

Received: 20th June-2013Revised: 05th July-2013Accepted: 08th July-2013

Research article

SYNTHESIS, SPECTRAL CHARACTERIZATION OF Cu (II) AND Ni (II) COMPLEXES WITH
THIOSEMICARBAZONES AND SEMICARBAZONES DERIVED FROM PYRIDINE-2-
CARBOXALDEHYDE

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ABSTRACT: Ni (II) and Cu (II) complexes were synthesized with L¹(Pyridine-2-carboxaldehydethiosemicarbazones) and L² (Pyridine-2-carboxaldehydesemicarbazones). These complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, IR, electronic and EPR spectral studies. The molar conductance measurements on the complexes in DMSO correspond to non electrolytes nature with L¹. The molar conductance measurements with L² lie in the range 210-226 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating the complexes were 1:2 electrolyte thus the complexes may be formulated as $[\text{M}(\text{L}_2)_2]\text{X}_2$ where M= Ni (II) and Cu (II) complexes. On the basis of spectral studies an octahedral geometry has been assigned for Ni (II) complexes. A tetragonal geometry suggested for Cu (II) complexes.

Key words: Spectral studies, Nickel (II) complexes, Cu (II) complexes, Semicarbazones and Thiosemicarbazones.

INTRODUCTION

Schiff bases are regarded as “privileged ligands” due to their capability to form complexes with a wide range of transition metal ions yielding stable and intensely colored metal complexes. Some of them have been shown to exhibit interesting physical and chemical properties and potential biological activities (Chandra et. al; 2009). Thiosemicarbazones are very versatile ligands. They can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt a variety of different coordination. Thio-semicarbazones and semicarbazones act as ligands because

1. They have better co-ordination tendency.
2. They form more stable complexes.
3. They have better selectivity.
4. They may form macrocyclic ligands
5. They have the ability to produce some new and unique complexes with enhanced biological and analytical properties. Thiosemicarbazones usually act as chelating ligands with transition metal ion bonding through the sulphur and hydrazine nitrogen atom. Thiosemicarbazones and their complexes have received considerable attention because of their pharmacological activities (Kothari and Sharma, 2011). Thiosemicarbazones and their complexes have received considerable attention because of their antifungal (Prasad and Agarwal, 2007), antitumor (Ainscough et.al.,1998), antibacterial (Chandra et.al.,2009), antiamebic, antimalarial, antiviral (Kolocouris et.al., 2002), radio protective and anti-inflammatory activities. Certain thiosemicarbazones are relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of chemotherapeutic agents against cancer (Sandercock et.al., 2007) Metal complexes of Ni (II) are found to act as a sensor (R Aruna et.al., 2010).

Thiosemicarbazones as chelating ligands with transition metal ions by binding through the thioketo sulphur and hydrazine nitrogen atoms and therefore this type of compounds can coordinate in vivo to metal ions. Because of such coordination, the thiosemicarbazones moiety undergoes a sterical reorientation that could favour its biological activity. The biological activity of thiosemicarbazones is also considered to involve the inhibition of ribonucleotide reductase, an obligatory enzyme in DNA synthesis. Ribonucleotide reductase is the enzyme that converts ribonucleotide to deoxyribonucleotide, a vital enzyme in DNA synthesis and a key target for the development of antineoplastic agents. Semicarbazones are reported to possess versatile structural features and very good antifungal, antibacterial, antitrypanosomal (Cerecetto H et al., 2000) and anticonvulsant properties (Dimmock J R et al., 2000). Rhenium (V) and Ruthenium (II) complexes of 5-nitrofurylsemicarbazone were tested against the trypanocidal activity (Otero L et al., 2006).

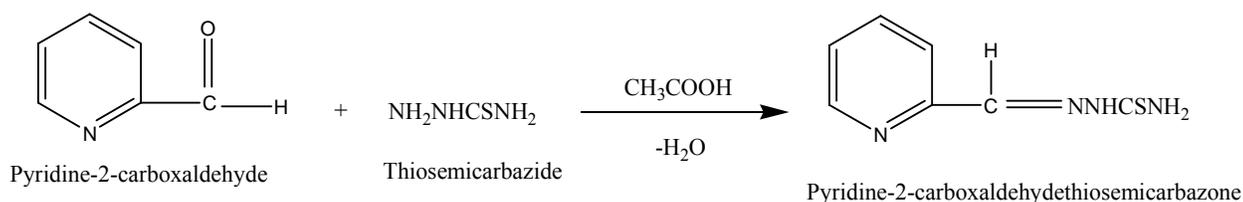
In present paper we report the synthesis and characterization of Ni (II) & Cu (II) complexes with thiosemicarbazones (L^1) and semicarbazones (L^2) derived from pyridine-2-carboxaldehyde.

MATERIAL AND METHODS

All the chemicals used in the present work were of analytical grade and procured from Sigma Aldrich. Metal salt were purchased from E. Merck and used as received. The solvent used were either spectroscopic pure SRL/BDH or purified by the recommended methods (Vogel, 1962)

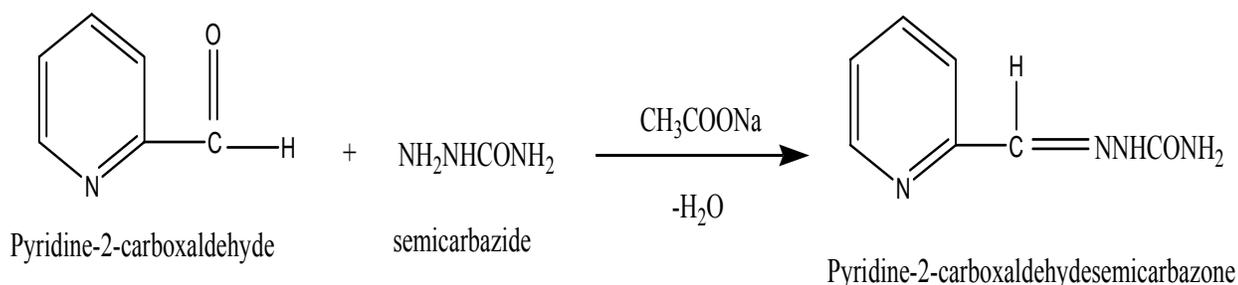
Synthesis of Schiff base ligand L^1 (Pyridine-2-carboxaldehydethiosemicarbazone)

Hot ethanolic solution (50 ml) of thiosemicarbazide (4.55 gm, 0.05 mol) and Pyridine - 2-carboxaldehyde (4.75 ml, 0.05 mol) mixed slowly with constant stirring in presence of acetic acid. This mixture was refluxed for 2 hours on a water bath. On cooling a cream colored compound was precipitated out. It was filtered washed with cold ethyl alcohol and dried under vacuum over P_4O_{10} . This reaction is a type of condensation reaction which takes place between aldehyde and thiosemicarbazide with elimination of water molecules which form thiosemicarbazones. The reaction can be represented as below.



Synthesis of Schiff base ligands L^2 (Pyridine -2-carboxaldehydesemicarbazones)

An aqueous solution (50 ml) of semicarbazide hydrochloride (5.55 gm, 0.05 mol) added in an ethanolic solution (50 ml) of corresponding aldehyde pyridine-2-carboxaldehyde (4.75 gm, 0.05 mol) in the presence of sodium acetate (4.1 gm, 0.05 mol). The reaction mixture was stirred vigorously for an hour in the magnetic stirrer. The crystalline product which formed was collected by filtration in each case washed several times with hot water and dried in vacuum over P_4O_{10} . This reaction is a type of condensation reaction which takes place between aldehyde and semicarbazide with elimination of water molecules which form semicarbazones. The reaction can be represented as below.



Synthesis of metal complexes

Hot ethanolic solution of metal salt (1mmol) e.g nickel chloride hexahydrate, nickel nitrate hexahydrate, copper chloride and copper nitrate were mixed separately with ethanolic solution of the corresponding ligands (2mmol in 20ml of absolute ethanol) e.g L¹ (Pyridine-2-carboxaldehydethiosemicarbazone (3.6 g, 0.02 mol) and L² (Pyridine-2-carboxaldehyde semicarbazone (3.28 g, 0.02 mol) than mixed together with constant stirring. The mixture was refluxed for 3-4 hour at 60-70^oc. On cooling solid colored complexes were precipitated out. The solid ppt. was filtered off, washed several times with ethanol and dried under vacuum over P₄O₁₀. Purity of the complexes was checked by the TLC color was noted, melting point was determined and yield of the complexes were calculated.

Table 1: Analytical data of ligands

Ligand	M.W	Color	M.P (^o C)	Yield (%)	Elemental analysis (%) found (Cal.)		
					C	H	N
C ₇ H ₈ N ₄ S(L ¹)	180	Shiny Yellow	178	68	46.68 (46.70)	4.46 (4.48)	31.14 (31.12)
C ₇ H ₈ N ₄ O(L ²)	164	White	135	64	51.30 (51.26)	4.84 (4.91)	34.17 (34.16)

PHYSICAL MEASUREMENTS

The C, H, N was analyzed on a carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the Elico (CM82T) conducting bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄.5H₂O as a calibrant. A mass spectrum was recorded on JEOL, JMS.DX-303 mass spectrometer. IR spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer.

RESULT AND DISCUSSION

L¹ (Pyridine- 2-carboxaldehydethiosemicarbazone)

The IR spectra of ligands show band around 3433 cm⁻¹ and 3260 cm⁻¹ which may be assigned to -NH₂ and -NH group respectively. The band due to [ν(C=N)] of pyridine ring and [ν(C=N)] of azomethane group appeared around at 620 and 1610 cm⁻¹. The mass spectrum of the free ligands (L¹) confirms the proposed formula by showing a peak at 179 amu (calculated atomic mass-180 amu) corresponding to the molecular ions (M⁺⁺¹).

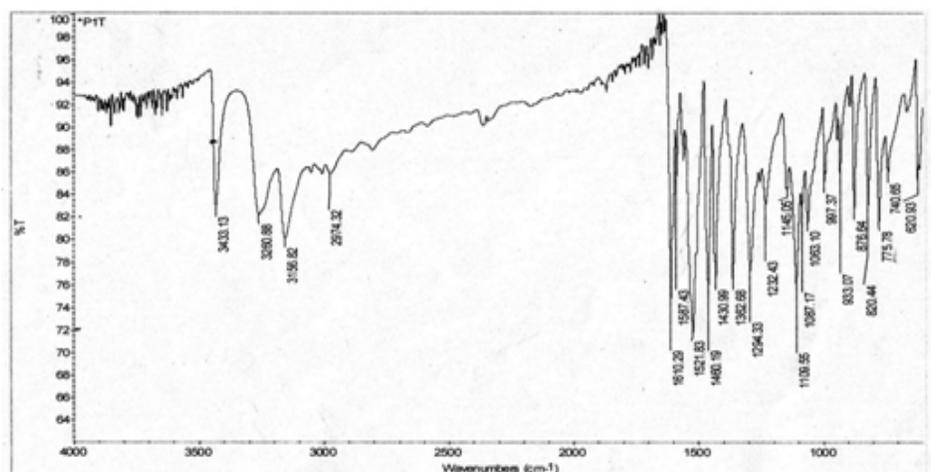


Figure 1: IR spectra of Pyridine-2-carboxaldehydethiosemicarbazone

L² (Pyridine-2-carboxaldehydesemicarbazones)

The IR spectra of ligands show bands around at 3384 cm⁻¹ and 3235 cm⁻¹ which may be assigned to -NH₂ and -NH group respectively. The band due to [ν(C=N)] and [ν(C=O)] appeared at around 1668 cm⁻¹ and 1695 cm⁻¹. The mass spectrum of the ligands L² confirm the proposed formula by showing a peak at 163 amu respectively corresponds to the molecular ions (M+⁺¹). It also shows a peak corresponding to the molecular ion (M+⁺¹). It also show a peak corresponds to loss of (-CONH₂) and various other fragments.

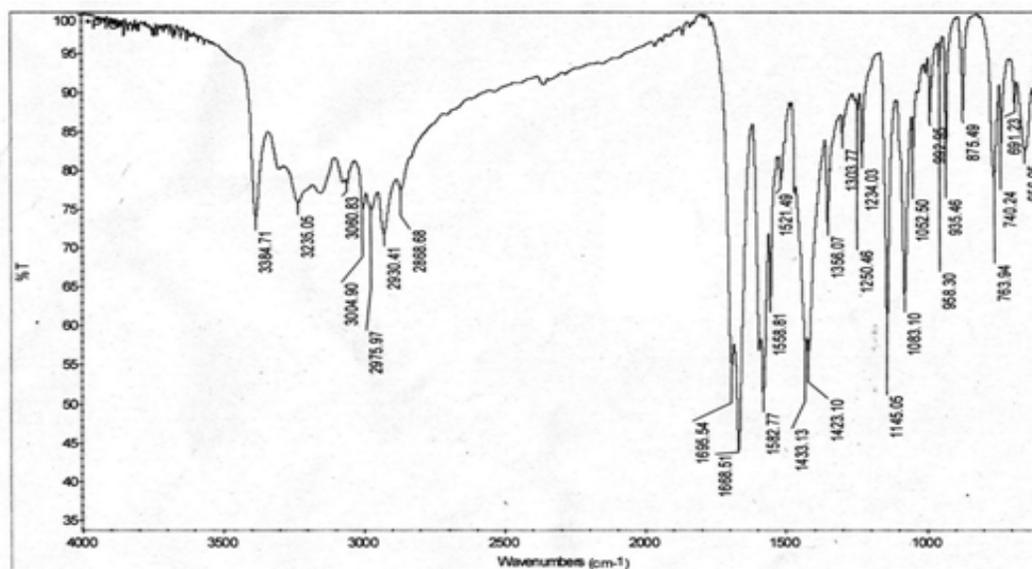


Figure 2: IR spectra of Pyridine-2-carboxaldehydesemicarbazone

¹H NMR spectra (δ, ppm) of ligands pyridine-2-carboxaldehydthiosemicarbazones (PCT)

¹H NMR spectrum of ligands L¹ (PCT) in DMSO show signal at 11.61s, (s, 1H, N (3) H); 8.53 (d, 1H, C (1) H); 7.33 (t, 1H, C(2) H); 7.80 (t, 1H, C(3) H); 8.25 (s, 1H, C (4) H); 8.07 (s, 1H, C (6) H); 8.31 (b, 2H, N (4) H)

¹H NMR spectra (δ, ppm) of ligands pyridine-2-carboxaldehydesemicarbazones (PCS)

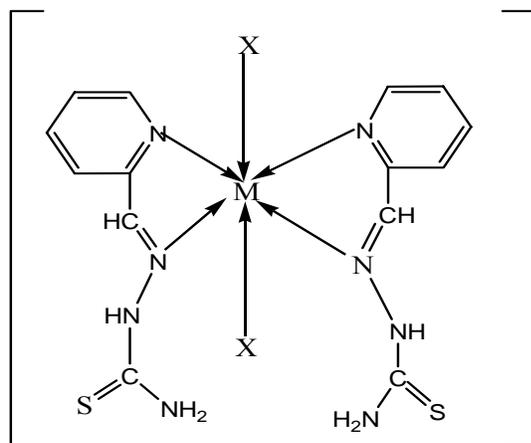
¹H NMR spectrum of ligands L² (PCS) in DMSO it show the signal at 10.51s, (s, 1H, N (3) H); 8.52 (d, 1H, C (1) H); 7.32 (t, 1H, C(2) H); 7.79 (t, 1H, C(3) H); 8.13 (s, 1H, C (4) H); 7.87 (s, 1H, C (6) H); 8.31 (b, 2H, N (4) H) Where s = singlet, d = doublet, t = triplet, b = broad

COMPLEXES

On complexation with L¹ (PCT) the bands corresponding to [ν(C=N)] shifted towards lower side while the pyridine rings vibration at around 620 cm⁻¹ shifted towards higher side due to increase in bond strength confirm the bidenting nature of the ligands coordinating through N of [ν(C=N)] azomethane and N atom of pyridine rings. On complexation with metal/metal ion with L² (PCS) the band corresponding to [ν(C=N)] and [ν(C=O)] shifted towards lower side but N atom of pyridine rings shifted towards higher side due to increase in bond strength indicate that L² (PCS) acts as a tridentate (three coordination side) ligands coordination through the pyridine N, imine N and Oxygen atom. In the IR spectra of nitrate complexes with L¹ (PCT) three bands are appeared at 1437-1467, 1316-1396 and 1064-1072 cm⁻¹ corresponding to the unidentate nature of the nitrate group which means the nitrate group are co-ordinate to the metal ion in a unidentate fashion. Structure of metal complexes with ligands L¹ (PCT) and can be represented as below. The position of the bands suggests that both the nitrates group is coordinated to the metal ion in a unidentate fashion. In the IR spectra of nitrate complexes with L² nitrate group is appeared at 1384-1394 cm⁻¹ suggest that nitrate group is uncoordinated and it is outside the coordination sphere so it do not participate in the bond formation with metal/metal ion.

Nickel (II) complexes

The value of magnetic moments for the complexes under study lies in the range from 2.85-2.92 B.M (table 3). Electronic spectra of the chloro and nitrate complexes show electronic spectral bands in the range 10,111-11,248, 14,705-14,836 and 23,364-25,906 cm^{-1} . These electronic spectral bands may be assigned to the spin allowed transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ corresponds to an octahedral geometry.



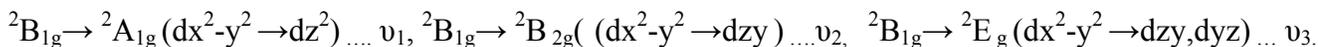
Suggested octahedral structure of the complexes with $L^1 [M(L^1)_2X_2]$ where $M=Ni(II)$ and $Cu(II)$ and $X=Cl^-$ and NO_3^-

Table 2: Elemental analysis and molar conductance data of complexes

Complex	M.W	Mol. Conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Color	M.P ($^{\circ}\text{C}$)	Yield (%)	Elemental analysis (%)			
						Found (calculated)			
						M	C	H	N
$[Ni(L^1)_2Cl_2]$	488.32	14	Green	230	60	11.86 (11.75)	34.28 (34.43)	3.26 (3.30)	22.86 (22.94)
$[Ni(L^1)_2(NO_3)_2]$	541.42	12	Green	250	62	10.52 (10.60)	30.98 (31.05)	2.94 (2.97)	25.76 (25.87)
$[Ni(L^2)_2]Cl_2$	456.32	220	Light Green	252	62	12.53 (12.58)	36.80 (36.85)	3.49 (3.53)	24.50 (24.55)
$[Ni(L^2)_2](NO_3)_2$	509.42	226	Bluish Green	280	63	11.22 (11.27)	29.93 (33.00)	3.10 (3.16)	27.40 (27.49)
$[Cu(L^1)_2]Cl_2$	494.44	12	Light Green	198	62	12.72 (12.85)	33.97 (34.00)	3.28 (3.26)	22.58 (22.66)
$[Cu(L^1)_2](NO_3)_2$	547.54	13	Green	195	60	11.68 (11.60)	30.69 (30.71)	2.91 (2.94)	25.52 (25.58)
$[Cu(L^2)_2]Cl_2$	462.44	210	Light Green	188	62	13.65 (13.74)	36.32 (36.36)	3.43 (3.48)	24.28 (24.23)
$[Cu(L^2)_2](NO_3)_2$	515.54	214	Shiny Green	186	61	12.28 (12.32)	32.58 (32.61)	3.09 (3.12)	27.12 (27.16)

Copper (II) complexes

Magnetic moment of all the Cu (II) complexes at room temperature lie in the range 1.82-1.92 BM corresponding to one unpaired electron (Table 3). The electronic spectra of six coordinated Cu^{2+} complexes have either D_{4h} or C_{4v} symmetry and the E_g and T_{2g} level, respectively. Thus three spin allowed transition are expected in the visible and near IR region. But only a few complexes are known in which such bands are resolved either by "Gaussian analysis" or by "single crystals polarization" studies. These Cu (II) complexes under study give rise absorption spectral band in the range 10,131-11,223 and 14,224-15,384 cm^{-1} and 25,316-25,641 cm^{-1} . These bands have been assigned to the following transition in order of increasing energy.



Electronic Paramagnetic Spectra

EPR spectra of Cu (II) complexes were recorded as polycrystalline sample on X-band at frequency 9.1 GHz under the magnetic field strength 3000 Gauss.

Table 3: Magnetic moment and electronic spectral data of complexes

Complexes	μ (B.M)	Electronic spectral data (cm^{-1})		
		ν_1	ν_2	ν_3
$[\text{Ni}(\text{L}^1)_2\text{Cl}_2]$	2.91	11,248	14,814	24,875
$[\text{Ni}(\text{L}^1)_2(\text{NO}_3)_2]$	2.92	11,198	14,836	23,364
$[\text{Ni}(\text{L}^2)_2\text{Cl}_2]$	2.85	10,172	14,814	25,380
$[\text{Ni}(\text{L}^2)_2(\text{NO}_3)_2]$	2.90	10,111	14,705	25,906
$[\text{Cu}(\text{L}^1)_2\text{Cl}_2]$	1.86	10,131	14,224	25,380
$[\text{Cu}(\text{L}^1)_2(\text{NO}_3)_2]$	1.82	11,223	15,384	25,316
$[\text{Cu}(\text{L}^2)_2\text{Cl}_2]$	1.92	10,288	14,224	25,380
$[\text{Cu}(\text{L}^2)_2(\text{NO}_3)_2]$	1.89	10,504	14,306	25,641

All the complexes show anisotropic EPR spectra. The g value has been calculated by Kivelson's method. $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between copper centers in the polycrystalline solid sample of the complex. According to Hathway (Hathway and Billing, 1970) if $G > 4$ the exchange interaction is negligible. If however the value of $G < 4$ than it indicates considerable exchange interaction in the solid complexes. In the complexes reported here the G value are less than 4 indicating the exchange interaction in solid complexes.

LIGANDS FIELDS PARAMETERS

Various field parameters are calculated for the complexes. The nephelauxetic parameter $\beta = B(\text{complex})/B(\text{free ion})$. Where B free ion for nickel (II) is 1041 cm^{-1} . The value of β lies in the range 0.29-0.65 (table 4). These values indicate the appreciable covalent character of metal ligands sigma bond.

Table 4: Ligands field parameters of complexes

Complexes	LFSE (kJ/mol)	Dq (cm ⁻¹)	β
[Ni(L ¹) ₂ Cl ₂]	161	1124	0.38
[Ni(L ¹) ₂ (NO ₃) ₂]	160	1119	0.29
[Ni(L ²) ₂ Cl ₂]	145	1017	0.61
[Ni(L ²) ₂ (NO ₃) ₂]	145	1011	0.65

CONCLUSION

The present work describes the synthesis of metal complexes with Schiff's base ligands PCT (L¹) and PCS (L²). The metal complexes of Ni (II) show the octahedral geometry while the metal complexes of Cu (II) show the tetragonal geometry. Molar conductance of metal complexes with L¹ indicate its non electrolytic nature as it has lower molar conductance value while metal complexes with ligands L² show its electrolytic nature as it has higher molar conductance value. In EPR spectrum G value of Cu (II) complexes less than 4 indicating the exchange interaction in solid complexes.

ACKNOWLEDGEMENTS

The authors are thankful to the principal, Zakir Husain Delhi College, University of Delhi and Mewar University Gangrar, Chittorgarh (Rajasthan) India-312901 for providing research facilities. IIT Mumbai for recording EPR spectra and IIT Delhi for recording NMR spectra

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