Synthesis, Characterization and Molecular Modeling of Nickel (II) Complexes with Semicarbazones and Thiosemicarbazones

Authors
Sulekh Chandra[1], Smriti Raizada[2], Sangeeta Sadwal[2]

[1]Department of Chemistry, Zakir Husain Delhi College (University of Delhi), New Delhi, India
Email: *schandra_00@yahoo.com*
[2]Department of Chemistry, M. M. H. College (C.C.S. University, Meerut), Ghaziabad, India
Email: *smriti_raizada@live.com*
Corresponding Author
Sangeeta Sadwal
Email: *sangita.sadwal@gmail.com*

Abstract
Ni (II) complexes of ligands pyridine-3-formamide thiosemicarbazone (L_1), pyridine-3-formamide semicarbazone(L_2), pyridine-2-formamide thiosemicarbazone (L_3) and pyridine-2 -formamide semicarbazone (L_4) have been synthesised. The ligands were characterised on the basis of elemental analyses, IR, ^1HNMR studies while that of the complexes were characterised by elemental analyses, molar conductance, magnetic moment, IR, electronic. On the basis of elemental analyses and molar conductance data the complexes were found to have general composition $[Ni(L)_2X_2]$ (where $L=L_1$, L_2, L_3 and L_4 , $X = Cl^-$,NO_3^-]. On the basis of IR, electronic spectra of complexes, octahedral geometries were found with planar coordination of the ligand around Ni^{2+} ion. Molecular modeling confirmed octahedral geometry.
Keywords: *octahedral, Nickel(II) complexes. IR, electronic spectrum..*

1. Introduction

Metal complexes of thiosemicarbazones and semicarbazones have been under recent attention due to their significant role in new drug discoveries. They are forerunner in latest pharmacological applications, found to be potent fungicidal agents, [1]antiviral [2],antitumor[3]and antiprotozoal[4] agents due to their enhanced chelating tendencies .

These ligands have shown meticulous disparity in their activities by substitution at [1]N and [4]N position in thiosemicarbazone moiety[] . Further, activity of ligands was found to be enhanced on complexation *esp* with Cu(II),Ni(II) ions .[5-8]

Ni(II) complexes have been synthesised due to their promising biochemical applications which stem from the fact that Ni(II) complexes have good lipophilic degree necessary for an efficient intake by cell for proliferation inhibition action against U937 cell line [9], MCF-7 human breast cancer cells[10] ,and due to their plasticity in coordination and redox chemistry [11] they are able to catalyze reactions in various biochemical systems . There has been constant pursuit of the synthesis and structural characterization of a variety of substituted and unsubstituted thiosemicarbazones and semicarbazones with different combinations of the aldehydes/ketones, with the aim to correlate their structural features with chelating ability [12]present paper is a novel pursuit of combination of thiosemicarbazones and semicarbazones with pyridine formamide (nicotinamide ,picolinamide) and their Ni(II) complexes.

In this paper we report the synthesis and spectral investigations of Ni(II) complexes with semicarbazide and thiosemicarbazide based

ligands : pyridine-3-formamide thiosemicarbazone (L_1), pyridine-3- formamide semicarbazone(L_2), pyridine- 2-formamide thiosemicarbazone (L_3) and pyridine-2 -formamide semicarbazone (L_4)

.

2. EXPERIMENTAL

Materials and methods

All the chemicals used were of Anal.R grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard/spectroscopic grade. C, H and N were analysed on a Carlo-Erba 1106 elemental analyser. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO4.5H2O as calibrant. ^{1}HNMR spectra was recorded at room temperature on a Bruker AdvanceDPX-300 spectrometer using DMSO-d[6] as a solvent. IR spectra (KBr) were recorded on FTIR spectrum BX-11 spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240spectrophotometer.
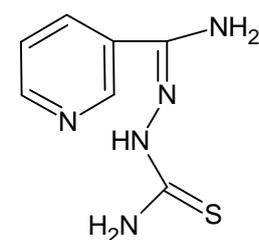
3. SYNTHESIS

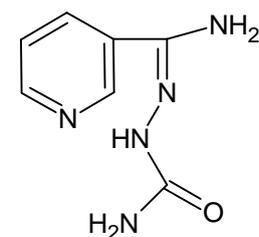### 3.1 Synthesis of ligands L_1-L_4

Hot ethanolic solution (20 mL) of pyridine-3-formamide for L_1 and pyridine-2 - formamide for L_2 (1.95 g, 0.01mol) was added to 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 L_1 and L_3 the yellow colored compounds were separated out and dried under vacuum over P_4O_{10}.

An aqueous solution (20 mL) of semicarbazide hydrochloride (1.11 g, 0.01 mol) added in an ethanolic solution (20 mL) of corresponding amide pyridine -3-formamide and pyridine-2- formamide (1.22 g, 0.01 mol) in the presence of sodium acetate (.83g, 0.01 mol). The reaction mixture was stirred vigorously for an hour. The crystalline
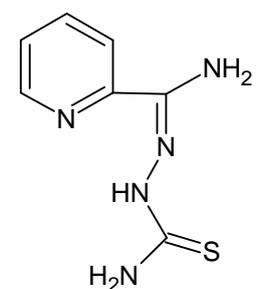
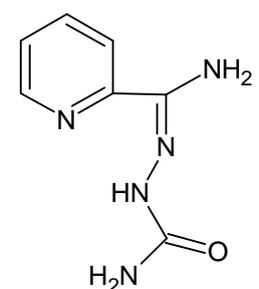products L_2, L_4 *resp*. formed were collected and dried in vacuum over P_4O_{10}. **[Fig 1]**

L_1

L_2

L_3

L_4

Fig. 1

3.2 Synthesis of complexes with ligands

Hot ethanolic solution (20 mL) of corresponding ligands $L_1 - L_4$, (0.002 mol,) was slowly added to aqueous solution (20 mL) of corresponding metal salts Ni(II) salts $NiCl_2.6H_2O, Ni(NO_3)_2.6H_2O$ (0.001mol) with continuous stirring. The mixture was refluxed for 8-10 hrs at 80-85ºC. On cooling colored complexes were precipitated out. They

were filtered, washed with hot ethanol and dried under vacuum over P_4O_{10}

4. RESULTS AND DISCUSSIONS
4.1 IR spectra
The significant IR spectral bands of the ligands L_1-L_4 clearly show the medium bands observed in the range 1030-1070 cm^{-1} are assigned to hydrazinic N—N bonds [13]. The 1600-1630 cm^{-1} region of the spectra of all ligands implies to –C=N bands. The –C=S group in L_1,L_3 shows stretching and bending vibrations at ~ 1320 and 801 cm^{-1} . The

strong bands at ~1684 cm^{-1} in L_2,L_4 can be assigned to ─C=O in semicarbazone moiety.

On complexation the bands corresponding to v(–C=N) and v(–C=S)/ (─C=O) shift towards the lower side (around ca. 20–50 cm^{-1}). This suggests that the all ligands act as bidentate chelating agent coordinating through nitrogen of C=N group for L_1-L_4 and sulphur of C=S for L_1,L_3 or oxygen of─C=O for L_2,L_4. The bands due to v(M-N) have come up at 400-700cm^{-1} shows coordination of metals. [**Table 1**]. [14]

Table 1: Important IR bands of ligands and their Ni (II) complexes

Compounds	v(C=N)	v(C=O)	v(NH)	v(C=S)	v(M-N)	v(M-O) v(M-S)
LIGAND(LI)	1618	-	3399	801		
[Ni(L1)2(Cl2)]	1602	-	3358	791	528	458
[Ni(L1)2(NO3)2]	1603	-	3466	693	588	429
LIGAND(L2)	1620	1684	3400	-		
[Ni(L2)2(Cl2)]	1619	1675	3606	-	-	413
[Ni(L2)2(NO3)2	1615	1657	3454	-	-	466
LIGAND(L3)	1628	-	3367	800		
[Ni(L3)2(Cl2)]	1589	-	3466	739	-	457
[Ni(L3)2(NO3)2]	1578	-	3348	785	-	-
LIGAND(L4)	1621	1684	3246	-		
[Ni(L4)2(Cl2)]	1616	1636	3428	-	-	-
[Ni(L4)2(NO3)2]	1613	1621	3302	-	-	455

4.2 ^{1}HNMR of ligands
In the spectra of L_1 and L_3 sharp singlets at 7.24 (L_1) and 8.02 ppm (L_3) corresponds to -CH proton. Absence of any coupling interactions by ─NH due to the unavailability of protons on neighboring atoms render singlet peak for the imine proton at 8.92 (L_1) and 8.56 ppm (L_1) are assigned to the ─NH protons. The ─CH protons adjacent to the ring nitrogen produces a triplet at 4.12 (L_1) and 4.41 ppm (L_3) due to coupling with nearby =CH─ protons. The spectra of ligands (L_2) show sharp singlets, which integrates as one hydrogen at ~ 10.08 ppm is assigned to the proton attached to the oxygen atom. Absence of any coupling interactions by ─NH renders singlet peak for the imine proton at 8.89 (L_2) and 8.58 ppm (L_4).

The presence of electron withdrawing azomethine group near to the CH proton leads to its resonance as a singlet at 7.28 (L_2) and 7.28 ppm (L_4).

4.3 CHN analysis and Molar Conductance
On the basis of elemental analyses (Table 2) all the complexes were found to possess Ni(L)$_2$X$_2$ (where L= L_1, L_2, L_3, L_4; X=Cl$^-$, NO$_3^-$, composition. Molar conductance of these complexes measured in DMSO solution(Table 2) corresponds to their non electrolyte nature. Thus the complexes may be formulated as [Ni (L)$_2$X$_2$] (where L= L_1, L_2, L_3, L_4; X=Cl$^-$, NO$_3^-$)

Table 2: Molar conductance and elemental analysis data of Ni(II) complexes

Complexes	MC *	colour	Element analysis Data calculated/(found)			
			M	C	H	N
[Ni(L$_1$)$_2$(Cl$_2$)]	20	Dark Green	11.28 (11.15)	32.33 (32.02)	3.48 (3.26)	26.93 (26.70)
[Ni(L$_1$)$_2$(NO$_3$)$_2$]	18	Dark Green	10.23 (10.98)	29.3 (28.6)	3.16 (3.02)	29.32 (29.00)
[Ni(L$_2$)$_2$(Cl$_2$)]	22	Bluish green	12.02 (11.89)	34.4 (33.92)	3.71 (3.66)	28.70 (28.53)
[Ni(L$_2$)$_2$(NO$_3$)$_2$]	16	Blue	10.84 (10.53)	31.07 (31.00)	3.35 (3.26)	31.06 (31.00)
[Ni(L$_3$)$_2$(Cl$_2$)]	20	Light Green	11.28 (11.25)	32.33 (32.29)	3.48 (3.33)	26.93 (26.62)
[Ni(L$_3$)$_2$(NO$_3$)$_2$]	21	Green	10.23 (10.18)	29.3 (29.00)	3.16 (3.06)	29.32 (28.89)
[Ni(L$_4$)$_2$(Cl$_2$)]	18	Green	12.02 (11.98)	34.4 (33.8)	3.71 (3.63)	28.70 (28.68)
[Ni(L$_4$)$_2$(NO$_3$)$_2$]	19	Green	10.84 (10.56)	31.07 (30.88)	3.35 (3.25)	31.06 (31.00)

* Molar Conductance Ω^{-1} cm^{-2}mol^{-1}

4.4 Magnetic moment

The magnetic moment observed for all the nickel(II) complexes is in range of 2.80-3.1 B.M which is consistent with the octahedral stereochemistry of the complex.[15] [Table 3]

4.5 Electronic spectra

The electronic spectra of nickel (II) complexes for the ligands (L$_1$-L$_4$) display three absorption bands in the range of ~10,700cm^{-1}, ~15,000cm^{-1}, and ~33,000cm^{-1}. The ground state nickel (II) in an octahedral coordination is $^3A_{2g}$. Thus, these bands may be assigned to three spin-allowed transition $^3A_{2g}(F)\rightarrow^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F)\rightarrow^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F)\rightarrow^3T_{1g}(P)(\nu_3)$ respectively. The position of bands suggest mostly of octahedral geometry [Table 3].[16]-[18]

Table 3: Magnetic moment and electronic spectral data of the Ni (II) complexes

Compounds	M$_{eff}$ B.M.	λ_{max} cm^{-1}
[Ni(L$_1$)$_2$(Cl$_2$)]	2.92	10870 , 32258
[Ni(L$_1$)$_2$(NO$_3$)$_2$]	2.85	10756 , 24330 , 27700
[Ni(L$_2$)$_2$(Cl$_2$)]	3.20	10192 ,15243 , 24752
[Ni(L$_2$)$_2$(NO$_3$)$_2$]	2.94	10705 , 27700
[Ni(L$_3$)$_2$(Cl$_2$)]	3.10	10406 , 30581
[Ni(L$_3$)$_2$(NO$_3$)$_2$]	2.84	10230 , 28248
[Ni(L$_4$)$_2$(Cl$_2$)]	2.93	10274 , 25906
[Ni(L$_4$)$_2$(NO$_3$)$_2$]	3.10	10123 , 30211

4.6 Molecular model of Metal Complexes

The structures were modeled using basic techniques of molecular modeling and refining them with software ACD/ChemSketch. ACD/ChemSketch is an integrated software package from Advanced Chemistry Development, Inc., (ACD/Labs) for drawing chemical structures, reactions, and schematic diagrams, and designing other chemistry-related reports and presentations.[19,20] Figs 2-5
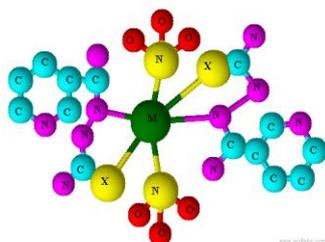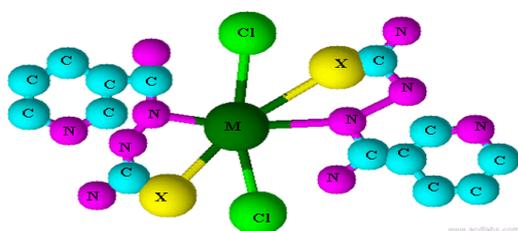

Fig 2. 3D structure of metal complexes of pyridine 3 formamide thiosemicarbazone L_1 (X=S) and pyridine 3 formamide semicarbazone L_2 (X=O)[M(L)$_2$(NO$_3$)$_2$] where L= L_1,L_2 ;m =Ni(II) H atoms have been removed for clarity .

Fig 3. 3D structure of metal complexes of pyridine 3 formamide thiosemicarbazone L_1 (X=S) and pyridine 3 formamide semicarbazone L_2 (X=O) [M (L)$_2$ (Cl)$_2$] where L= L_1,L_2 ;m = Ni(II) .H atoms have been removed for clarity.
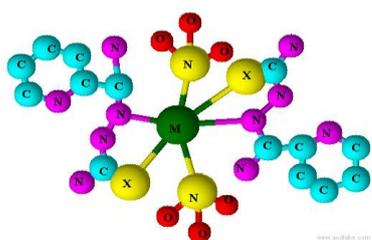

Fig 4 3D structure of metal complexes of pyridine 2 formamide thiosemicarbazone L_3 (X=S) and pyridine 2 formamide semicarbazone L_4 (X=O) ,

[M (L)$_2$ (NO$_3$)$_2$] where L= L_3,L_4 ;m = Ni(II).H atoms have been removed for clarity
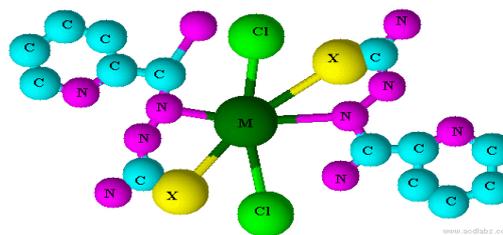

Fig 5 3D structure of metal complexes of pyridine 2 formamide thiosemicarbazone L_3 (X=S) and pyridine 2 formamide semicarbazone L_4 (X=O) , [M (L)$_2$ (Cl)$_2$] where L= L_3,L_4 ;M = Ni(II), .H atoms have been removed for clarity

5. CONCLUSION

Ni (II) complexes containing ligands pyridine-3-formamide thiosemicarbazone (L_1), pyridine-3-formamide semicarbazone (L_2), pyridine-2-formamide thiosemicarbazone (L_3) and pyridine-2-formamide semicarbazone (L_4) were synthesised and characterised. On the basis of spectral studies octahedral geometries were found with planar coordination of the ligand around Ni^{2+} ion for all complexes.

REFERENCES

1. U. Kumar, S. Chandra, J. Saudi Chem. Soc. 15 (2011) 19
2. V.H Patil, A.D. Kulkarni, P.S. Badami . Spectrochim. Acta A,75(2010) 347.
3. K. Sharma, R. Singh, N. Fahmi, R.V. Singh. Spectrochim. Acta A,75(2010)422.
4. A.A. Al-Amiery, Y.K. Al-Majedy H. Abdulreazak H.Abood, Bioinorg. Chem. Appl. 1(2011) 6.
5. J. Wiecek, D. Kovala-Demertzi, Z. Ciunik, M. Zervou and M.A. Demertzis,Bioinorg. Chem. Appl. 1(2010)9.
6. K.O. Ferraz, S.M.S.V. Wardell, J.L.Wardell, S.R.W. Louro, H. Beraldo, Spectrochim. Acta A, 73(2011)140.
7. N. Raja, R. Ramesh, Spectrochim. Acta A. 75(2010) 713.

8. D.R .Kumar , M. Ayesha, Res. J. Chem. Environ. 15(2011)5.

9. Bisceglie F, Baldini M, Belicchi-Ferrari M, et al. Eur J Med Chem 42 (2007) 627-34.

10. J Chen, Y Huang, G Liu,. Toxicol Appl Pharmacol 40 (2004) 197.

11. A Buschini, S Pinelli, C Pellacani,.J. Inorg. Biochem. 66 (2009) 103.

12. A.P. Mishra, R. Mishra, R. Jain, S. Gupta, Mycobiol. 40 (2012) 20. X. G. Gu, X. Z. Wan, B. Jiang, Biorg. Med. Chem. Lett. 9 (1999) 569.

13. S. Munde, V. A. Shelke, S. M. Jadhav, A. S. Kirdant, S. R. Vaidya, S. G. Shankarwar,T. K. Chondhekar, Adv. Appl. Sci. Res. 3 (2012) 175.

14. R. Jain, A. P. Mishra, Jordan J.Chem. 7 (2012) 9.

15. S. Chandra, D. Jain, A. K. Sharma, P. Sharma, Mol.14 (2009) 174

16. S. Chandra ,S. Raizada, M. Tyagi P.K. Sharma. Spectrochim. A. 69 (2008) 816

17. S Chandra, A. Kumar. J. Saudi Chem. Soc 14 (2012) 12

18. S. Chandra ,M. Tyagi, S. Agrawal .J. Saudi Chem. Soc. 15 (2011) 49

19. S. Goel,S. Chandra, S. Dhar, J. Chem. 6 (2013)7

20. ACD/ChemSketch, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com,11(2014)