



Synthesis, thermal and spectral studies of Co(II), Ni(II) and Cu(II) complexes of Schiff base ligand derived from 1,6-diaminohexane and salicylaldehyde

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ABSTRACT: Cobalt(II), Nickel(II) and Copper(II) complexes, with Schiff base ligand derived from 1,6-diaminohexane and salicylaldehyde (salhex) have been synthesized and characterized by elemental analysis, conductance measurements, magnetic susceptibility measurements, IR, electronic spectra, ESR spectral studies and thermal analysis. IR spectra suggested that salhex acts as tetra dentate dibasic ligand. The possible geometries of the complexes are assigned on the basis of ESR, electronic spectra as well as the magnetic moment values. The thermal behaviour of Cu(II) complexes is studied using thermogravimetric analysis (TGA) technique. The different thermodynamic and kinetic parameters are calculated using Coats – Redfern method.

Keywords: Schiff base, complexes, spectral, thermal study.

1- Introduction

Schiff base ligands and their metal complexes are of significant interest for their pharmacological properties as anti-bacterial, anti-cancer, anti-viral and anti fungal agents [1-5]. Also, Schiff base ligands and their metal complexes have a variety of analytical and industrial applications [6-9] in addition to their important role in catalysis and organic synthesis [10-12]. Metal complexes of Schiff bases derived from substituted salicylaldehyde and different amines have been widely investigated [13-18].

In view of this, we report the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of Schiff base ligand (salhex) derived from 1,6-diaminohexane and salicylaldehyde. The coordination behaviour of Schiff base towards transition metal salts of Co(II), Ni(II) and Cu(II) is investigated via IR, electronic spectra, ESR spectra, magnetic moment and conductance measurements as well as the thermal analysis.

2- Experimental

2.1: Synthesis of Schiff base (salhex):

The Schiff base ligand was prepared by refluxing an ethanolic solution of salicylaldehyde (20 mmol) with 1,6- diaminohexane (10 mmol) on a water bath for 1h. On cooling, yellow compound was obtained and recrystallised from ethanol. The yellow Schiff base product obtained (m.p = 68^oC) was subjected to elemental analysis (Calc for C₂₀H₂₄N₂O₂: C 74.1; H 7.41; N 8.68), (Found: C 73.8; H 7.3; N 8.48 %).

2.2: Preparation of complexes:

All the metal complexes were prepared using a 2:1 (metal : ligand) molar ratio following a general method. To 20 ml of an ethanolic solution of corresponding metal salts (2 mmol) an ethanolic solution (20 ml) of Schiff base (1 mmol) was added and the resulting mixture

was refluxed on water bath for 2 hrs. The coloured complexes separated out, filtered, washed with ethanol and dried over CaCl_2 and then subjected to elemental analysis. The analytical data are given in Table (1).

2.3. Measurements:

Microanalyses of C, H and N were made using Heraeus CHN elemental analyzer. The IR spectra were recorded as KBr discs on a Perkin Elmer 1430 spectrophotometer in the $4000\text{--}200\text{ cm}^{-1}$ range. The electronic spectra were recorded using a Shimadzu 240 UV-Vis spectrometer. The X-band ESR spectra of the complexes were recorded at room temperature on a JOEL-X-band spectrometer equipped with an E 101 microwave bridge. Diphenyl picryl hydrazide free radical (DPPH) was used as internal standard ($g = 2.0023$). Magnetic susceptibilities were measured by employing the Faraday balance technique. The equipment was calibrated with $\text{Hg}[\text{Co}(\text{CNS})_4]$. Diamagnetic corrections were calculated from Pascal constants. The thermal analysis (TGA) was carried out using computerized Shimadzu TG-50 thermal analyzer up to $800\text{ }^\circ\text{C}$ at a heating rate $10\text{ }^\circ\text{C}/\text{min}$. in an atmosphere of N_2 .

3. Result and Discussion:

The stoichiometry and formulation of Schiff base complexes of different Cu(II) salts (chloride, acetate and nitrate) as well as Co(II) and Ni(II) are based on their elemental analyses, molar conductance and IR spectral data. The complexes are stable in air, soluble in the coordinated solvents as DMF or DMSO and have higher m.p.s than that of the free ligand. The higher m.p of the complexes can be taken as an evidence for the bonding to the M(II) ion with chelate ring formation .

Nonelectrolytic nature of the complexes is indicated by their low conductance values ($6\text{--}11\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) [19]. The analytical data (Table 1) are in agreement with 1:2 (ligand : metal) stoichiometry. These result were confirmed from the chemical analysis where Cl ions are not precipitated by addition of AgNO_3 solution.

3.1. IR spectra:

The IR spectrum of the Schiff base (salhex) compared to Cu(II) (1-3) complexes showed a broad band at 3422 cm^{-1} and a strong band at 1626 cm^{-1} assigned to the $\nu(\text{OH})$ and $\nu(\text{C}=\text{N})$, respectively. The participation of the $\text{C}=\text{N}$ group in complex formation is ascertained from the shift of $\nu\text{C}=\text{N}$ to lower frequencies in the complexes by $6\text{--}10\text{ cm}^{-1}$. Also, the participation of the OH group in complex formation, is apparent from the lower shift in position of the $\delta(\text{OH})$ in-plane vibration (1366 cm^{-1} in free ligand) to $1313\text{--}1333\text{ cm}^{-1}$ and the change in the $\nu(\text{C}-\text{O})$ stretching vibration in the free ligand (1226 cm^{-1}) to lower value in complexes ($1200\text{--}1206\text{ cm}^{-1}$). The participation of the azomethine nitrogen and phenolic oxygen is also confirmed by the appearance of new bands in the spectra of complexes in the $454\text{--}463$ and $512\text{--}517\text{ cm}^{-1}$ regions which may be assigned to M-N and M-O stretching vibrations, respectively [20].

The IR spectra of all Cu(II) complexes showed a strong broad band in the $3434\text{--}3465\text{ cm}^{-1}$ region which confirms the presence of water molecules coordinated to the metal ion. The presence of strong band at $853\text{--}851\text{ cm}^{-1}$ in all Cu(II) complexes attributed to the rocking vibration motion (H_2O) of coordinated water molecules. This notification was also supported by thermal analysis. The IR spectrum of nitrate complex showed three ($\text{N}-\text{O}$) stretching bands at $1455(\nu_5)$, $1333(\nu_1)$ and $1033(\nu_2)\text{ cm}^{-1}$. The separation of two highest

frequency bands ($\nu_5 - \nu_1$) is 122 cm^{-1} suggesting that nitrate group is coordinated to the central metal ion in unidentate manner [21]. In acetate complex, the acetate group displayed the asymmetric and symmetric vibrations at 1533 and 1333 cm^{-1} with $\Delta \nu = 200 \text{ cm}^{-1}$ characteristic of their monodentate nature [22].

The IR spectrum of Ni (II) complex (4) showed that the $\nu(\text{C}=\text{N})$ stretching vibration of the free ligand undergoes a shift to lower frequency by 6 cm^{-1} . This is indicative of nitrogen coordination of the azomethine nitrogen to Ni(II) ion. The coordination of the o-OH group to Ni(II) ion through deprotonation can be elucidated by the shift of $\nu(\text{C}-\text{O})$ to lower value by 19 cm^{-1} in the spectrum of Ni(II) complex. The appearance of new bands at 455 and 530 cm^{-1} assigned to $\nu(\text{Ni}-\text{N})$ and $\nu(\text{Ni}-\text{O})$ confirmed the involvement of the phenolic and azomethine nitrogen atoms in complex formation. The broad band at 3420 cm^{-1} assigned to the stretching vibration of noncoordinated water molecules.

The IR spectrum of Co(II) complex (5) showed that the position of $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ is shifted to lower wavenumber by 10 and 15 cm^{-1} respectively. This indicated that the coordination occurs through nitrogen and oxygen atoms of $\text{C}=\text{N}$ and phenolic oxygen group. This coordination behaviour is also proved by the appearance of IR bands due to $\nu(\text{Co}-\text{N})$ and $\nu(\text{Co}-\text{O})$ vibrations at 459 and 520 cm^{-1} , respectively. The observable new bands at $3448, 756$ and 590 cm^{-1} are attributed to coordination water [23].

3.2. Electronic spectra and magnetic measurements:

The magnetic moments of Cu (II) complexes listed in Table (2) fall in the normal range for Cu(II) species. Magnetic moment values are in the range $1.78 - 1.89 \text{ BM}$ and this confirms that Cu(II) complexes have square planar geometry [24]. Also, these values indicated that Cu(II) complexes are monomeric in nature and the absence of metal-metal interaction. The Nujol mull spectra of Cu(II) complexes showed different bands within the ranges $26316 - 27027$, $22222 - 22727$ and $17241 - 17544 \text{ cm}^{-1}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, respectively suggesting square planar geometry.

The Nujol mull spectrum of Ni(II) complex exhibited two absorption bands at 19231 and 23810 cm^{-1} corresponding to square planar geometry. These bands may be assigned to the spin allowed transitions ${}^1\text{A}_{1g} (\text{D}) \rightarrow {}^1\text{B}_{2g} (\text{G}) \nu_2$ and ${}^1\text{A}_{1g} (\text{D}) \rightarrow {}^1\text{E}_g (\text{G}) \nu_3$, respectively [25]. The Ni(II) complex exhibited diamagnetic character denoting square planar geometry.

The electronic spectrum of Co(II) complex showed spectral bands at 18519 and 20833 cm^{-1} . These bands are assigned to ${}^4\text{T}_{1g} (\text{F}) \rightarrow {}^4\text{A}_{2g} (\text{F}) (\nu_2)$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g} (\text{P}) (\nu_3)$ transitions respectively, characteristic of octahedral geometry [26]. The observed magnetic moment value of the Co(II) complex is 4.1 BM which suggested an octahedral geometry.

3.3. ESR Spectra:

The ESR spectra of Cu(II) complexes were recorded as polycrystalline sample at room temperature. The g tensor value (Table 2) can be used to derive the ground state. From the observed values $g_{11} > g_{\perp} > 2.0023$ indicating that the Cu site has a $d_{x^2-y^2}$ ground state characteristic of square planar. Kivelson and Neiman [27] have reported that the g_{11} value in a copper(II) complex can be used as a measure of the covalent character of the metal ligand bond (g_{11} value < 2.3 for covalent character of the metal-ligand bond and > 2.3 for ionic character). The g_{11} values reported are in the range indicating considerable covalent bonding characters.

$G = (g_{11} - 2) / (g_{\perp} - 2)$ which measure the exchange interaction between the Cu centers have been calculated. According to Hathaway [28], if $G > 4$ the exchange interaction is negligible whereas when the value of $G < 4$ indicates considerable exchange interaction in the solid complexes. The values of G in Table (2) indicate that there is no direct Cu-Cu interaction in the solid state.

3.4. Thermal analysis (TGA):

Selected complexes were thermally investigated and their plausible degradation schemes are represented in Table (3). The TG thermogram of Cu(II) complex (2) is taken as a representative example.

The thermal decomposition of Cu(II) complex (2) showed three steps. The first step of decomposition within the temperature range 207-305°C corresponds to the loss of 2 moles of coordinated water molecules (Found 6.4, Calc. 6.48 %) The second step occurs in the temperature rang 307-491 °C corresponding to partial decomposition with the loss of 2Cl (Found 13.41, Calc 13.65 %). The final step of decomposition is consistent with the formation of CuO as a final product from which the Cu content was calculated and was found to be in agreement with those obtained from elemental analysis.

The kinetic parameters of decomposition process of the complexes namely, activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and free energy of the decomposition (ΔG^*) as well as the order (n) are evaluated graphically by using Coats-Redfern [29] equations were used for evaluating the kinetic parameters.

Coats-Redfern equation:

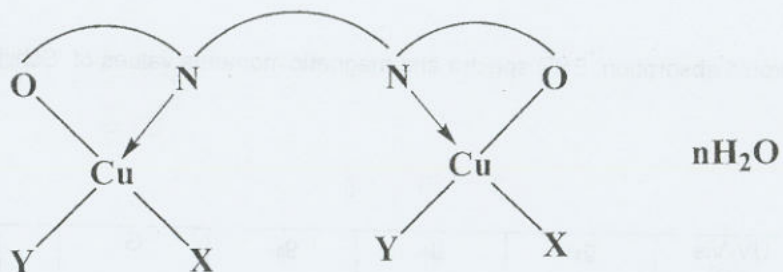
$$\ln \left[\frac{1 - \alpha^{1-n}}{1 - n\phi} \right] = \frac{M}{T} + B \quad \text{for } n \neq 1$$

$$\ln \left[\frac{1 - \alpha}{\phi} \right] = \frac{M}{T} + B \quad \text{for } n = 1$$

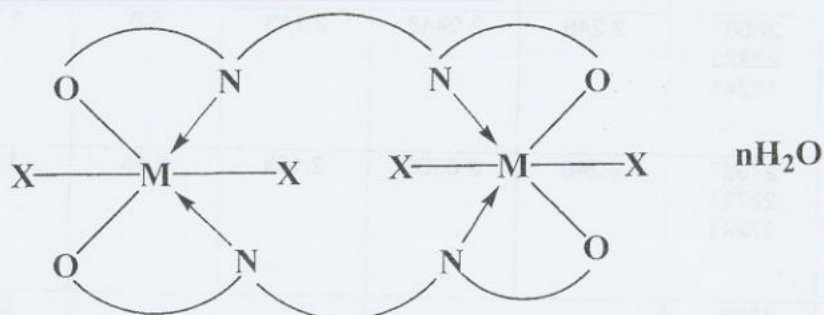
Where $M = -E/R$ and $B = \ln(ZR/be)$ where E , R , Z and ϕ are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

The correlation coefficient r was computed by using the least square method for the above equations. Linear curves were drawn for different values of n equal 0, 0.33, 0.5, 0.66 and 1. The values of n , which gave the best fit, were chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the L.H.S. vs. $1/T$ of Coats-Redfern equation, as shown in (Fig.1). The calculated values of n , E^* , A , ΔS^* , ΔH^* and ΔG^* for the decomposition steps are given in Table (4). The ΔS^* values for complexes were found to be negative. This indicates that the activated complex is more ordered than the reactants and/or the reactions are slow [30]. The positive values of ΔH means that the decomposition processes are endothermic.

Based on the information gained in the present study, the structures of the complexes are given in Schemes 1.



- For complex (1) $n = 1$, $X = \text{AcO}$, $Y = \text{H}_2\text{O}$
 (2) $n = 0$, $X = \text{Cl}$, $Y = \text{H}_2\text{O}$
 (3) $n = 0$, $X = \text{NO}_3$, $Y = \text{H}_2\text{O}$



- for complex (4), $n = 1$, $X = \text{zero}$
 for complex (5), $n = 0$, $X = \text{H}_2\text{O}$

Scheme (1) Structures of the metal complexes

Table (1): Elemental Analysis, Molecular Formula and Molar Conductance of Schiff base complexes

NO	Complex	Colour	% Found (Calc)				Ω
			C	H	N	M	
1	$[\text{Cu}_2\text{L}(\text{AcO})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	green	46.19 (46.40)	5.28 (5.50)	4.39 (4.50)	20.2 (20.4)	8
2	$[\text{Cu}_2\text{L}(\text{Cl})_2(\text{H}_2\text{O})_2]$	green	43.01 (43.17)	4.59 (4.68)	4.98 (5.04)	(22.70) (22.84)	10
3	$[\text{Cu}_2\text{L}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	green	39.19 (39.40)	4.05 (4.30)	9.0 (9.20)	(20.97) (20.90)	11
4	$[\text{NiL}]_2 \cdot \text{H}_2\text{O}$	green	61.29 (61.59)	5.67 (5.90)	7.0 (7.19)	14.99 (15.06)	7
5	$[\text{CoL}(\text{H}_2\text{O})_2]_2$	Brown	57.21 (57.57)	5.98 (6.24)	6.79 (6.42)	14.0 (14.13)	6

$$\Omega = \text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

Table (2): Electronic absorption, ESR spectra and magnetic moments values of Schiff base complexes.

Complex	UV-Vis cm ⁻¹	g ₁₁	g _⊥	g _{av}	G	μ _{eff} BM
1	26316 22222 17544	2.2124	2.0448	2.101	4.74	1.83
2	26667 22222 17241	2.249	2.0448	2.113	5.6	1.78
3	27027 22727 17241	2.249	2.0386	2.109	6.45	1.89
4	19231 23810					Dia
5	18519 20833	-	-	-	-	4.01

Table (3): Thermal decomposition data of Cu(II) complexes.

Complex	Temp. °C	Mass Loss %		Assignment
		Estimate	Calc.	
1	25- 90	2.83	2.9	Loss of 1H ₂ O
	110- 205	5.84	5.96	Loss of 2H ₂ O
	250-300	20.66	20.80	Loss of 2AcO
	350-750			Loss of ligand
2	207-305	6.4	6.48	Loss of 2H ₂ O
	307-491	13.41	13.65	Loss of 2Cl
	491-750			Loss of ligand
3	120-250	5.68	5.91	Loss of 2H ₂ O
	261-355	21.21	21.61	Loss of 2NO ₃
	356-454			Loss of ligand

Table (4): Temperatures of decomposition and activation parameters (KJmol⁻¹) of decomposition for Cu(II) complexes under investigation.

Complex	T(K)	Coast-Redfern					
		n	r	E*	ΔH*	-ΔS* ^a	ΔG*
1	833	1	0.988	11.7	4.52	0.082	72.65
2	376	0	0.994	18.5	11.10	0.081	82.97
3	662	0	0.994	36.4	30.86	0.112	104.58

^a KJ mol⁻¹ K⁻¹.

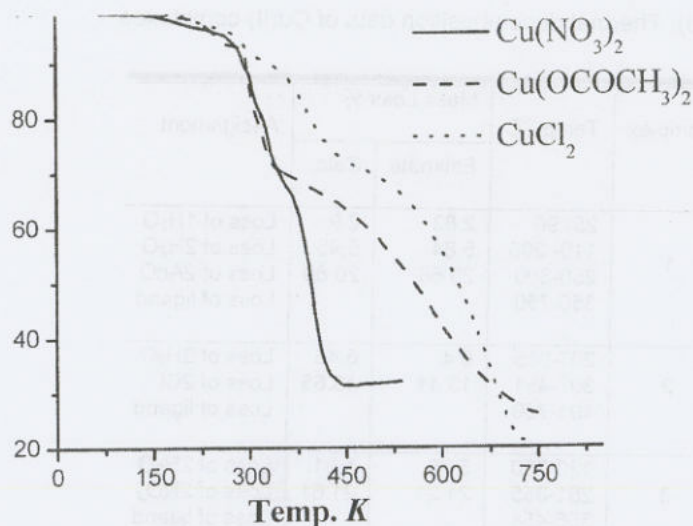


Fig 1a: TGA curve of Cu(II)-complexes.

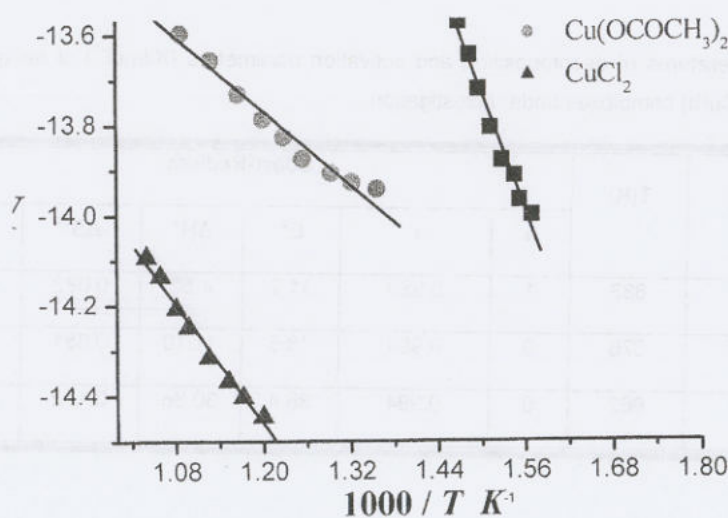


Fig. 1 b: Coats-Redfern plots for the decomposition steps

$$Y = \ln \left[\frac{1 - (1-x)^{1-n}}{(1-n)T^2} \right] \text{ for } n \neq 1 \quad \text{or} \quad \ln \left[\frac{-\ln(1-x)}{T^2} \right] \text{ for } n = 1$$

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تحضير ودراسات طيفيه وحراريه لمتراكبات الكوبلت والنيكل والنحاس ثنائي التكافؤ مع مرتبطات ثنائي السن

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تم تحضير منراكبات الكوبلت والنيكل والنحاس ثنائي التكافؤ لقاعده شيف المشتقه من 6و1 ثنائي امينو هكسان وتم دراسه هذه المتراكبات بالتحليل العنصرى والتوصيل الكهربى والقابليه المغناطيسيه والاشعه تحت الحمراء وفوق البنفسجيه والتحليل الحرارى وكذلك تم دراسه الاشكال الفراغيه للمتراكبات بالطرق المختلفه مثل الاشعه فوق البنفسجيه وقيم العزم المغناطيسى