

COBALT (II), NICKEL (II), AND COPPER (II) CHELATES OF N-ISONICOTINAMIDO-SALICYLALDIMINE

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The 1:1 and 1:2 (metal to ligand) complexes of N-isonicotinamidosalicylaldimine with Co(II), Ni(II) and Cu(II) have been prepared. Stoichiometry and stability of the complexes have been tested in solution using electronic spectral and conductometric methods. Characterization of the complexes has been accomplished by elemental analysis, molar conductance, electronic and infrared spectral measurements. It is concluded that the chelate formation takes place through the C=N and C=O with 1:2 ratio and through the C=N and enol form with 1:1 complexes. The different bands observed in the electronic spectra of the complexes in DMF solutions have been assigned to the $\pi - \pi^*$, $L \rightarrow MCT$ and d-d electronic transitions.

Key words : Transition metals, Chelate formation, Complexation.

Introduction

The ligands pyridine-4 carboxaldehyde isonicotinoyl hydrazone, pyridine-2-carboxaldehyde isonicotinoyl hydrazone and N-isonicotinamidosalicylaldimine are expected to exhibit variable bonding and stereochemical behaviour in their complexes because of the presence of several alternate bonding donor sites and the possibility of ketoenol tautomerism. Several studies were reported [1-3] on the synthesis and characterization of some complexes of these ligands. The reported [3] study on the complexes of N-isonicotinamidosalicylaldimine seems to be not complete. Therefore, the present paper aims to synthesis and characterization the complexes of N-isonicotinamidosalicylaldimine with Co(II), Ni(II) and Cu(II) using several tools e.g. elemental analyses, molar conductance, electronic and infrared spectral measurements. Moreover, the stoichiometry and stability of the formed complexes in solution were tested using electronic spectral and conductometric titration methods.

Experimental

Reagent grade metal salts and organic solvents were used. The ligand N-isonicotinamidosalicylaldimine, L was prepared by refluxing isonicotinoylhydrazine and salicylaldehyde in 1:1 molar ratio in absolute ethanol. The solid product was filtered off and recrystallized from ethanol. The purity was confirmed by elemental analysis and infrared spectra (Tables 1 and 2). The structure formula of the ligand is given in Fig. 1.

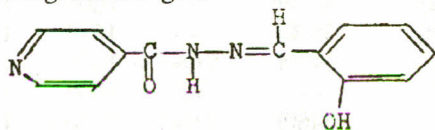


Fig. 1

The metal complexes were prepared by adding an ethanolic solution of the metal salt ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) to an ethanolic solution of the ligand, L in 1:1 and 1:2 metal to ligand molar ratios. The mixture was refluxed for ~ 3 hr. The solid complex was filtered off, washed with ethanol and stored in a desiccator over dry silica gel.

For spectral and conductance measurements, 1×10^{-3} mol.dm⁻³ stock solutions of the ligand as well as of the metal salts were prepared by dissolving the accurately weighed amount of each in absolute ethanol. More dilute solutions of the reagents were obtained as required by accurate dilution. The metal ion solutions were standardized by recommended methods of analysis [4].

The electronic spectra were recorded with Cecil CE 599 recording spectrophotometer using 1cm matched silica cells. The infrared spectra of the ligand and its complexes were recorded on Perkin-Elmer 599 spectrophotometer as KBr discs. Molar conductance and conductometric titrations were performed with a WPA, Saffron Walden CM 25 conductivity meter.

Results and Discussion

The complexes isolated are given in Table 1. The elemental analysis data reported in this Table reveal that the anion of the ligand, L (enol form) is coordinated to the metal ion for 1:1 ratio, while with 1:2 the neutral ligand (keto form) coordinated to the metal ion. The general formula of 1:1 complexes is $[(L-H)MXH_2O]$ and for 1:2 is $[(L_2M)X_2(H_2O)_n]$ where M=Co (II), Ni (II) and Cu (II), X=Cl⁻ or CH₃COO⁻.

Molar conductance values given in Table 1 in DMF solutions lies in the range 32.46 - 39.00 for 1:1 complexes and for 1:2 lies between 128.47 - 189.99 ohm⁻¹cm² mole⁻¹.

It is reported [5] that 1:1 electrolytes in DMF solutions have molar conductance value in the range 65 - 90. Accordingly, it can be deduced that the complexes 1:2 are electrolytic i.e. the chloride is present as a counter ion. This is in accordance within the formulae $[(L)_2M]X_2(H_2O)_n$ suggested before. In case of 1:1 complexes, the conductivity results imply that $[M(L-H)X(H_2O)]$ dissociates partly to $[M(L-H)(dmf)_2]^+$ in dimethyl formamide. This behaviour can presumably be ascribed to the displacement of X and H_2O ($X=Cl^-, CH_3COO^-$) by DMF molecules upon dissolution.

Assignment of the important infrared bands, which aids in understanding of the bonding of the complexes are presented in Table 2. The ν_{OH} band [6] of the ligand appears as a broad band at 3180 cm^{-1} . This is in consistency with the expected involvement of this group with the azomethine nitrogen through intramolecular hydrogen bonding. On complexation, a broad band is appeared in the region

$3010 - 3080\text{ cm}^{-1}$. The increase in bond order of N-H band ($\sim 10\text{-}20\text{ cm}^{-1}$) is strongly indicates that N-H group is not involved in bonding in 1:2 complexes while the proton of this group is involved in enolization and is consequently deprotonated on coordination to the metal ions in 1:1 complexes. The strong band at 1610 cm^{-1} in the IR spectra of free ligand is assigned [11] to C=N stretching frequency. On complexation, this band in most cases is shifted to lower frequency confirming the coordination of the azomethine nitrogen. Such the structure of the different complexes obtained can be represented in Fig. 2.

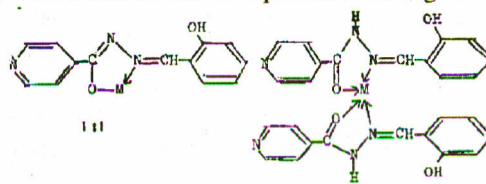


Fig. 2

TABLE 1. ANALYTICAL DATA, COLOUR, DECOMPOSITION TEMPERATURE AND MOLAR CONDUCTANCE VALUES ($\text{Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) OF THE LIGAND L AND ITS COMPLEXES.

Compound	Colour	Dcomp. Temp. °C	Molar conduc.	Calc. (Found) %			
				C	H	N	Cl
$C_{13}H_{11}N_3O_2L$	Pale yellow	250	—	64.73 (64.70)	4.59 (4.80)	17.42 (16.90)	—
$[(L-H)CoCl(H_2O)]$	Brown	320	32.46	44.28 (44.80)	3.43 (3.50)	11.92 (11.70)	10.05 (9.62)
$[(L-H)Ni(CH_3COO)(H_2O)]$	Brown	300	34.55	47.92 (48.10)	4.02 (4.50)	11.18 (11.50)	—
$[(L-H)CuCl(H_2O)]$	Brown	350	37.00	43.71 (43.50)	3.38 (3.30)	11.76 (11.60)	9.92 (10.80)
$[(L)_2Co]Cl_2H_2O$	Brown	347	166.67	49.54 (49.20)	3.83 (4.04)	13.33 (12.96)	11.25 (10.94)
$[(L)_2Ni](CH_3COO)_2$	Brown	360	128.47	54.66 (55.10)	4.28 (3.70)	12.75 (12.20)	—
$[(L)_2Cu]Cl_2H_2O$	Green	349	189.99	49.18 (48.80)	3.81 (3.20)	13.24 (12.90)	11.17 (10.90)

$3300 - 3500\text{ cm}^{-1}$. This suggests that water molecules are coordinated to the central metal ion. This is supported by the results of elemental analysis of the synthesized complexes (Table 1). The C-O phenolic group [7,8] band of the free ligand appeared at 1210 cm^{-1} . Upon complexation, this band is practically unaffected indicating that the O-H group is not involved in the bonding with the metal ions. The band observed at 1675 cm^{-1} in the IR spectra of free ligand is assigned [9] to C=O stretching vibration. This band is totally disappeared on chelation with 1:1 complexes, while with 1:2 type, the intensity of C=O band is decreased and the position is unaffected. On the other hand, the C-H and N-H bands [9,10] are observed at

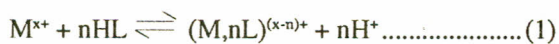
TABLE 2. SOME INFRARED FREQUENCIES (cm^{-1}) OF THE LIGAND, L AND ITS COMPLEXES.

Compound	Frequency(cm^{-1})			
	ν_{O-H} and H_2	$\nu_{C=O}$	$\nu_{C=N}$	ν_{phenyl}
Free ligand, L	3180	1675	1610	1210
Co(II)-1(L-H)	3440b	—	1605	1210
Ni(II)-(L-H)	3420b	—	1605	1210
Cu(II)-(L-H)	3500b	—	1610	1205
Co(II)-(L) ₂	3450b	1680	1610	1210
Ni(II)-(L) ₂	—	1680	1600	1215
Cu(II)-(L) ₂	3480b	1680	1610	1210

b = broad

The spectrophotometric job's continuous variation method [12] has been applied to detect the stoichiometry of the complexes formed in ethanolic solution. In this method, an ethanolic solution having the same concentration of ligand as that of the complex solution was used as blank. The total concentration is 8.9×10^{-4} mol. dm⁻³. On plotting the absorbance values at the selected wavelength versus the mole fraction of the ligand, the curves represented in Fig. 3 are obtained which exhibit a shoulder at 0.5 for Co(II) and Cu(II) and at 0.6 for Ni(II) and a maximum at 0.7 for the three metal ions. This indicates the possible formation of the two types of complexes in solution with 1:1 and 1:2 stoichiometric ratios.

Determination of the apparent stability constant. The stability of the complexes in solution was inspected by determining their apparent formation constant [13] values using the results of continuous variation method. If the equilibrium sets in solution are given as follows:



$$\beta = \frac{[(M,nL)^{(x-n)+}] [H^+]^n}{[M^{x+}] [HL]^n} \dots\dots\dots(2)$$

$$\beta = \frac{A/A_m}{[(1-A)/A_m] n^2 C_{HL}^n} \dots\dots\dots(3)$$

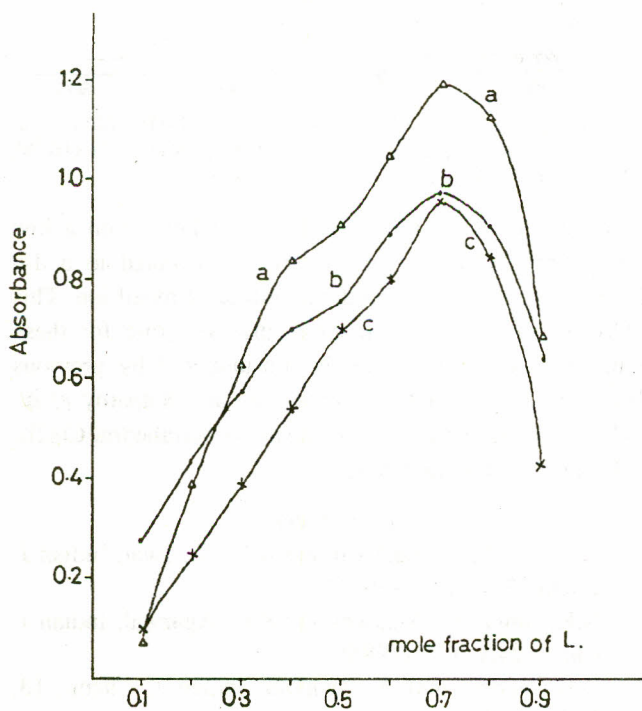


Fig. 3. Job's continuous variation plots of the metal complexes of ligand, L with a:Co(II), $\lambda =400$ nm, b:Cu(II), $\lambda =410$ nm, and c:Ni(II), $\lambda 430$ nm. The total concentration is 8.9×10^{-4} M.

where β = apparent stability constant, A = absorbance, A_m = absorbance at saturation, n= number of ligand groups in the complex, and C_{HL} is the concentration of the ligand. The values of β obtained are given in Table 3 which are in agreement with the general order of stability of complexes of Co(II), Ni (II) and Cu (II) metal ions which is established before by Grinberg *et al.* [14] and Irving *et al.* [15].

TABLE 3. APPARENT FORMATION CONSTANT VALUES β OF N-ISONICOTINAMIDOSALICYLALDIMINE COMPLEXES.

1:1			1:2		
Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
53.4×10^5	72.8×10^5	145.9×10^5	1.99×10^{11}	5.55×10^{11}	2.82×10^{12}

The stoichiometry is also confirmed by conductometric titration of 25 ml of 1×10^{-3} M of each of the metal ions with 5×10^{-3} M of the ligand in absolute ethanol. As shown in Fig. 4 the specific conductance - molar ratio curves are straight lines for the majority of the points recorded with breaks denoting the formation of 1:1 and 1:2 (M(II):L) types of complexes. It is obvious that the conductometric titration experiments confirmed the Job's plot results for Co-L, Co-L₂, Ni-L₂, Cu-L but not for Ni-L and Cu-L₂ which may be due to an experimental errors.

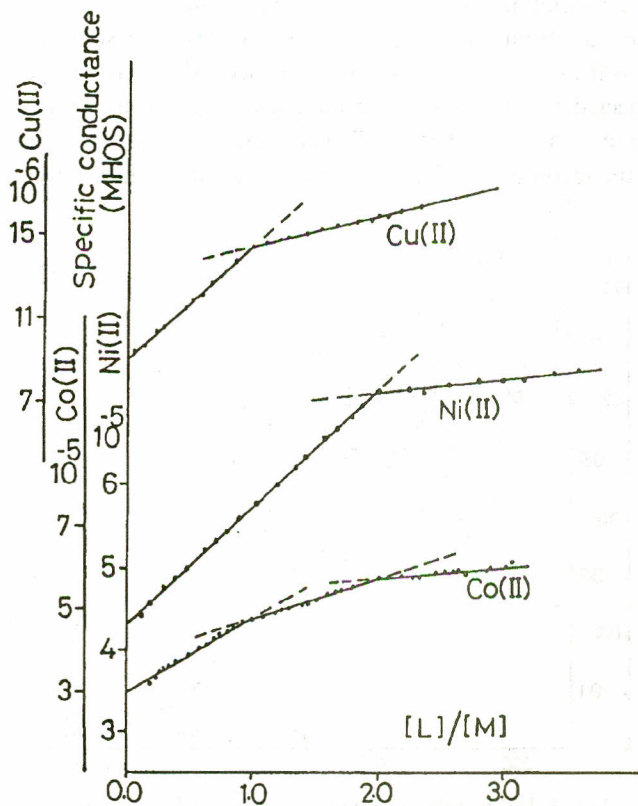


Fig. 4. Conductometric titration of 25ml of 1×10^{-3} M metal ions with 5×10^{-3} M ligand L.

TABLE 4. ELECTRONIC SPECTRAL DATA OF THE LIGAND, L AND ITS COMPLEX SOLUTIONS IN DMF.

Ligand, L	$\lambda_{\max.}, \text{nm}$ ($\epsilon_{\max.} \times 10^{-3} \text{ mole}^{-1} \text{ cm}^2$)					
	1:1 Complexes			1:2 Complexes		
	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
292(8.33)	—	293b(2.58)	—	—	284b(13.89)	295(10.33)
304(8.33)	—	—	—	—	—	305(9.99)
335(8.80)	346sh(6.40)	369(2.38)	335(5.57)	342sh(12.90)	330b(20.80)	338(9.76)
402(5.15)	439b(6.89)	412(2.02)	422b(2.04)	426b(13.66)	411b(36.50)	405b(3.59)
—	—	—	454sh(1.90)	—	—	—

b = broad and sh = shoulder

The UV-visible spectra of the DMF solutions of the different complexes were recorded as shown in Fig.5 and 6. The $\lambda_{\max.}$ and $\epsilon_{\max.}$ values of the different absorption bands observed are listed in Table 4. The spectrum of the ligand shows absorption bands at 292, 304, 335 and 402 nm. The first two bands are assigned [4] to the $\pi-\pi^*$ transitions of the aromatic and pyridyl groups. The bands at 335 and 402 nm are ascribed to an intramolecular charge transfer transitions taking place within the ligand molecule. The observed visible bands in the recorded spectra of the different complexes in the range 330 - 454 nm can be assigned to an charge transfer transitions arising from ligand-metal interactions, i.e. $L \rightarrow MCT$. This assignment is evidenced from the observed high intensities of these bands as well as the fact that this type of electronic transition is expected to be easier in the complexed ligand due to the positive charge of the coordinated metal ion. Moreover, in all the recorded spectra of the complexes, the longer wave-

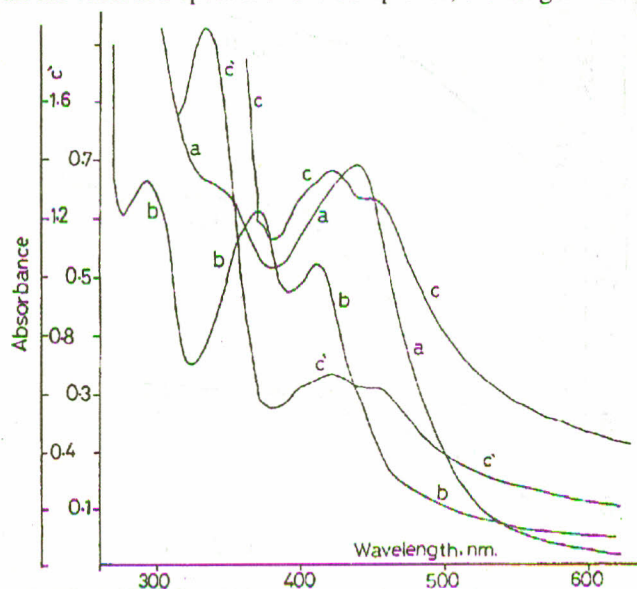


Fig. 3. UV-visible absorption spectra of DMF solutions of 1:1 L-H complexes with a:Co (II), $1 \times 10^{-4} \text{M}$, b:Ni (II), $2.5 \times 10^{-4} \text{M}$, and c:Cu(II), $3.33 \times 10^{-4} \text{M}$.

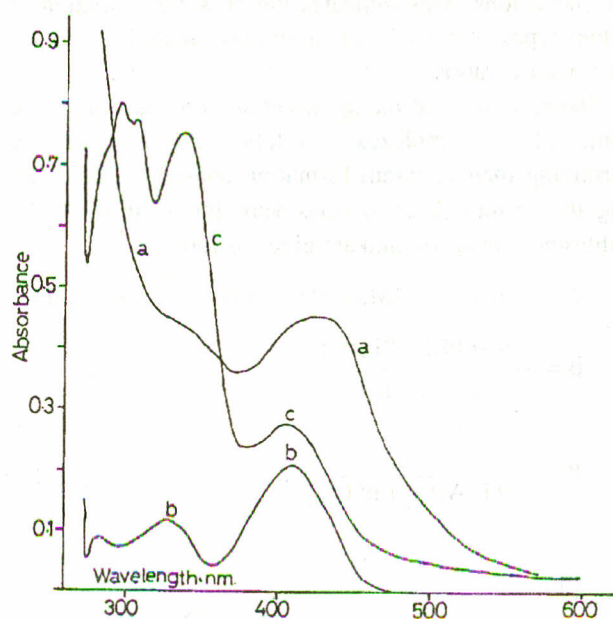


Fig. 4. UV-visible absorption spectra of DMF solutions of 1:2 L-complexes with a:Co(II), $3.33 \times 10^{-3} \text{M}$, b:Ni(II), $5.76 \times 10^{-6} \text{M}$, and c:Cu(II), $7.79 \times 10^{-5} \text{M}$.

length side of $L \rightarrow MCT$ band is associated with a low energy broad shoulder which can be attributed to a d-d electronic transition within the coordinated metal ion. This behaviour may suggest an tetrahedral structure for these complexes. This suggestion is substantiated by previous observations described by Lever [16] and Satpathy *et al.* [17] concerning the electronic spectra of tetrahedral Co(II), Ni(II) and Cu(II) complexes.

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