



Received on 06 April 2014; received in revised form, 14 June 2014; accepted, 10 July 2014; published 01 November 2014

SYNTHESIS AND SPECTROSCOPIC STUDIES OF COBALT (II) COMPLEXES WITH NITROGEN- OXYGEN AND NITROGEN SULPHUR DONOR LIGANDS

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Keywords:

Pyridine carboxamide,
Thiosemicarbazone, Semicarbazone,
Schiff bases

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ABSTRACT: CoII complexes of ligands pyridine3carboxamide thiosemicarbazone (L₁), pyridine 3 carboxamide semicarbazone (L₂), pyridine2carboxamide thiosemicarbazone (L₃) and pyridine 2 carboxamide semicarbazone (L₄) have been synthesized. The ligands were characterized based on elemental analyses, IR, ¹HNMR studies while the complexes were characterized by elemental analyses, molar conductance, magnetic moment, IR, electronic and EPR spectral studies. The complexes are not soluble in ordinary organic solvent but highly soluble in dimethylsulfoxide. The conductivity data show the nonelectrolytic nature of the complexes. Based on elemental analyses, molar conductance data and other spectral studies the complexes were found to have general composition [Co (L)₂X₂] (where L=L₁, L₂, L₃ and L₄, X = Cl⁻, ½SO₄²⁻, NO₃⁻) and exhibit distorted octahedral geometries.

INTRODUCTION: Nitrogen-containing metal chelates esp. schiff base ligands (-CH=N-) form important physiologically and pharmacologically compounds. Schiff bases are widely studied for their unparalleled recognition in biological systems ¹ to comprehend the structures of biomolecules ². Schiff bases can accommodate different metal centers esp. transition metals by different coordination modes allowing successful synthesis of homo and heterometallic complexes with wide-ranging stereochemistry ³.

Schiff bases derived from thiosemicarbazide, semicarbazide, and their metal complexes are of great significance for their pharmacological properties such as antimicrobial ⁴, antifungal ⁵, antitumor, antiviral ^{6,7}, anticancer ⁸⁻¹⁴.

It is documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems, being a component of several vitamins and drugs such as nicotinamide. Nicotinamide (pyridine -3-carboxamide) is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). Nicotinamide is a bioligand for human health which plays an important role in the metabolism of living cells, and some of its metal complexes are biologically active as antibacterial or insulin-mimetic agents.

<p>QUICK RESPONSE CODE</p> 	<p>DOI: 10.13040/IJPSR.0975-8232.5(11).4718-23</p> <hr/> <p>This article can be accessed online on www.ijpsr.com</p> <hr/> <p>DOI link: http://dx.doi.org/10.13040/IJPSR.0975-8232.5(11).4718-23</p>
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Therefore, the structure of nicotinamide has been the subject of many studies. It is currently in the trial as a potential means of preventing the onset of Type I (insulin-dependent) diabetes mellitus in high-risk, first-degree relatives.

It has been classed as a food additive rather than a drug. Nicotinamide and picolinamide also serve as model compounds for the conformations of polypeptides and nucleic acids. The amide groups in picolinamide and nicotinamide can adopt a variety of tautomeric and rotameric structures in addition to forming interesting molecular associations *via* hydrogen bonding. Picolinamide (pyridine -2- carboxamide) introduces a novel twist in the carboxamide potential by its ability to form an intramolecular hydrogen bond between the amide and the pyridine ring.

The extensive research has been done in our lab¹⁵ elucidating the coordination behavior of transition metal complexes (3d, 4d, 5d) with thiosemicarbazone which has been proved to be potent antitumor, antiviral, anticarcinogenic, antituberculosis¹⁶, antioxidant, antibacterial activities, bactericidal and fungicidal agents^{17,18}.

Recently thiosemicarbazone based ligands have been studied for their use as sensors¹⁹. In this paper, we report the synthesis and spectral investigations of Co (II) complexes with semicarbazide and thiosemicarbazide based ligands: (L₁), pyridine-3-carboxamide semicarbazone (L₂), pyridine-2-carboxamide thiosemicarbazone (L₃) and pyridine-2-carboxamide semicarbazone (L₄) to study their structure-activity relation.

EXPERIMENTAL: All the chemicals used in the present work were of high purity, Anal. R grade, and procured from Sigma-Aldrich. Metal salts were purchased from E. Merck and used as received. The solvents used were either spectroscopic pure from SRL/BDH or purified by the recommended methods.

Synthesis of Ligands: Hot ethanolic solution (20 mL) of pyridine-3- carboxamide and pyridine-2 -carboxamide (0.91g, 0.01mol) was added to a hot ethanolic solution of thiosemicarbazide (1.22g, 0.01mol) in the presence of 0.5 mL acetic acid. The contents were refluxed at 70–80 °C for about 8-10 hrs on a water bath with constant stirring. On

cooling the contents L₁ and L₃ the yellow-colored compounds were separated. The completion of the reaction was confirmed by the TLC. The solvent was removed using a rotary evaporator, and light yellow colored solid was obtained. It was washed with cold ethanol and dried under vacuum over P₄O₁₀, yield 68%, melting point-198-200 °C, soluble in water **Fig. 1**.

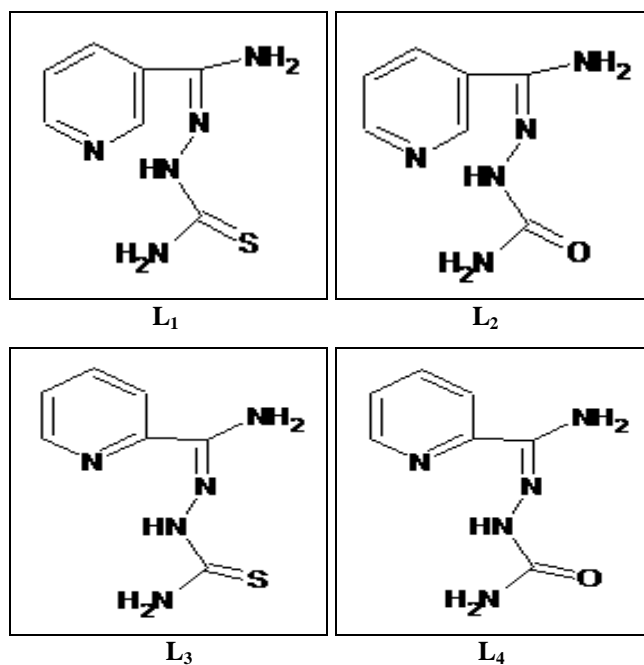


FIG. 1

An aqueous solution (50 mL) of semicarbazide hydrochloride (5.55 g, 0.05 mol) added in an ethanolic solution (50 mL) of corresponding amide pyridine -3-carboxamide and pyridine-2-carboxamide (4.75 gm, 0.05 mol) in the presence of sodium acetate (4.1 g, 0.05 mol). The reaction mixture was stirred vigorously for an hour. The crystalline product L₂, L₄ which formed was collected by filtration in each case washed several times with hot water and dried in vacuum over P₄O₁₀ **Fig. 1**.

The characterization details are tabulated in **Table1**.

Preparation of Metal Complexes: Hot ethanolic solution of metal salts (1 mmol), cobalt chloride hexahydrate (0.237 g), or cobalt nitrate hexahydrate (0.291 g), was mixed with a hot ethanolic solution of the corresponding ligand (2 mmol) (L₁, L₂, L₃, L₄). The mixture was refluxed for 8-10 h at 70–80 °C. On cooling the contents, the complex separated out in each case. It was filtered, washed with 50%

ethanol, and dried under vacuum over P_4O_{10} . The characterization details are tabulated in **Table 1**.

Physical Measurements: The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as calibrant IR spectra (KBr) were recorded on an FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. The 1H NMR spectrums were recorded on a Jeol FT-NMR Spectrometer using DMSO as a solvent. Thermogravimetry (TG) and Differential thermogravimetric analysis (DTA) for the metal complexes were carried out on a Perkin Elmer

Diamond TG-DTA spectrometer for the determination of complex entrapped water.

RESULTS AND DISCUSSIONS:

Physical Properties: The analytical data of the ligands and its complexes with their physical properties are given in **Table 1**. All the complexes have shown good solubility in DMSO but they were found insoluble in ether, water, acetone, and benzene. The interaction of the ligand with metal salts in 1:1 molar ratio in EtOH yielded stable solid.

The elemental analysis and molar conductance of complexes in DMSO correspond to non-electrolyte nature with general composition. $[Co(L)_2X_2]$ (Where $L = L_1, L_2, L_3, L_4$; $X = Cl^-, NO_3^-, \frac{1}{2}SO_4^{2-}$).

TABLE 1: MOLAR CONDUCTANCE AND ELEMENTAL ANALYSIS DATA OF CO II COMPLEXES

Complexes	Colour	Molar conductance	Yield %	Melting Point °C	Elemental analysis data found (Calculated)			
					M	C	H	N
Ligand (L_1, L_3) $C_7H_9N_5S$	Pale yellow	-	73	198	-	43.0 (42.95)	4.61 (4.60)	35.8 (35.4)
Ligand (L_2, L_4) $C_7H_9N_5O$	white	-	64	190-194	-	46.91 (46.92)	5.01 (5.02)	39.11 (39.10)
$[Co(L_1)_2Cl_2]$	Pink	19	59	258	11.30 (11.32)	32.27 (32.31)	3.45 (3.48)	26.89 (26.91)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								
$[Co(L_1)_2SO_4]$	Pink	20	63	235	10.76 (10.80)	30.6 (30.8)	3.31 (3.32)	25.5 (25.6)
$CoC_{14}H_{18}N_{10}S_3O_4$								
$[Co(L_1)_2(NO_3)_2]$	Reddish	19	68	234	10.24 (10.27)	29.31 (29.32)	3.15 (3.16)	29.22 (29.3)
$CoC_{14}H_{18}N_{12}S_2O_6$	pink							
$[Co(L_2)_2Cl_2]$	Pink	20	65	220	12.06 (12.07)	34.42 (34.44)	3.61 (3.71)	28.65 (28.69)
$CoC_{14}H_{18}N_{10}O_2Cl_2$								
$[Co(L_2)_2SO_4]$	Bluish	17	58	222	11.45 (11.48)	32.74 (32.75)	3.51 (3.53)	27.12 (27.2)
$CoC_{14}H_{18}N_{10}O_6S$	pink							
$[Co(L_2)_2(NO_3)_2]$	Reddish	15	57	246	10.84 (10.88)	31.01 (31.06)	3.32 (3.35)	31.04 (31.05)
$CoC_{14}H_{18}N_{12}O_8$	pink							
$[Co(L_3)_2Cl_2]$	Purple	15	60	255	11.30 (11.34)	32.27 (32.35)	3.45 (3.42)	26.89 (26.89)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								
$[Co(L_3)_2SO_4]$	Purple	21	62	274	10.76 (10.78)	30.6 (30.9)	3.31 (3.35)	25.5 (25.7)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								
$[Co(L_3)_2(NO_3)_2]$	Reddish	21	59	251	10.24 (10.25)	29.31 (29.31)	3.15 (3.15)	29.22 (29.25)
$CoC_{14}H_{18}N_{10}S_2Cl_2$	pink							
$[Co(L_4)_2Cl_2]$	Red	19	58	253	12.06 (12.05)	34.42 (34.48)	3.61 (3.66)	28.65 (28.67)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								
$[Co(L_4)_2SO_4]$	Red	20	60	211	11.45 (11.47)	32.74 (32.74)	3.51 (3.52)	27.12 (27.14)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								
$[Co(L_4)_2(NO_3)_2]$	Red	18	61	284	10.84 (10.86)	31.01 (31.08)	3.32 (3.33)	31.04 (31.06)
$CoC_{14}H_{18}N_{10}S_2Cl_2$								

IR Spectra: IR spectra of the ligands show bands at $\sim 3200-3300$ and $3100-3400\text{ cm}^{-1}$ which may be assigned to $[(NH_2)]$ and $[(NH)]$ groups, respectively. The bands due to $[\nu(C=S)]$ appeared

at $\sim 801\text{ cm}^{-1}$, $[\nu(C=O)]$ at ~ 1684 and the bands at $\sim 1618\text{ cm}^{-1}$ may be assigned to symmetric or asymmetric $[\nu(C=N)]$ group.

The assignments of the significant IR spectral bands of the metal complexes are shown in **Table 2** which clearly show the shifting of the bands corresponding to ν ($-\text{C}=\text{N}$), ($-\text{C}=\text{S}$) and $\nu(\text{C}=\text{O})$ in ligands towards the lower side (around ca. 20–50

cm^{-1}) on complexation. This suggests that the ligands act as bidentate chelating agent coordinating through the nitrogen of $\text{C}=\text{N}$ group, sulfur of $\text{C}=\text{S}$ group and oxygen of $\text{C}=\text{O}$.

TABLE 2: IMPORTANT IR BANDS AND ASSIGNMENT OF SEMICARBAZONE AND THIOSEMICARBAZONE BASED LIGANDS AND THEIR CO (II) COMPLEXES

Compound	ν (C=N)	ν (C=O)	ν (NH)	ν (C-S)	ν (M-O/M-S)
(L ₁)	1618	-	3399	801	
[Co(L ₁) ₂ Cl ₂]	1574	-	3269	764	430
[Co(L ₁) ₂ SO ₄]	1560	-	3292	756	
[Co(L ₁) ₂ (NO ₃) ₂]	1580	-	3307	782	434
(L ₂)	1620	1684	3400	-	
[Co(L ₂) ₂ Cl ₂]	1565	1678	3101	-	
[Co(L ₂) ₂ SO ₄]	1549	1652	3102	-	
[Co(L ₂) ₂ (NO ₃) ₂]	1591	1656	3258	-	
(L ₃)	1628	-	3367	800	
[Co(L ₃) ₂ Cl ₂]	1583	-	3275	780	-
[Co(L ₃) ₂ SO ₄]	1563	-	3307	768	
[Co(L ₃) ₂ (NO ₃) ₂]	1565	-	3332	773	-
(L ₄)	1621	1684	3246	-	
[Co(L ₄) ₂ Cl ₂]	1591	1679	3160	-	
[Co(L ₄) ₂ SO ₄]	1594	1666	3175	-	

Electronic Spectra and Magnetic Moment: The magnetic moments of all the Co II complexes lies in the range 4.89-5.02 BM corresponding to three unpaired electrons. This indicates that the coordination takes place through the nitrogen atoms of the imine group, sulfur atom of $>\text{C}=\text{S}$, oxygen atom of $>\text{C}=\text{O}$ group which corresponds to octahedral symmetry **Table 3**.

TABLE 3: MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF COII COMPLEXES

Complexes	μ_{eff} (BM)	λ_{max} (cm^{-1})
[Co(L ₁) ₂ Cl ₂]	4.95	8801, 18609, 22460
[Co(L ₁) ₂ (NO ₃) ₂]	4.89	8876, 19502, 23575
[Co(L ₂) ₂ Cl ₂]	4.92	8865, 18880, 22550
[Co(L ₂) ₂ (NO ₃) ₂]	5.02	8863, 19525, 22375
[Co(L ₃) ₂ Cl ₂]	4.96	8831, 20809, 22600
[Co(L ₃) ₂ (NO ₃) ₂]	5.00	8890, 18725, 2676
[Co(L ₄) ₂ Cl ₂]	4.95	8873, 21000, 22515
[Co(L ₄) ₂ (NO ₃) ₂]	4.98	8843, 19767, 23950

EPR Spectra: The X band EPR spectra of Co (II) complexes display the broad signal value of $g_{\parallel} = 2.0001-2.0069$, $g_{\perp} = 1.9763-2.0076$ and $g_{\text{iso}} = 1.9895-2.0064$ corresponding to the tetragonal symmetry around Co(II) atoms²⁰.

Thermal Analysis of Metal Complexes: Crystal water content in complex [Co (L₁)₂Cl₂] (1) and its thermal stability was determined by the TGA and DTG techniques **Fig. 2**. The metal complex (1)

show major weight loss above 133 °C which shows that it is free of any entrapped water. The data obtained for other complexes was reprehensible. The complex (1) decomposes in two steps by oxidative degradations; in the final step (>690 °C) results in the metallic oxide Co₃O₄ as stable residue. Data from the thermal analysis sustains the molecular formulas assigned for these complexes. It shows a total mass loss of 85.6% at 133-280 °C, 50.9% at 280 °C, 14.39% at 690 °C.

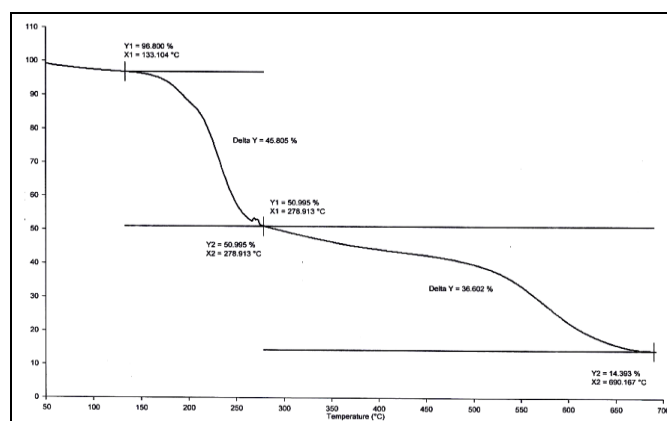
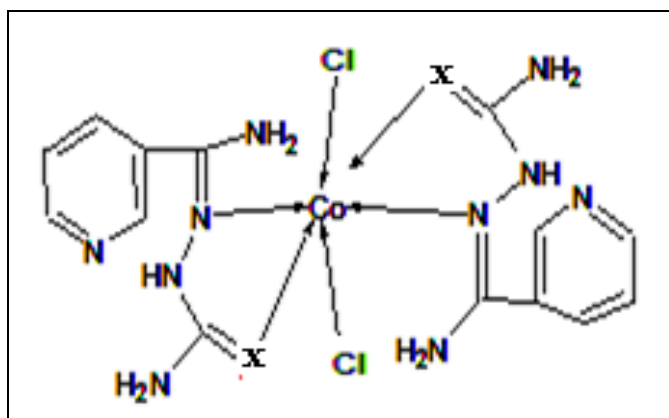
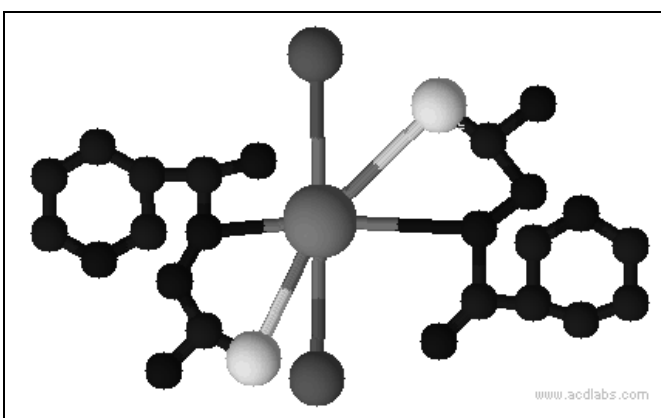
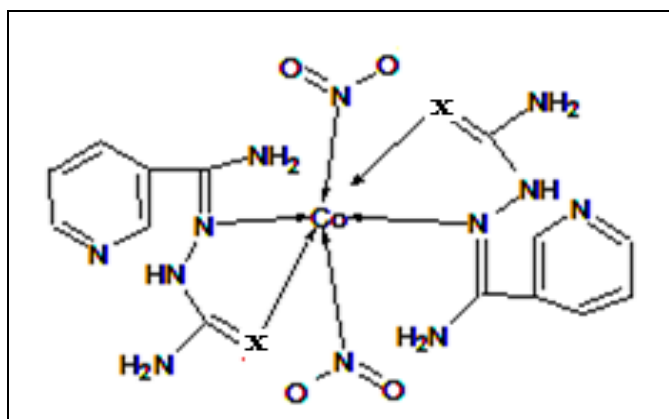
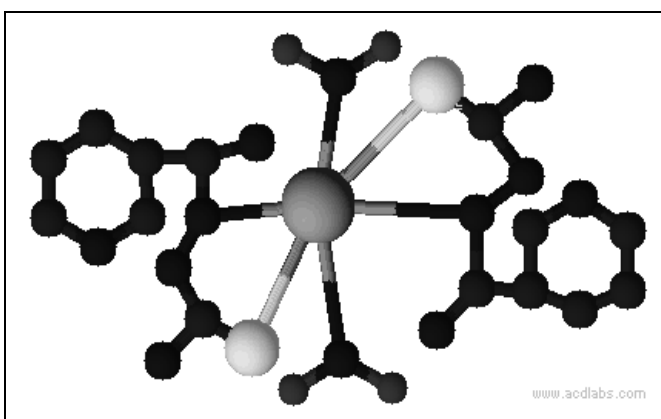


FIG. 2: THERMO GRAVIMETRIC ANALYSIS (TGA) OF COBALT COMPLEX [Co (L₁)₂(Cl)₂]

Suggested Structure of the Complexes: On the basis of the above spectral studies the following structure may be suggested for the complexes **Fig. 3, 4**.

FIG. 3A: STRUCTURE OF $[Co(L_1)_2(Cl)_2]$ FIG. 3B: SUGGESTED 3D STRUCTURE OF $[Co(L_1)_2(Cl)_2]$ FIG. 4A: STRUCTURES OF $[Co(L_1)_2(NO_3)_2]$ FIG. 4B: SUGGESTED 3D STRUCTURE OF $[Co(L_1)_2(NO_3)_2]$

CONCLUSION: The present work describes the facile synthesis of metal complexes with newly synthesized ligands. Spectral data confirms that the ligands are bidentate and metal complexes have distorted octahedral geometry which may be formulated as $[Co(L)_2X_2]$ (where $L = L_1, L_2, L_3, L_4$; $X = Cl^-, NO_3^-, 1/2SO_4^{2-}$). An interesting fact is that the ligand being water-soluble can be further studied for their applications as chelating agents, work for which is being carried out in our lab.

ACKNOWLEDGEMENT: The authors are thankful to the UGC New Delhi for financial assistance, IIT Mumbai, for recording EPR spectra and IIT Delhi, for recording NMR spectra.

CONFLICT OF INTEREST: Nil

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How to cite this article:

Chandra S, Raizada S and Sadwal S: Synthesis and spectroscopic studies of Cobalt (II) complexes with nitrogen- oxygen and nitrogen sulphur donor ligands. Int J Pharm Sci & Res 2014; 5(11): 4718-23. doi: 10.13040/IJPSR.0975-8232.5(11).4718-23.

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