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SYNTHESIS, CHARACTERIZATION AND PHYSICOCHEMICAL STUDIES OF Ni(II) AND Cu(II) COMPLEXES WITH SOME NITROGEN- OXYGEN AND NITROGEN SULPHUR DONOR LIGANDS

Sulekh Chandra*[1] and Prem Ballabh [2]

Department of Chemistry Zakir Husain Delhi College University of Delhi [1], J.L.N. Marg New Delhi-110002, India
Department of Chemistry Mewar University [2], Gangrar, Chittorgarh-312 901, Rajasthan, India

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Correspondence to Author:

Dr. Sulekh Chandra

Associate Professor, Department of Chemistry Zakir Husain Delhi College University of Delhi, J.L.N. Marg New Delhi-110002, India

E-mail: schandra_00@yahoo.com

ABSTRACT: Ni(II) and Cu(II) complexes of Schiff base thiosemicarbazones (L^1) and semicarbazones (L^2) derived from pyrrole-2-carboxaldehyde. These complexes are characterized by elemental analysis, molar conductance measurements, magnetic suscepectibility measurements, mass, IR, electronic and EPR spectral studies. The molar conductance measurements of the complexes in DMSO determine the non-electrolytes and electrolytes nature of the complexes based on their molar conductance value as higher value indicates the electrolytes nature of the complexes and lower value of the molar conductance indicates the non-electrolytes nature of the complexes. On the basis of spectral studies an octahedral geometry may be assigned for Ni(II) complexes except $[Ni(L^1)_2](NO_3)_2$ which are of tetrahedral geometry. A tetragonal geometry may be suggested for Cu(II) complexes.

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 [1, 2, 3, 4, 5, 6] activities.

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 modes.

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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 [7].

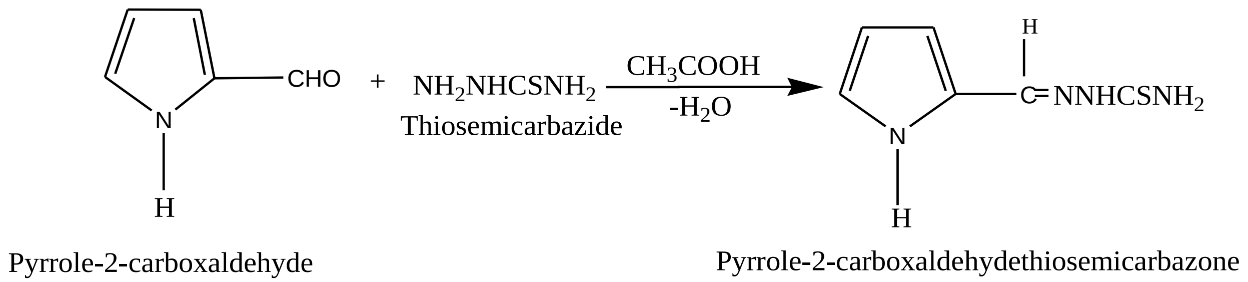
Thiosemicarbazones and their complexes have received considerable attention because of their antifungal [8, 9, 10 ,11, 12], antitumor [13, 14, 15] antibacterial [16] antiamoebic, antimalarial, antiviral, radio protective and anti-inflammatory activities. Certain thiosemicarbazones are relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of chemotherapeutic agents against cancer [17]. Metal complexes of Ni(II) are found to act as a sensor [18] and also nanoparticle act as a sensor [19].

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 pyrrole-2-carboxaldehyde.

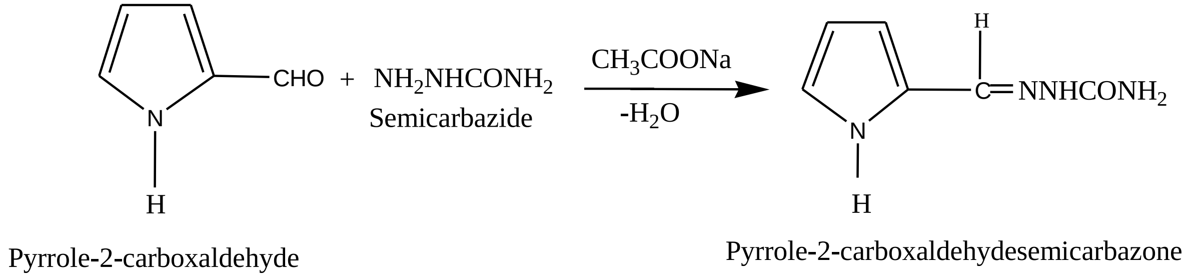
MATERIAL AND METHODS:

Chemicals: All the chemicals used in the present work were of analytical grade and procured from Sigma Aldrich Banglore India. 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 (Pyrrole-2-carboxaldehyde thiosemicarbazone): Hot ethonolic solution (50 ml) of thiosemicarbazide (4.55 gm, 0.05 mol) and pyrrole-2-carboxaldehyde (4.75 gm, 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/ketone and thiosemicarbazide with elimination of water molecules which form thiosemicarbazones. The reaction can be represented as below.



Synthesis of Schiff base ligands L^2 (Pyrrole-2-carboxaldehyde semicarbazones): An aquouse solution (50 ml) of semicarbazide hydrochloride (5.55 gm, 0.05 mol) added in an ethonolic solution (50 ml) of corresponding aldehyde pyrrole-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/ketone 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 (0.238g), nickel nitrate hexahydrate (0.292 g) were mixed with ethanolic solution of the corresponding ligands (2mmol in 20ml of absolute ethanol) e.g. pyrrole-2-carboxaldehyde thiosemicarbazone (1.9g, 0.02 mol). The mixture was heated under refluxed for 40 hour at room temperature. The solid ppt. was filtered off, washed several times with ethanol and dried over calcium (II) chloride.

Crystals were obtained by dissolving the complex in DMSO and allowing slow evaporation over a period of 6 weeks. Purity of the complexes was checked by the TLC color was noted, melting point was determined and yield of the complexes were calculated.

Physical Measurements: C, H, N were 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 $CuSO_4.5H_20$ 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:

L^1(P2CTS): The IR spectra of ligands show band around 3448 cm^{-1} and 3267 cm^{-1} which may be assigned to $–NH_2$ and –NH group respectively. The band due to [υ(C=S)] and [υ(C=N)] group appeared around at 1109 and 1587 cm^{-1}.

TABLE 1: ANALYTICAL DATA OF LIGANDS

Ligand	M.W.	Color	M.P. (^oC)	Yield (%)	Elemental analysis (%) found (Cal.)		
					C	H	N
$C_6H_8N_4S(L^1)$	168	White	152-155	73	43 (42.8)	4.7 (4.8)	33.6 (33.3)
$C_6H_8N_4O(L^2)$	152	White	204-206	78	47.5 (47.3)	5.0 (5.3)	36.7 (36.8)

The mass spectrum of the free ligands (L^1) confirms the proposed formula by showing a peak at 169 amu corresponding to the molecular ions (M^+ +1). It also show a peak corresponds to loss of ($-CSNH_2$) and various other fragments.

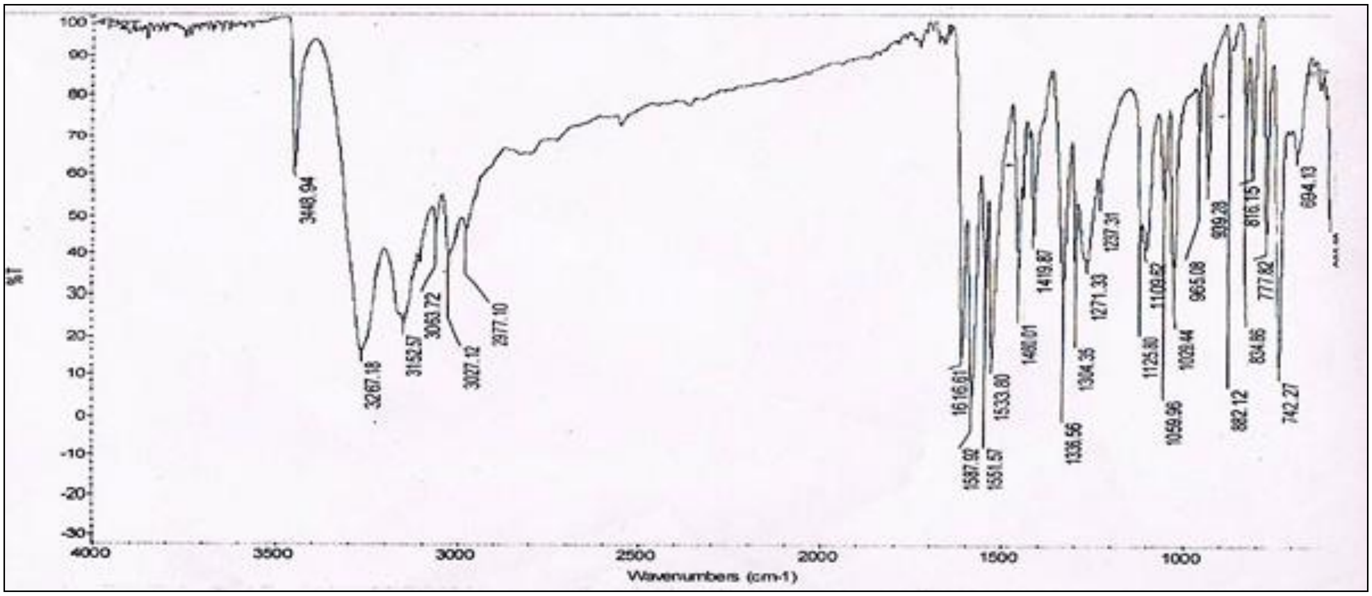


FIGURE 1: IR SPECTRA OF PYROLLE-2-CARBOXALDEHYDETHIOSEMICARBAZONE

L^2(P2CS): The IR spectra of ligands show bands around at 3448 cm^{-1} and 3325 cm^{-1} which may be assigned to $-NH_2$ and -NH group respectively. The band [υ(C=N)] appeared at around 1631 cm^{-1}. The mass spectrum of the ligands L^2 confirm the proposed formula showing a peak at 153 Amu respectively corresponds to the molecular ions ($M+^{+1}$). It also shows a peak corresponding to the molecular ion ($M+^{+1}$).

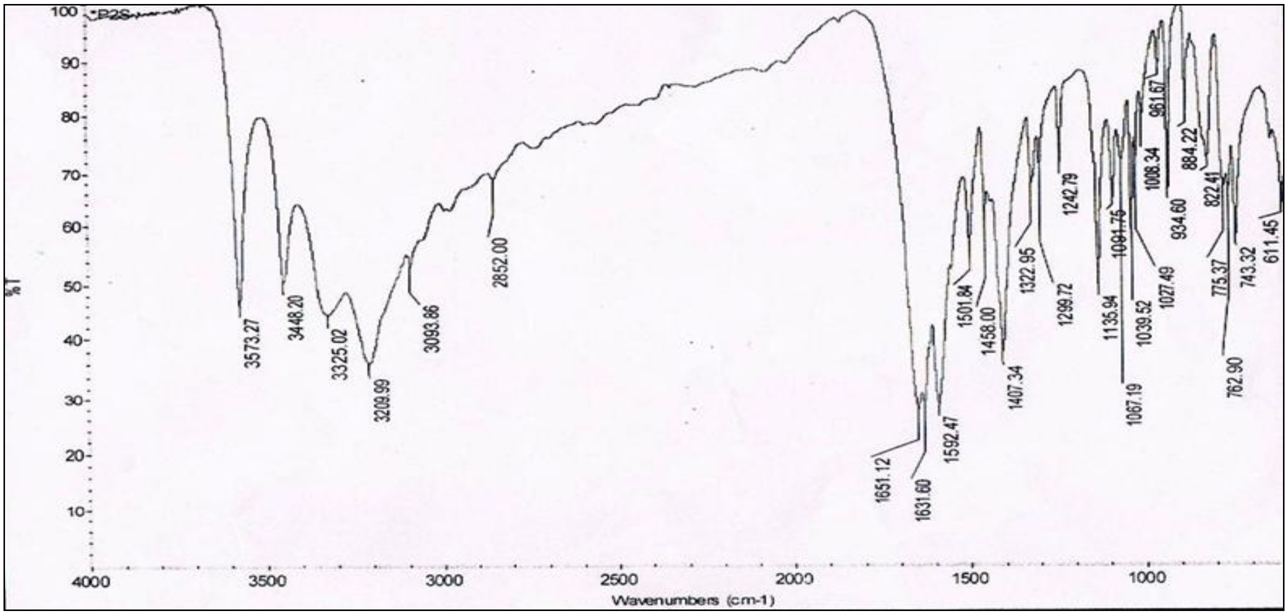


FIGURE 2: IR SPECTRA OF PYROLLE-2-CARBOXALDEHYDE SEMICARBAZONE

^{1}H NMR Spectra of L^1(P2CTS) and L^2(P2CS): The ^{1}H NMR Spectrum of the ligands L^1(P2CTS) and L^2(P2CS) were recorded in DMSO. Chemical shift (δ, ppm) were listed in **table 2**. The spectrum of L^1(P2CTS) and L^2(P2CS) exhibit two resonance for the N(4) H_2 proton showing that rotation about the C(S)-N(4)H_2 and C(O)-N(4)H_2 is prevented by its partial double bond character. The signal at δ 7.80 and δ 7.62 is attributed to the methine proton.

TABLE 2: ^{1}H NMR SIGNAL (δ, ppm) OF L^1(P2CTS) AND L^2(P2CS)

Ligand	N(1)	N(3)	N(4)	C(5)	C(1)	C(2)	C(3)
$C_6H_8N_4S$ (L^1)	11.33	11.21	8.05 7.85	7.80	6.94	6.37	**6.08**
$C_6H_8N_4O$ (L^2)	11.52	11.20	8.35 7.83	7.62	6.97	6.47	**6.039**

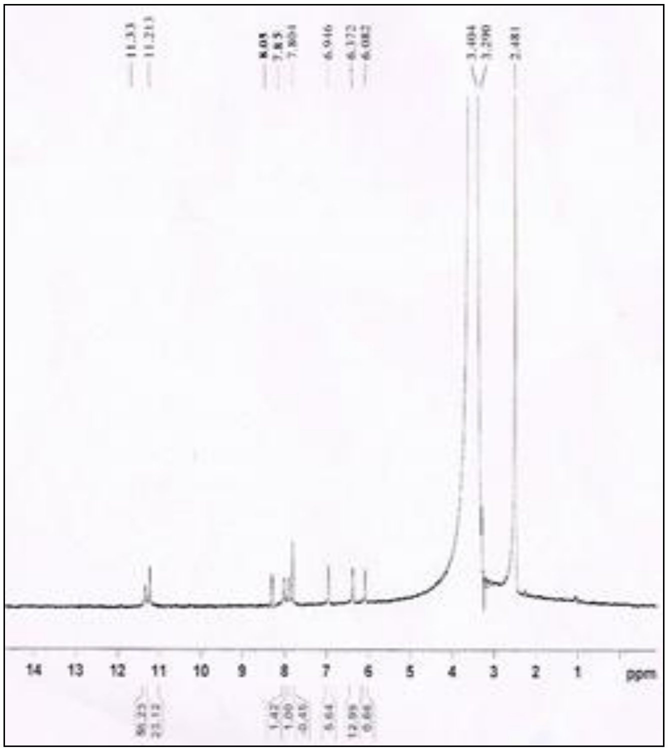


FIGURE 3: ^{1}H NMR SPECTRA OF L^1(P2TCS)

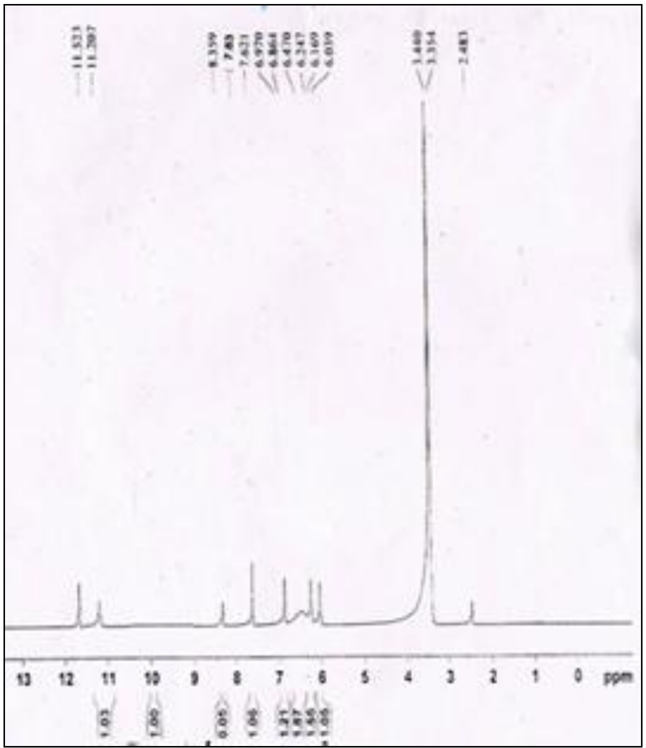


FIGURE 4: ^{1}H NMR SPECTRA OF L^2(P2TCS)

Complexes: On complex formation most of the bands in the IR spectrum of the ligands undergoes frequency shift towards lower side (around 20-30 cm^{-1}) suggests that the ligands act as bidenting chelating agents coordinating through nitrogen of [υ(C=N)] group and sulphur of [υ(C=S)] group.

In case of thiosemicarbazones the bands of [υ(C=N)] and [υ(C=S)] shifted towards lower side acts as bidentate chelating agents coordinating through nitrogen of [υ(C=N)] group and sulphur of [υ(C=S)] group. In case of semicarbazones the bands of [υ(C=N)] and [υ(C=O)] shifted towards lower side acts as bidentate chelating agent coordination through nitrogen of [υ(C=N)] and oxygen of [υ(C=O)] group. On the basis of elemental analysis the complexes were found to have the composition shown in **table 3**. The molar conductance measurements of all the complexes in DMSO corresponds to non-electrolyte nature except $[Ni(L^1)_2](NO_3)_2$ which is 1:2 electrolyte because anion do not participate in the bond formation with central metal/metal ion.

The complexes may be formulated as $[M(L)_2X_2]$ where M = Ni (II), Cu(II), L= L^1,L^2 and X = Cl^-, NO_3^-. The value of the molar conductance of complexes is mainly based on the mobility of the ions in the solution. The larger value of conductance indicates the higher mobility of the ions and smaller value of conductance indicates lower mobility of the ions in the solution. It is also temperature dependent because as the temperature increases kinetic energy of the complexes ions in the solution increases which leads the higher mobility of the complexes ions as a result the molar conductance of the complexes increases in the solution in which it is dissolves. The value of molar conductance of Ni(II) and Cu(II) complexes are listed in table 3.

IR spectra of $[Ni(L^1)_2](NO_3)_2$ complex show sharp and strong band at 1384 cm^{-1} indicate that the nitrate group is uncoordinated. IR spectra of nitrate complexes with ligands L^2 display three absorption bands around at 1420-1440, 1290-1320 and 1020-1050 cm^{-1} suggesting that both the nitrate group are coordinated to the metal ion.

TABLE 3: ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCE DATA OF COMPLEXES

Complex	M.W.	Mol. Conductance (Ω^{-1} cm^{2}mol^{-1})	Color	M.P (^{0}C)	Yield (%)	Elemental analysis (%) Found (calculated)			
						M	C	H	N
$[Ni(L^1)_2Cl_2]$	464.32	12	Bluish brown	202	60	12.44 (12.36)	31.10 (31.04)	3.61 (3.47)	24.29 (24.13)
$[Ni(L^1)_2](NO_3)_2$	517.43	150	Dark green	204	63	11.54 (11.09)	27.58 (27.85)	3.28 (3.11)	26.92 (27.07)
$[Ni(L^2)_2Cl_2]$	432.32	14	Brown	246	62	13.32 (13.28)	33.54 (33.33)	3.43 (3.73)	25.59 (25.91)
$[Ni(L^2)_2(NO_3)_2]$	485.43	14	Light green	238	62	11.80 (11.82)	29.36 (29.69)	3.03 (3.32)	28.74 (28.85)
$[Cu(L^1)_2Cl_2]$	470.44	24	Brown	190	64	13.87 (13.50)	30.60 (30.63)	3.40 (3.42)	23.58 (23.81)
$[Cu(L^1)_2(NO_3)_2]$	523.55	13	Black	188	60	12.35 (12.13)	27.74 (27.52)	3.22 (3.08)	26.58 (26.75)
$[Cu(L^2)_2Cl_2]$	438.44	16	Dark Green	236	62	14.26 (14.49)	32.72 (32.87)	3.42 (3.67)	25.31 (25.55)
$[Cu(L^2)_2(NO_3)_2]$	491.55	18	Black	229	61	12.69 (12.92)	29.51 (29.32)	3.50 (3.28)	28.68 (28.49)

Nickel (II) complexes: The value of magnetic moments of Ni(II) complex at room temperature lies in the range from 2.92-3.96 B.M (**table 4**). These values are in tune with a high spin configuration and show the presence of an octahedral environment around the Ni^{2+} ion in the complex. Electronic spectra of the chloro and nitro complexes (except nitrate complexes with ligands (L^1) show electronic spectral bands in the range 9551-13,000, 11,000-20,000 and 19,000-27,000 cm^{-1}. The ground state Ni(II) is an octahedral coordination is $^3A_{2g.}$ These value are in a tune with the spin allowed transitions $^3A_{2g}$ (F) → $^3T_{2g}$(F), $^3A_{2g}$ (F) → $^3T_{1g}$ (F), $^3A_{2g}$ (F) →$^3T_{1g}$ (P) corresponds to an octahedral geometry. The nitrates complexes of Ni(II) with ligands L^1 have medium intensity electronic spectral band around at

9000 cm^{-1} assigned as υ_1. The band at 14,640 cm^{-1} corresponds to υ_2 is not splits. As the excited state is an orbitally non degenerate. The υ_3 data appears at 24,000 cm^{-1} indicates tetrahedral geometry.

Copper (II) complexes: At room temperature Cu(II) complex show magnetic moment in the range 1.86-2.08 B.M corresponding to one unpaired electron (**table 4**). The electronic spectra of six coordinated Cu^{2+} have both D4h or C4v 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 13,227-15,748 and 16,600-19,400 cm^{-1} corresponds to the tetragonal geometry. These bands have been assigned to the following transition in order of increasing energy.

$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2B_{2g}$

EPR spectra of Cu(II) complexes were recorded polycrystalline solid sample on X-band frequency 9.1 GHz under the magnetic field strength 3000 Gauses. All the complexes show anisotropic EPR spectra of the complex. According to Hathway if G>4 the exchange interaction is negligible but G<4 indicate considerable exchange interaction in the solid complex. The complexes reported here has the G value are less than 4 indicating the exchange interaction in solid complexes. The g value has been calculated by Kivelson’s method. $G = (g_{\parallel}-2)/(g_{\perp}-2)$, which measure the exchange interaction between copper center in the polycrystalline solid sample of the complex.

TABLE 4: MAGNETIC MOMENT (B.M) AND ELECTRONIC SPECTRAL DATA (CM^{-1}) OF COMPLEXES

Complexes	μ (B.M.)	Electronic spectral data(cm^{-1})		
		υ_1	υ_2	υ_3
$[Ni(L^1)_2Cl_2]$	2.92	9551	14,224	23,809
$[Ni(L^1)_2](NO_3)_2$	2.96	8928	14,640	24,000
$[Ni(L^2)_2Cl_2]$	3.03	9746	14,814	25,380
$[Ni(L^2)_2(NO_3)_2]$	3.96	9746	14,306	25,380
$[Cu(L^1)_2Cl_2]$	2.08	13,297	16,680	-
$[Cu(L^1)_2(NO_3)_2]$	1.96	13,227	16,640	-
$[Cu(L^2)_2Cl_2]$	1.86	15,748	16,600	-
$[Cu(L^2)_2 (NO_3)_2]$	1.92	15,290	19,400	-

Ligands fields Parameters: Various ligands field parameters were calculated for the complexes and are listed in table 4. The nephelauxetic parameter β= B (complex)/B (free ion). Where B free ion for Nickel(II) is 1041 cm^{-1}. The value of β lies in the range 0.60-0.75 (**table 5**). These values indicate the appreciable covalent character of metal ligands sigma bond.

TABLE 5: LIGAND FIELD PARAMETERS OF COMPLEXES

Complexes	LFSE (kj/mol)	Dq (cm^{-1})	β
$[Ni(L^1)_2Cl_2]$	137	955	0.60
$[Ni(L^1)_2](NO_3)_2$	85	892	0.75
$[Ni(L^2)_2Cl_2]$	139	974	0.69
$[Ni(L^2)_2(NO_3)_2]$	139	974	0.66

CONCLUSION: Ni(II) and Cu(II) complexes of Schiff base derived from pyrrole-2-carboxaldehyde were synthesized and characterized using various spectral techniques. The IR result demonstrate that on complexation with L^1 the bands corresponding [v(C=N)], [v(C=S)] and on complexation with L^2 the bands corresponding [v(C=N)], [v(C=O)] shifted towards lower side suggest the bidenting nature of ligands L^1 and L^2. Electronic spectra and magnetic measurement indicate that the complex exhibit octahedral geometry except $[Ni(L^1)_2](NO_3)_2$ which has tetrahedral geometry.

A tetragonal geometry may be suggested for Cu(II) complexes. EPR of the Cu complex measures the exchange interaction which is less than 4.

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