $490-497\text{ cm}^{-1}$  and  $529-530\text{ cm}^{-1}$  respectively. Two new additional bands were appeared at  $822-826\text{ cm}^{-1}$  correspond to  $\delta_r(\text{H}_2\text{O})$  rocking and  $\delta_w(\text{H}_2\text{O})$  wagging vibrations of coordinated water molecules. Further a broad band also appeared at  $3352-3373\text{ cm}^{-1}$  due to  $\nu(\text{H}_2\text{O})$  stretching vibrations. These bands were not seen in the ligand. The presence of water molecules was also supported by TG analysis [16-17]

### Electronic spectra and magnetic moment

The nature of the ligand field around the metal ion has been deduced from the electronic spectra.  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_3]$  exhibits three bands at  $10988$ ,  $19725$  and  $25818\text{ cm}^{-1}$  corresponding to transitions  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  respectively. The magnetic moment is 2.77 B.M. These findings are in favour of an octahedral geometry for the Ni(II)-complex. The  $[\text{Cu}(\text{L})(\text{H}_2\text{O})]$  exhibits two bands appears at  $12992$  and  $19230\text{ cm}^{-1}$  corresponding to transition  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  respectively. The magnetic moment is 1.91B.M. These findings favor a square planar geometry for this complex (Table. 3) [18-19].

**Table 1** Physical and analytical data of ligand and its metal complexes

S. No.	Ligand/Complex (Mol. Formula)	Colour	Yield %	MP/Dec. Temp. ( $^{\circ}\text{C}$ )	Elemental Analysis (%)				$\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$	$\mu_B$
					C	H	N	M		
1.	dcp ( $\text{C}_{12}\text{H}_8\text{Cl}_3\text{NO}_2$ )	Orange	79	>200	49.28 (49.29)	2.54 (2.54)	4.42 (4.38)	--	--	
2.	$[\text{Ni}(\text{L})(\text{H}_2\text{O})_3]$ ( $\text{C}_{13}\text{H}_7\text{Cl}_3\text{NNiO}_5$ )	Brownish Red	68	120	36.59 (36.60)	2.82 (2.80)	3.27 (3.25)	13.79 (13.76)	15.4	
3.	$[\text{Cu}(\text{L})(\text{H}_2\text{O})]$ ( $\text{C}_{13}\text{H}_7\text{Cl}_3\text{CuNO}_5$ )	Gray	71	110	39.39 (39.35)	2.03 (2.00)	3.53 (3.49)	16.03 (16.04)	11.2	



**Figure 1** Synthesis of Ligand and its Ni(II) and Cu(II) complexes.

**Table 2** Infra red absorptions of ligand and its metal complexes

Compounds	Assignments (in $\text{cm}^{-1}$ )						
	$\nu\text{C=C}$	$\nu\text{C-O}$	$\nu\text{C=N}$	$\nu\text{O-H str/}$ def. (phenolic)	$\nu\text{O-H}$ (water)	$\nu\text{M-N}$	$\nu\text{M-O}$
dcp	1476	1276	1606	3426/ 1371	-	-	-
$[\text{Ni}(\text{L})(\text{H}_2\text{O})_3]$	1474	1243	1592	-	3352/826	490	530
$[\text{Cu}(\text{L})(\text{H}_2\text{O})]$	1473	1271	1597	-	3373/822	497	529

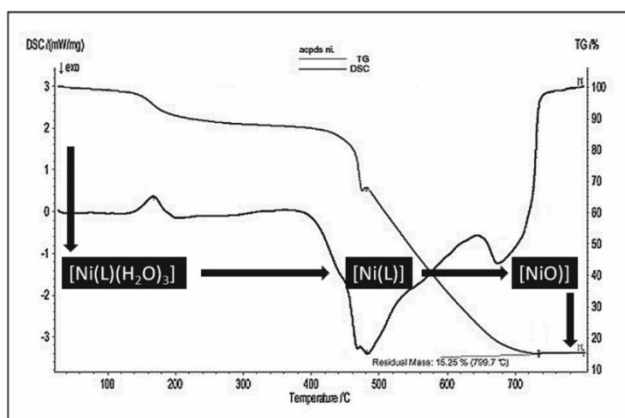
**Table 3** Electronic spectral data and magnetic moment of complexes.

S. No.	Compounds	Band Assignments	$\lambda_{max}$ (cm-1)	Proposed Geometry	$\mu_{eff}$ (BM)
1.	[Ni(L)(H <sub>2</sub> O) <sub>3</sub> ]	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> (F)	10988	Octahedral	2.77
		<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)	19725		
		<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	25818		
2.	[Cu(L)(H <sub>2</sub> O)]	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>	12992	Square planar	1.91
		<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	19230		

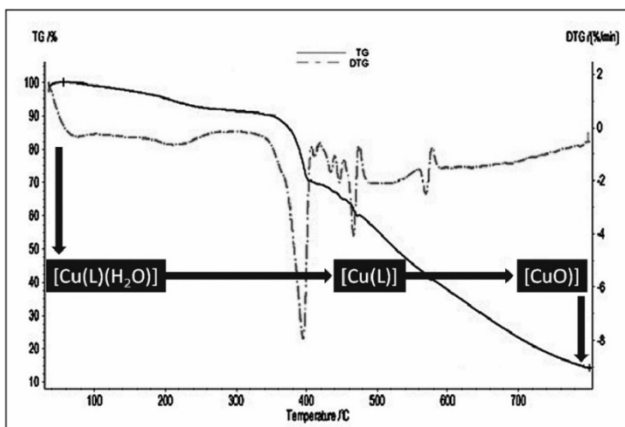
**Thermal analyses**

The thermal analysis helps in evaluating the thermal stability of the metal complexes, corresponding to thermal degradation vs structural changes. The TGA curve of the [Ni(L)(H<sub>2</sub>O)<sub>3</sub>] (Fig. 2) does not show any loss in weight upto 119 °C. This indicates the absence of lattice water molecules. A weight loss has been observed between 120-237 °C. This corresponds to loss of three coordinated water molecules in the complex (Remaining Wt.%, Obs./Calcd., 89.54/89.59). After that, complex does not show any appreciable loss in weight upto 367 °C and then a rapid weight loss has been observed upto 480 °C corresponding to non-chelated part of the ligand (Remaining Wt.%, Obs./Calcd., 69.26/69.06). Above 736 °C, a constant weight region has been observed due to metal oxide, as a final pyrolysis product (Remaining Wt.%, Obs./Calcd., 16.48/16.37).

The thermal degradation behavior of the [Cu(L)(H<sub>2</sub>O)] (Fig. 3) has been studied by TGA analysis. The TGA curve of the complex shows three stages of decomposition between the temperature range of 110-800 °C. The complex does not show any loss in weight upto 110 °C, which indicates the absence of lattice water molecules.



**Figure 2** Thermogram of Ni(II)-Complex



**Figure 3** Thermogram of Cu(II)-Complex

An elimination of one coordinated molecule of water has been observed between the temperature range 110-185 °C (Remaining Wt.%, Obs./Calcd., 97.21/96.99). After 185 °C, a weight loss has been observed up to 415 °C, which indicates decomposition of non-coordinated part of the ligand (Remaining Wt.%, Obs./Calcd., 70.65/70.61). Above 790 °C a horizontal curve has been observed suggesting the ultimate pyrolysis product as metal oxide (Remaining Wt.%, Obs./Calcd., 16.29/16.37) [20-22].

**Kinetic study**

On the basis of thermal decomposition, the kinetic analysis parameter such as activation energy (E\*), pre-exponential factor (Z), entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and free energy of activation ( $\Delta G^*$ ) were calculated by using C-R, P-N and H-M equations. The kinetic parameter data are summarized in Table 4 & 5.

The high values of activation energies reflect the thermal stability of the complexes. The complexes have positive entropy, which indicates that the decomposition reactions proceed with a higher rate than the normal ones. The positive value of entropy also indicates that the activated complexes have a less ordered and less rigid structure than the reactants or intermediates. The positive values of the entropies of activation are compensated by the values of enthalpies of activation, leading to almost the same values for the free energy of activation [23-25].

**Table 4** Non-isothermal kinetic parameters of [Ni(L)(H<sub>2</sub>O)<sub>3</sub>]complex

S. No.	Step	Temp. Range (K)	Method	$\Delta E^*$ (kJ/mol)	$\Delta S^*$ (JK <sup>-1</sup> mol <sup>-1</sup> )	Z (S <sup>-1</sup> )	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta G$ (Jmol <sup>-1</sup> )
1.	I	155-200	PN	89.282	206.486	5.337x10 <sup>2</sup>	93.032	-93.077
			CR	79.589	184.971	3.889x10 <sup>2</sup>	83.338	-83.365
			HM	91.509	211.428	2.972x10 <sup>2</sup>	95.259	-95.228
2.	II	435-470	PN	1.723	173.498	4.873x10 <sup>4</sup>	-4.329	-126.311
			CR	1.206	173.132	4.049x10 <sup>4</sup>	-4.846	-126.045
			HM	1.634	158.851	2.989x10 <sup>4</sup>	-4.418	-115.648
3.	III	510-640	PN	213.462	260.001	7.117x10 <sup>5</sup>	220.520	-220.684
			CR	188.154	230.162	6.449x10 <sup>5</sup>	195.212	-195.330
			HM	176.957	216.961	6.072x10 <sup>5</sup>	184.015	-184.110

**Table 5** Non-isothermal kinetic parameters of [Cu(L)(H<sub>2</sub>O)]complex

S. No.	Step	Temp. Range (K)	Method	$\Delta E^*$ (kJ/mol)	$\Delta S^*$ (JK <sup>-1</sup> mol <sup>-1</sup> )	Z (S <sup>-1</sup> )	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta G$ (Jmol <sup>-1</sup> )
1.	I	396-582	PN	30.558	296.058	2.173x10 <sup>2</sup>	26.493	-144.746
			CR	31.028	290.665	2.009x10 <sup>2</sup>	27.963	-142.107
			HM	32.524	263.137	1.952x10 <sup>2</sup>	28.458	-128.645
2.	II	635-677	PN	2.757	171.474	1.811x10 <sup>3</sup>	-2.696	-112.490
			CR	1.646	168.829	1.343x10 <sup>3</sup>	-3.807	-110.756
			HM	1.527	152.530	0.909x10 <sup>3</sup>	-3.926	-100.063
3.	III	734-1026	PN	13.230	234.343	3.016x10 <sup>5</sup>	5.914	-206.216
			CR	18.214	221.781	1.324x10 <sup>5</sup>	10.898	-195.156
			HM	19.265	199.381	0.772x10 <sup>5</sup>	11.949	-175.443

**CONCLUSION**

In the present research studies, our efforts are to synthesize some new compounds and characterize them by various physicochemical, spectral and thermal analyses. The synthesized Schiff base ligand binds with the metal ions in a tridentate manner, with ONO donor sites of deprotonated phenolic-O and azomethine-N. Thermal data show degradation pattern of the complexes.

### Acknowledgement

We are thankful to Head, Department of Chemistry, Dr. H.S.G. University, Sagar for laboratory facilities. We are grateful to Dr. R. Kumar (Department of Physics, Dr. H.S.G. University, Sagar) for Thermal analysis.

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### How to cite this article:

Anjali Tiwari *et al* (2018) 'Synthesis, Characterization, Thermal And Non-Isothermal Degradation Studies Of Two Mononuclear Nickel And Copper Complexes Containing Schiff Base Moiety', *International Journal of Current Advanced Research*, 07(4), pp. 11606-11609. DOI: <http://dx.doi.org/10.24327/ijcar.2018.11609.2014>

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