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# Electronic, epr and magnetic studies of Co(II), Ni(II) and Cu(II) complexes with thiosemicarbazone (L<sup>1</sup>) and semicarbazone (L<sup>2</sup>) derived from pyrole-2-carboxyaldehyde

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#### Abstract

Co(II), Ni(II) and Cu(II) complexes are synthesized with thiosemicarbazone (L<sup>1</sup>) and semicarbazone (L<sup>2</sup>) derived from pyrole-2-carboxyaldehyde. These complexes are characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, mass, IR, electronic and EPR spectral studies .The molar conductance measurements of the complexes in DMSO correspond to non-electrolytic nature except  $Co(L^1)_2(NO_3)_2$  and  $Ni(L^1)_2(NO_3)_2$  complexes which are 1:2 electrolytes. All the complexes are of high-spin type. On the basis of spectral studies an octahedral geometry may be assigned for Co(II) and Ni(II) complexes except  $Co(L^1)_2(NO_3)_2$  and  $Ni(L^1)_2(NO_3)_2$  which are of tetrahedral geometry. A tetragonal geometry may be suggested for Cu(II) complexes. © 2006 Elsevier B.V. All rights reserved.

Keywords: Anti HIV; Molar conductance; IR spectrum

# 1. Introduction

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 [1]. The metal complexes show more activities as compared to the free thiosemicarbazones and semicarbazones. They may have numerous applications, e.g. anticancer [2], fungicides, antibacterial [3,4], antiviral [5,6], antifungal [7,8], anti HIV [9], antitumour [10] and other biological activities [11–13]. Particularly first row of transition metal complexes with such ligands have a wide range of biological activities [14–18].

In view of the above applications it is highly desirable to synthesize and characterize transition metal complexes with such ligands. In the present paper we report the synthesis and characterization of complexes with thiosemicarbazone ( $L^1$ ) and semicarbazone ( $L^2$ ) (Fig. 1) derived from pyrole-2-carboxyaldehyde.

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# 2. Experimental

All the chemicals used were of analytical grade and procured form Sigma–Aldrich. Metal salts were purchased from E. Merck and were used as received.

## 2.1. Preparation of ligands

Ligands  $L^1$  and  $L^2$  were prepared by following methods.

## 2.1.1. Ligand $L^1$

Hot ethanolic solution (20 mL) of a pyrole-2-carboxyaldehyde (0.95 g, 0.01 mol) was mixed with hot ethanolic solution of thiosemicarbazide (0.95 g, 0.01 mol). The contents were refluxed for about 2–3 h on a water bath. On cooling the contents the white colored compound separated out. The same was filtered, washed with 50% ethanol and dried in vacuum over  $P_4O_{10}$ . Yield 72%, mp 153–155 °C. Elemental analysis found % C 43.0, H 4.6, N 33.5 calculated for C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>S (molecular mass 168 amu) % C 42.8, H 4.8, N 33.31.

# 2.1.2. Ligand $L^2$

An aqueous solution (20 mL) of semicarbazone HCl (1.11 g, 0.01 mol) was added to a ethanolic solution (20 mL) of pyrole-

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Fig. 1. Structure of ligands: Y = S, for  $L^1$ ; Y = O, for  $L^2$ .

2-carboxyaldehyde (0.95 g, 0.01 mol) in the presence of sodium acetate (1.36 g, 0.01 mol). The reaction mixture was stirred vigorously for around an hour. The crystalline white product which formed was collected by filtration, washed several times with hot water and dried in vacuum over  $P_4O_{10}$ . Yield 78%, mp 203–206 °C. Elemental analysis found % C 47.8, H 5.0, N 36.9 calculated for  $C_6H_8N_4O$  (molecular mass 152 amu) % C 47.36, H 5.3, N 36.8.

#### 2.2. Synthesis of complexes

Hot ethanolic solution (20 mL) of corresponding metal salts (0.005 mol for each case) was mixed with hot ethanolic solution of the respective ligand (0.01 mol) and refluxed for 3–4 h on a water bath. On cooling the contents, the colored complex separated out in each case. The same was filtered, washed with 50% ethanol and dried in vacuum over  $P_4O_{10}$ . Purity of the complexes was checked by TLC.

#### 2.3. Physical measurements

The C, H, N was analyzed on a Carlo-Erba1106 elemental analyzer. Molar conductance was measured on the Eleco (CM82T) conducting bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO<sub>4</sub>·5H<sub>2</sub>O as a calibrant. Mass spectra were recorded on JEOL, JMS.DX-303 Mass spectrophotometer. 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. EPR spectra of the complexes were recorded as polycrystalline sample at LNT for Co(II) complexes and at room temperature for Cu(II) complexes on E4-EPR spectrometer using DPPH as the g-marker.

#### 3. Results and discussion

# 3.1. Ligand $L^1$

The IR spectrum of ligand L<sup>1</sup> shows bands at 3380 and  $3171 \text{ cm}^{-1}$  which may be assigned to  $-\text{NH}_2$  and -NH groups, respectively. The bands due to  $\nu(-\text{C=S})$  and  $\nu(-\text{C=N})$  groups appeared at 1107 and 1597 cm<sup>-1</sup>. The mass spectrum of free ligand L<sup>1</sup> confirms the proposed formula by showing a peak at



169 amu corresponding to the molecular ion  $(M^+ + 1) C_6 H_8 N_4 S$ . It also shows a peak at 108 amu corresponding to loss of  $(-\text{CSNH}_2)$  and various other fragments (Fig. 2).

# 3.2. Ligand $L^2$

The IR spectrum of ligand  $L^2$  shows bands at 3380 and  $3171 \text{ cm}^{-1}$  which may be assigned to  $-\text{NH}_2$  and -NH group, respectively. The band  $\nu(-\text{C=N})$  appeared at 1601 cm<sup>-1</sup>. The mass spectrum of free ligand  $L^2$  confirm the proposed formula by showing a peak at 153 amu corresponding to the molecular ion  $(M^+ + 1) C_6H_8N_4O$ . It also shows a peak corresponding to loss of  $(-\text{CONH}_2)$  at 108 amu and various other fragments (Fig. 3).

# 3.3. Complexes

On complexation the bands corresponding to  $\nu(-C=N)$  and  $\nu(-C=S)$  (in case of thiosemicarbazone) shifted towards lower side (around Ca 20–30 cm<sup>-1</sup>) suggest that the ligand acts as bidentate chelating agent coordinating through nitrogen of  $\nu(-C=N)$  group and sulphur of  $\nu(-C=S)$  group. In case semicarbazone the band of  $\nu(-C=N)$  and the band of  $\nu(-C=O)$  shifted towards lower side (around Ca 20–30 cm<sup>-1</sup>) suggests that the ligand also acts as bidentate chelating agent coordinating through nitrogen of  $\nu(-C=N)$  group and oxygen of  $\nu(-C=O)$  group.

On the basis of elemental analysis the complexes were found to have the composition as shown in Table 1.



 Table 1

 Elemental analysis and molar conductance data of complexes

Complex	Molar conductance $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$	Color	mp (°C)	Yield (%)	Elemental analysis data found (calculated)			
					М	С	Н	Ν
$\overline{\text{Co}(\text{L}^1)_2\text{Cl}_2}$	11	Purple	195	67	12.40 (12.64)	30.72 (30.90)	3.20 (3.43)	24.27 (24.03)
$Co(L^1)_2(NO_3)_2$	120	Black	200	65	10.25 (10.73)	26.00 (26.23)	2.68 (2.91)	25.28 (25.50)
$Co(L^2)_2Cl_2$	15	Black	243	62	13.35 (13.58)	33.41 (33.18)	3.46 (3.68)	26.08 (25.81)
$Co(L^2)_2(NO_3)_2$	10	Pink	245	60	12.36 (12.10)	29.23 (29.57)	3.53 (3.28)	28.53 (28.75)
$Ni(L^1)_2Cl_2$	14	Bluish brown	200	60	12.43 (12.60)	30.70 (30.92)	3.60 (3.43)	24.28 (24.04)
$Ni(L^1)_2(NO_3)_2$	150	Dark brown	205	62	11.55 (11.31)	27.59 (27.76)	3.29 (3.08)	26.73 (26.99)
$Ni(L^2)_2Cl_2$	12	Brown	245	62	13.31 (13.53)	33.53 (33.20)	3.42 (3.68)	25.58 (25.82)
$Ni(L^2)_2(NO_3)_2$	145	Light green	238	61	12.28 (12.06)	29.34 (29.58)	3.03 (3.28)	28.53 (28.76)
$Cu(L^1)_2Cl_2$	22	Brown	190	62	12.88 (12.69)	22.54 (28.76)	3.42 (3.19)	22.59 (22.37)
$Cu(L^1)_2(NO_3)_2$	13	Black	187	59	12.36 (12.13)	27.77 (27.50)	3.23 (3.05)	26.57 (26.74)
$Cu(L^2)_2Cl_2$	16	Dark green	235	62	14.24 (14.48)	32.71 (32.83)	3.40 (3.64)	25.30 (25.53)
$Cu(L^2)_2(NO_3)_2$	175	Black	227	60	12.68 (12.92)	29.52 (29.29)	3.50 (3.25)	28.69 (28.48)

The molar conductance measurements of the complexes in DMSO correspond to non-electrolytic nature [19] except  $Co(L^1)_2(NO_3)_2$  and  $Ni(L^1)_2(NO_3)_2$  complexes which are 1:2 electrolyte. Thus all the complexes may be formulated as  $[M(L)_2X_2]$  where M = Cu(II), Co(II) and Ni(II) and  $X = Cl^-$ ,  $NO_3^- [L = L^1$  and  $L^2$ ] except  $[Co(L^1)_2](NO_3)_2$  and  $[Ni(L^1)_2]$   $(NO_3)_2$ .

IR spectra of  $Co(L^1)_2(NO_3)_2$  and  $Ni(L^1)_2(NO_3)$  complexes show sharp and strong band at 1384 cm<sup>-1</sup> indicate that the nitrate group is uncoordinated. IR spectra of nitrate complexes of Co(II) and Ni(II) with L<sup>2</sup> display three absorption bands around at 1415–1440, 1290–1320 and 1020–1050 cm<sup>-1</sup> suggesting that both the nitrate groups are coordinated to the metal ion (Fig. 4) [20–23].



Fig. 4. IR spectral bands of the anions.

Table 2 Magnetic moment (BM) and electronic spectral data  $(cm^{-1})$  of complexes

Complex	$\mu$ eff BM	Electronic spectral data			
		$\nu_1$	$\nu_2$	ν <sub>3</sub>	
$\overline{\text{Co}(\text{L}^1)_2\text{Cl}_2}$	4.87	9,400	14,380	21,090	
$Co(L^1)_2(NO_3)_2$	4.91	5,590	14,890	21,000	
$Co(L^2)_2Cl_2$	4.88	9,396	14,420	21,360	
$Co(L^2)_2(NO_3)_2$	4.90	6,115	15,500	21,150	
$Ni(L^1)_2Cl_2$	2.92	9,620	14,560	25,060	
$Ni(L^1)_2(NO_3)_2$	2.95	7,900	14,640	24,000	
$Ni(L^2)_2Cl_2$	3.01	9,770	15,250	24,600	
$Ni(L^2)_2(NO_3)_2$	3.98	9,620	14,525	24,000	
$Cu(L^1)_2Cl_2$	2.06	13,280	16,680	_	
$Cu(L^1)_2(NO_3)_2$	1.98	13,220	16,640	_	
$Cu(L^2)_2Cl_2$	1.88	15,742	16,600	_	
$Cu(L^2)_2(NO_3)_2$	1.90	15,290	19,400	-	

#### 3.4. Copper (II) complexes

Magnetic moment of all the Cu(II) complexes at room temperature lie in the range 1.88–2.06 BM corresponding to one unpaired electron (Table 2). The electronic spectra of six coordinated Cu<sup>2+</sup> complexes have either D<sub>4h</sub> or C<sub>4v</sub> symmetry and the E<sub>g</sub> and T<sub>2g</sub> levels of the <sup>2</sup>D free ion term will split into B<sub>1g</sub>, A<sub>1g</sub>, B<sub>2g</sub>, E<sub>g</sub> levels, 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 crystal polarization" studies. These Cu(II) complexes under study give rise absorption spectral band in the range 13,220–15,750 and 16,260–20,000 cm<sup>-1</sup>. These bands have been assigned to the following transition in order of increasing energy [24,25]:

$${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}, \qquad {}^{2}B_{1g} \rightarrow {}^{2}A_{2g}.$$

EPR spectra of Cu(II) complexes were recorded as polycrystalline sample on X-band at frequency 9.5 GHz under the magnetic field strength 3400 Gauss. All the complexes show anisotropic EPR spectra [26]. The g values have been calculated by Kivelson's method [27].  $G = (g_{11} - 2)/(g_1 - 2)$ , which measures the exchange interaction between copper centers in the polycrystalline solid sample of the complex have also been calculated. According to Hathaway [28,29] if the value of *G* is above four then exchange interaction is negligible, if however the value of *G* is less than four 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.

#### 3.5. Nickel(II) complexes

The value of magnetic moments for the complexes under study lies in the range from 2.92 to 3.98 BM (Table 2). Under study electronic spectra of the chloro and nitrate complexes (except nitrate complex with ligand  $L^1$ ) show electronic bands in the range 8580–13,000, 11,000–20,000 and 19,000–27,000 cm<sup>-1</sup> and may be assigned to the spin allowed

transitions  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}$ ,  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ ,  ${}^{3}A_{2g}(P) \rightarrow {}^{3}T_{1g}(P)$  corresponding to an octahedral geometry The nitrato complex of Ni(II) with L<sup>1</sup> under study have medium intensity band around at 9000 cm<sup>-1</sup> assigned as  $\nu_1$ . The band at 10,000–15,000 cm<sup>-1</sup> corresponds to  $\nu_2$  and it is not split, as the excited state is orbitally non-degenerates. The  $\nu_3$  transition appears at 14,000–25,000 cm<sup>-1</sup> indicates tetrahedral geometry.

#### 3.6. Cobalt(II) complexes

At room temperature all the complexes under study show magnetic moment in the range 4.87-4.91 BM (Table 2) corresponding to three unpaired electrons. The electronic spectra of Co(II) complexes (except nitrate complex with L<sup>1</sup>) display electronic spectral bands in the range 7000-9500, 14,000-17,000 and  $20,000-21,500 \text{ cm}^{-1}$ . These may be assigned to the following transitions  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ ,  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ ,  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$  characteristic to an octahedral geometry whereas the nitrate complex with  $L^1$  show three electronic spectral bands around 5000, 8000 and 19,000 cm<sup>-1</sup> corresponding to the following transitions  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}(F)$ ,  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$ ,  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$  characteristic to tetrahedral geometry. The  ${}^{4}F$ State of d<sup>7</sup> in an octahedral crystal field is split into three states. Since these states are connected by the spin orbit coupling the spin lattice relaxation times are short making epr measurements possible only at very low temperature. EPR spectra of the complexes recorded as polycrystalline sample at liquid nitrogen temperature and g values are given in Table 3.

#### 3.7. Ligand field parameters

Various ligand field parameters are calculated for the complexes. The value of Dq in Co(II) complexes were calculated from transition energy ratio diagram using the  $v_3/v_2$  ratio[30]. The Nephelauxetic parameter  $\beta$  was readily obtained by using the relation  $\beta = B$  (complex)/B (free ion), where B free ion for Ni(II) is 1041 cm<sup>-1</sup> and for Co(II) is 1120 cm<sup>-1</sup> [31,32]. The  $\beta$  lies in the range of 0.61–0.95 (Table 3). These values indicate the appreciable covalent character of metal ligand  $\sigma$ bond.

Table 3	
Ligand field parameter and g value of complexes	

Complex	g	LFSE (K J mol <sup><math>-1</math></sup> )	$Dq (cm^{-1})$	β
$\overline{\text{Co}(\text{L}^1)_2\text{Cl}_2}$	1.95	134	940	0.84
$Co(L^1)_2(NO_3)_2$	1.87	80	559	0.76
$Co(L^2)_2Cl_2$	1.88	134	939	0.86
$Co(L^2)_2(NO_3)_2$	1.83	87	611	0.70
$Ni(L^1)_2Cl_2$	_	137	962	0.68
$Ni(L^{1})_{2}(NO_{3})_{2}$	_	113	790	0.95
$Ni(L^2)_2Cl_2$	_	140	977	0.67
$Ni(L^2)_2(NO_3)_2$	_	137	962	0.61
$Cu(L^1)_2Cl_2$	1.98	_	_	_
$Cu(L^{1})_{2}(NO_{3})_{2}$	2.00	_	_	_
$Cu(L^2)_2Cl_2$	2.07	-	_	_
$Cu(L^2)_2(NO_3)_2$	2.04	-	-	-

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