

SPECTROSCOPIC STUDY AND SYNTHESIS OF SCHIFF'S BASE LIGAND OF 2-BENZOYLPIRIDINE SEMICARBAZIDE HYDROCHLORIDE AND ITS Cu(II) AND Ni(II) TRANSITION METAL COMPLEXES

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ABSTRACT

Transition metal complexes of Cu(II) and Ni(II) with 2-benzoylpyridinesemicarbazide hydrochloride with general composition ML_2X_2 (where M= Cu(II) and Ni(II), L= 2-benzoylpyridine and semicarbazide hydrochloride ligand, X= Cl^- , NO_3^- , SO_4^{2-} , OAc^-) have been synthesised and characterised by elemental analysis, magnetic moment, conductivity measurement, mass spectrometry, IR spectrometry, UV-Vis spectroscopy, and EPR spectral studies. The magnetic moment values indicate that these are high spin complexes. The IR spectral study indicates that ligand is bidentate and coordinated through N and O. On the basis of spectral study Octahedral geometry was proposed for Ni(II) complexes and tetragonal geometry was proposed for Cu(II) complexes.

Keywords: Semicarbazone, bidentate, Cu(II), Ni(II)

INTRODUCTION

Coordination chemistry is the most important branch of chemistry because of its immense importance in various fields like medicine, agriculture etc. Semicarbazone are nitrogen and oxygen donors and are found to be less reactive as anticarcinogenic agent in comparison to thiosemicarbazone and thiosemicarbazide complexes. This difference is attributed to the fact that thiosemicarbazone complexes have less chelating property than semicarbazone complexes. Semicarbazones compounds have adaptable features and can coordinate either as neutral ligand or deprotonated ion to metal[1]. Semicarbazones molecules also hold great importance due to their pharmacological properties such as antibacterial, antifungal, antihypertensive, hypolipdemic, antineoplastic, hypnotic and anticonvulsant [2-5]. A large variety of Semicarbazones and their complexes shows anti protozoa activity also. They represent these properties due to their remarkable variation in their stereochemistry and their mode of bonding through azomethine and oxygen. Semicarbazones drags the attention of researchers because of their unusual coordination modes, high pharmacological potentiality and good chelating property. Ketones and aldehydes due to their additional donor atoms enhances the coordination possibilities in semicarbazones[6-7]. In present paper we report the synthesis and characterisation of Ni(II) and Cu(II) complexes with 2-benzoylpyridinesemicarbazone

ligand (Fig.1)

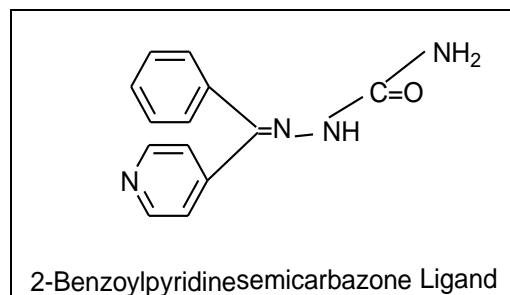


Fig.1 Structure of 2-Benzoylpyridine-semicarbazide ligand

Experimental Section

All reagents were commercially available and used without further purification and were purchased from sigma Aldrich and metal salts were purchased from E-Merck and were used as received. Solvent were either spectroscopy pure from SRL/VDH or purified by recommended methods.

Preparation of ligand

Semicarbazone (0.11mol) and sodium acetate (0.11) were dissolved in little amount of distilled water and added to alcoholic solution of 2-benzoylpyridine with constant stirring and refluxed for 7-8 hrs. at 78-80°C according to (fig.1). The resultant solution was cooled for 24 hrs. On cooling white shiny crystals were separated out which were washed with ethanol and ether several time to remove excessive reactant and dried over P_4O_{10} .

Preparation of transition metal complexes

Hot ethanolic solution (20 ml) of corresponding metal salts (0.01mol) were mixed with hot ethanolic solution of the ligand (0.01mol) with constant

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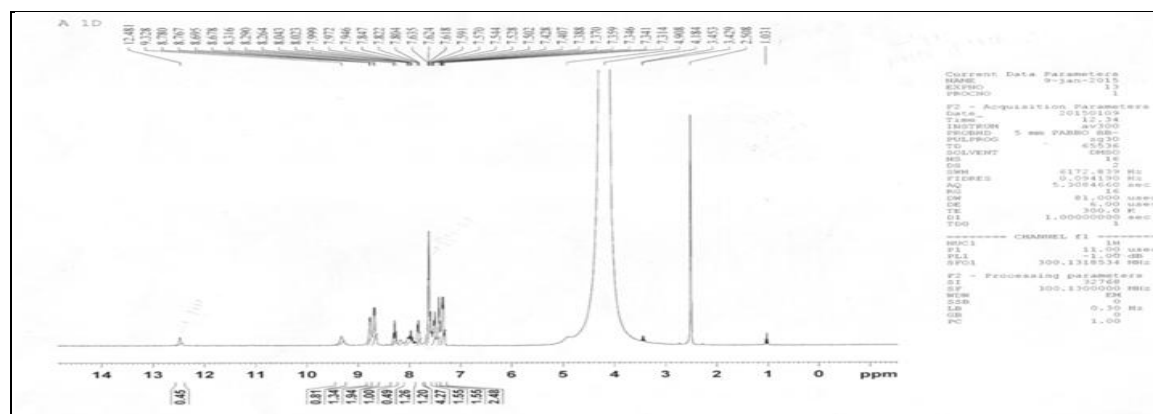


Fig. 1(a) : NMR of Ligand

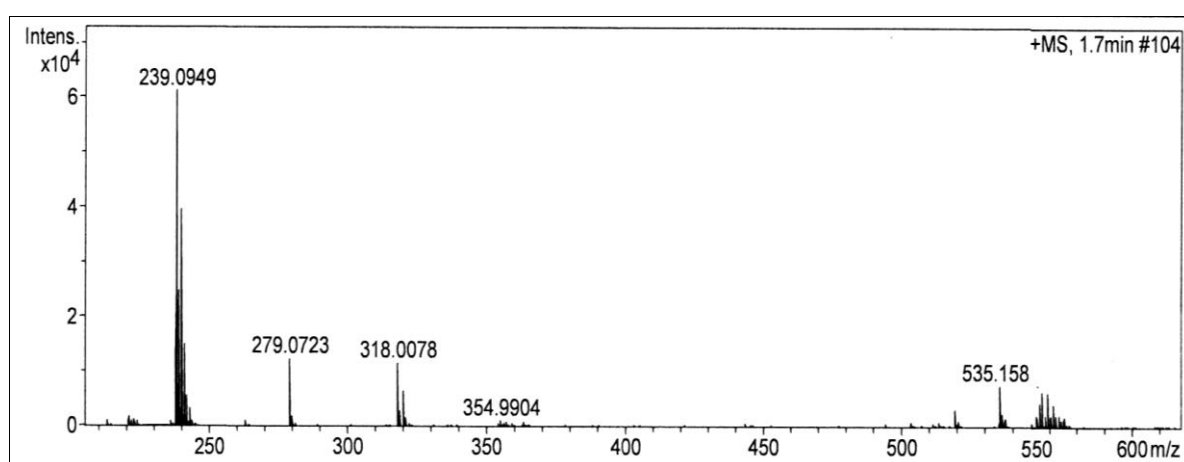


Fig. 1b. Mass Spectrum of Ligand

stirring and refluxed for 7-8 hrs. at 78-80°C. On cooling the contents, the coloured precipitates were separated out in each case. It was filtered, washed with ethanol and ether. The resultant mixture was dried over P_4O_{10} .

Analytical and physical measurement

Elemental (CHN) analysis was carried out on a Perkin Elmer sercise-II-2400. IR was recorded using a Thermo scientific Nicolet 6700 FT-IR on KBr disc in the wave number ranged 4000-400 cm^{-1} . Mass spectrum was recorded using Bruker microtop-QII. 1H NMR spectra were recorded on Bruker Advanced DPX-300 spectrometer using $DMSO-d_6$ as a solvent and TMS as an internal solvent. Electronic spectral studies were conducted on a perkinelmer-lambda 25, UV spectrophotometer. The EPR spectra were recorded in solid as polycrystalline sample at room temperature on E_4 -EPR spectrometer using DPPH as g marker.

Result and discussion

All the nickel and copper complexes were synthesised by condensation reaction between

ligand and corresponding metal salts. For Ni(II) and Cu(II) complexes were synthesised at 6-7pH range. The synthesised complexes were coloured and stable at room temperature and were found soluble in DMSO and DMF. The molar conductivity value lies in the range from 3.6-11.8 ($ohm^{-1}cm^2 mol^{-1}$) which indicates their non electrolytic nature and indicates that complexes have stoichiometry of the type $[ML_2X_2]$ where $M = Cu(II), Ni(II), L = ligand$ and $X = Cl^-, NO_3^-, SO_4^{2-}$ and OAc^- which is further supported by elemental analysis values. The physical and analytical data together of synthesised complexes is listed in table 1.

1H NMR of ligand

1H NMR of ligand was done in DMSO on 44-300 MHz NMR (Fig.1a). The aromatic proton appears as set of singlet, doublet and multiplet in the range 7.40-8.78ppm. The singlet for NH proton appears at 9.32ppm while two NH_2 protons [8] resonates as a multiplet at 7.34-7.38 ppm. The NH_2 and NH protons are confirmed by their D_2O spectra. All the protons are found in their expected region.

Table 1 : Elemental Analysis, Colour and Formula of Copper and Nickel complexes

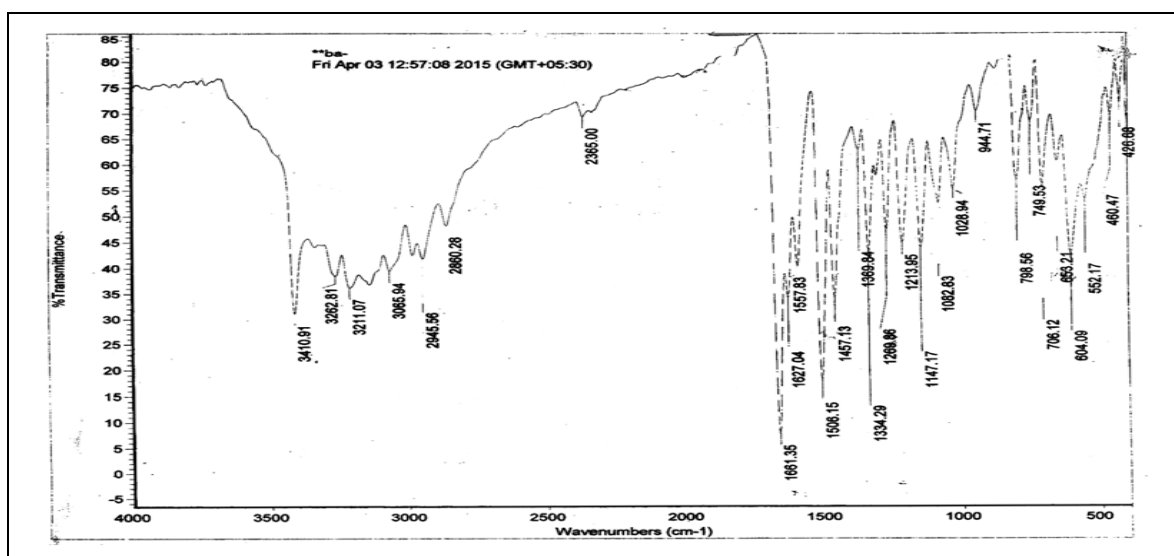
	Colour	Found	Calc.	%
		C	H	N
[Cu(L) ₂ Cl ₂]	Black	50.81 (50.25)	3.91 (3.19)	18.24 (18.32)
[Cu(L) ₂ (SO ₄) ₂]	Black	42.42 (42.65)	3.26 (3.38)	18.24 (18.59)
[Cu(L) ₂ (NO ₃) ₂]	Black	51.53 (51.60)	3.96 (3.72)	20.81 (20.01)
[Cu(L) ₂ (OAc) ₂]	Brown	54.42 (54.91)	4.53 (4.61)	16.93 (16.14)
[Ni(L) ₂ Cl ₂]	Shiny Brown	51.81 (51.61)	3.93 (3.05)	18.37 (18.45)
[Ni(L) ₂ (SO ₄) ₂]	Shiny Brown	42.70 (42.70)	3.28 (3.56)	15.33 (15.32)
[Ni(L) ₂ (OAc) ₂]	Shiny Brown	54.82 (54.27)	4.57 (4.65)	17.06 (17.26)
[Ni(L) ₂ (NO ₃) ₂]	Shiny Brown	48.10 (48.03)	3.70 (3.89)	19.43 (19.99)

Table 2 : IR Spectral Data of Copper and Nickel Complexes

Compound	v(C=N)	v(C=S)	v(M-N)
Ligand	1660	1577	
[Cu(L) ₂ Cl ₂]	1627	1557	420
[CuL ₂ (OAc) ₂]	1618	1550	419
[CuL ₂ (SO ₄) ₂]	1642	1539	419
[CuL ₂ (NO ₃) ₂]	1636	1547	403
[NiL ₂ Cl ₂]	1621	1535	429
[NiL ₂ (SO ₄) ₂]	1640	1552	418
[NiL ₂ (OAc) ₂]	1636	1555	427
[Ni(L) ₂ (NO ₃) ₂]	1619	1549	405

Magnetic Moment

The magnetic moment of synthesised complexes was calculated at room temperature on Guoy Chapman's balance by using CuSO₄.5H₂O as calibrant listed in table3. The magnetic moment of Cu(II) complexes was found to be in the range 1.49-1.53B.M. This value of magnetic moment indicates one unpaired electron in case of Cu(II) complexes (table3). For Ni(II) complexes the magnetic moment values lies between 2.54-3.10B.M. This value of magnetic moment corresponds to three unpaired electron. This shows that complexes under study are high spin complexes.

**Fig. 2a : IR Spectrum of [Cu(L₂)Cl₂]**

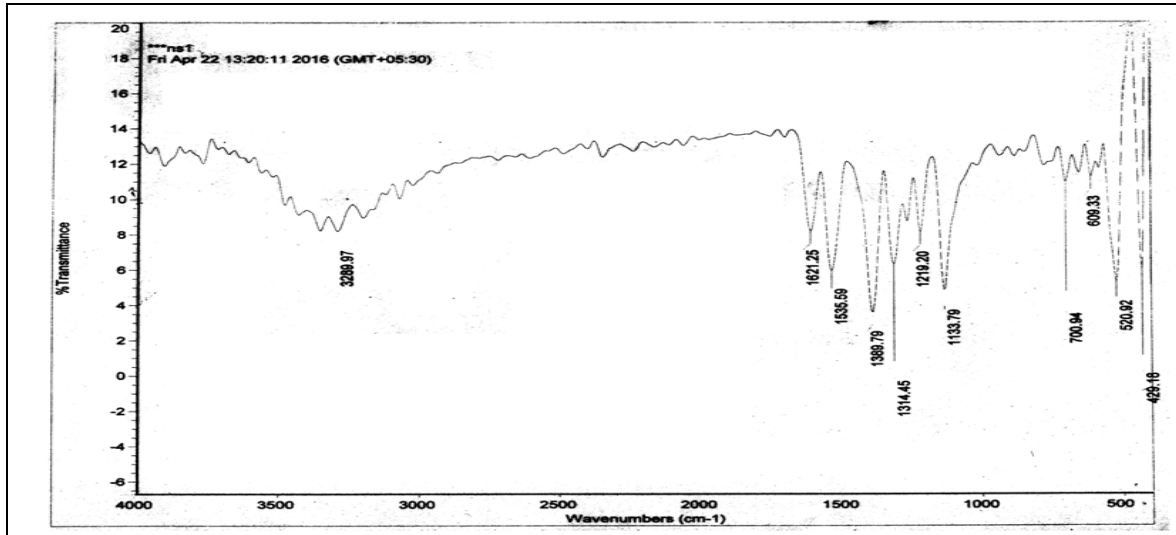


Fig. 2b: IR Spectrum of $[Ni(L_2)Cl_2]$

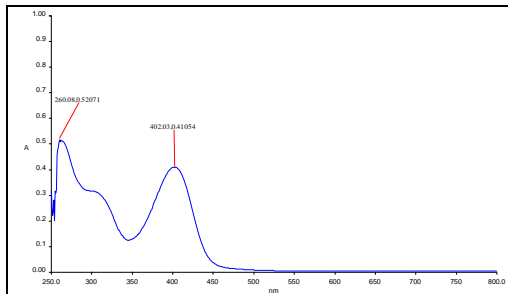


Fig. 3a : UV Spectrum of $[Cu(L_2)Cl_2]$

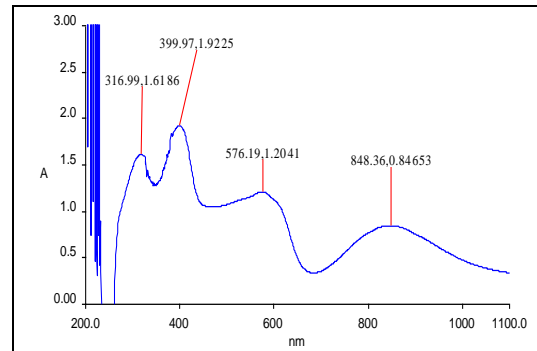


Fig. 3b : UV Spectrum of $[Cu(L_2)(NO_3)_2]$



Fig. 4a: EPR Spectrum of Copper

Mass spectra

Mass spectra gives the relevant information

about the proposed formula of the synthesised complexes. Mass spectrum of ligand (fig. 1a) shows a molecular ion peak at $m/z=239$ amu corresponding

Table 3 : Magnetic Moment and Electronic Spectral Bands of Copper and Nickel Complexes

Complexes	λ max	μ_{eff}	Dq	B	β	LFSE
[Cu(L ₂)Cl ₂]	12316,24827,32653, 38249	1.43	-	-	-	-
[Cu(L ₂)(OAc) ₂]	14262,18444,22026,	1.53	-	-	-	-
[Cu(L ₂)(SO ₄) ₂]	12315, 24973, 38554	1.41	-	-	-	-
[Cu(L ₂)(NO ₃) ₂]	12318, 24873, 38449	1.46	-	-	-	-
[Ni(L ₂)Cl ₂]	11787,17355,25001, 31546	2.93	1178	466	0.448	169
[Ni(L ₂)SO ₄]	11790,17360,25011,31362	2.96	1179	466	0.448	169
[Ni(L ₂)OAc ₂]	11877,17540, 24718, 30975	3.01	1187	441	0.424	170
[Ni(L ₂)(NO ₃) ₂]	11576,17667,22936, 30700	2.98	1157	391	0.376	166

TABLE 4 : EPR spectral data of Cu(II) Complexes

Complexes	g_{\parallel}	g_{\perp}	g_{iso}	G
[Cu(L ₂)Cl ₂]	2.167	2.044	-	3.79
[Cu(L ₂)(OAc) ₂]	2.043	2.012	-	3.58
[Cu(L ₂)(SO ₄) ₂]	2.240	2.134	-	1.791
[Cu(L ₂)(NO ₃) ₂]	2.234	2.114	-	2.048

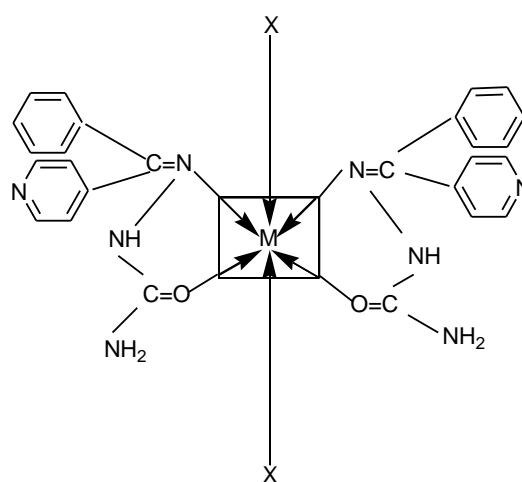
to species [C₁₃H₁₁N₄O]⁺. The peak at m/z= 255 amu indicates M-1 peak. This value favours the proposed formula of the ligand. The mass spectrum of the complex [CuC₂₆H₂₃O₂N₈Cl₂]⁺ shows a molecular ion peak at m/z = 645.6 amu which justifies the proposed formula of the complex.

IR Spectra

In table 2 the most characteristic IR bands of ligand and complexes are shown between 4000-400cm⁻¹. A band at 1660 cm⁻¹ may be assigned to $\nu(\text{C}=\text{O})_{\text{carbonyl}}$ [9] group and another band at 1577 cm⁻¹ which corresponds to $\nu(\text{C}=\text{N})_{\text{azomethine}}$ [10] group. In IR of complexes these value are shifted towards lower side from 25-45 cm⁻¹. This indicates that both $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{O})$ groups are coordinated to central metal ion in complex formation (Fig.2a and 2b). The coordination of $\nu(\text{C}=\text{O})$ group is further supported by appearance of new $\nu(\text{M}=\text{O})$ band which appeared in the region from 403-420 cm⁻¹ [11]. Thus the ligand is bidentate and coordinated through sulphur and oxygen with central metal ion.

IR Bands due to anion

In nitrate complexes of Cu(II) four bands appeared at 1412(ν_1), 1319(ν_2), 1031(ν_3), 1287(ν_5) and the difference between ν_5 and ν_1 is 125 cm⁻¹ which indicates unidentate behaviour of nitrate group [12]. In sulphato complexes of Cu(II) the bands appeared are 1123, 1064, 935cm⁻¹ suggesting the monodentate coordination of sulphate group [13]. In acetato complexes the band corresponds

**Fig. 4b: Proposed structure of complex**

to $\nu_{\text{C}=\text{O}}$ appeared at 1483 and $\nu_{\text{C}=\text{O}}$ at 1266 cm⁻¹, $\Delta\nu=217\text{cm}^{-1}$ [14-16] indicates monodentate coordination of acetate group. In IR spectra of nitrate complexes of Ni(II) three bands appeared at 1434 (ν_1), 1315 (ν_2), 1266 (ν_3) cm⁻¹, $\Delta\nu=168\text{cm}^{-1}$ suggests that nitrate group is attached in unidentate manner to central metal ion. The IR spectra of acetato complexes of Ni(II) shows $\nu\text{C}=\text{O}$ band at 1412 and $\nu\text{C}=\text{O}$ band at 1264 cm⁻¹ which indicates that both the acetates are attached in unidentate manner [18]. In IR spectra of sulphato complexes three bands appeared at 1640 (ν_1), 1552 (ν_2), 418 (ν_3) represent unidentate behaviour of sulphate group.

Electronic spectra

The electronic spectra of Cu(II) complexes displays three bands in the region 12316-14262 cm⁻¹ (ν_1), 18444 cm⁻¹ (ν_2), 22026-24973 cm⁻¹ (ν_3) (Fig.3a) which may be assigned to following transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ ($d_{x^2-y^2} \rightarrow d_{zy}$) (ν_2) and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ ($d_{x^2-y^2} \rightarrow d_{zy}, d_{yz}$) (ν_3) [19] which supports the tetragonal geometry and the other bands are due to charge transfer. The electronic spectra of Ni(II) complexes also displays three bands in the region from 11576-11877cm⁻¹ (ν_1), 17355-17667 cm⁻¹ (ν_2),

22936-25011 cm^{-1} (ν_3) (Fig.3b) which suggests the transitions as: ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ respectively [20] and other bands may be due to charge transfer. The position of these bands suggests the octahedral geometry of Ni(II) complexes. Ligand field parameter are calculated and listed in table 3.

EPR Spectra

The EPR spectra of the synthesised complexes under study was recorded as polycrystalline sample at room temperature. The g value obtained from the epr spectra are represented in table 4. The g value of Cu(II) complexes can be use to obtain ground state [21]. In tetragonal geometry the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^2B_{1g}$ ground state with $g_{\parallel} > g_{\perp}$. The trend $g_{\parallel} > g_{\perp} > g_e$ observed for these complexes indicates that the unpaired electron is localised in $d_{x^2-y^2}$ orbital of the Cu(II) ions and the spectral features are the characteristics of axial symmetry [22] and tetragonal geometry. Along with this the G values which is the exchange coupling interaction between two copper centres obtained from Hathway [23] expression $G = g_{\parallel} - 2/g_{\perp} - 2$. If the value of G is greater than 4 than exchange interaction is negligible and if the value of G is less than 4 than a considerable interaction is possible. The G values obtained for Cu(II) complexes under study is less 4 indicates considerable interaction in solid complexes. The calculated G values follows the order $\text{Cl}^- > \text{CH}_3\text{COO}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The lower G values for sulphate indicates that sulphate has large interaction than acetate, nitrate and chloride complexes.

According to the above spectral study the proposed structure of complex is following:(Fig.4b

CONCLUSION

The synthesised ligands and complexes were characterised by elemental analysis, IR spectroscopy, mass spectroscopy, UV-Vis, ${}^1\text{H}$ NMR spectroscopy and EPR spectral studies. The proposed study of complexes indicates octahedral geometry for nickel complexes and tetragonal geometry for copper complexes. Ligand was found to be bidentate which coordinates to metal through azomethine group as $\nu(\text{C}=\text{N})$ and through oxygen as $\nu(\text{C}=\text{O})$ group.

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REFERENCES

1. Kurup MRP, Varghese B, Sithambaresan M, Krishnan S, Sheeja SR, Suresh E. Synthesis, spectral characterization and crystal structure of copper(II) complexes of 2-benzoylpyridine-N(4)-phenylsemicarbazone. *Polyhedron*. 2011 Jan;30(1):70–8. Available from: <http://dx.doi.org/10.1016/j.poly.2010.09.030>
2. West DX, Liberta AE, Padhye SB, Chikate RC, Sonawane PB, Kumbhar AS, et al. Thiosemicarbazone complexes of copper(II): structural and biological studies. *Coordination Chemistry Reviews*. 1993 Feb;123(1-2):49–71. Available from: [http://dx.doi.org/10.1016/0010-8545\(93\)85052-6](http://dx.doi.org/10.1016/0010-8545(93)85052-6).
3. H. Beraldo BSP, D. Gambinob BSP. The Wide Pharmacological Versatility of Semicarbazones, Thiosemicarbazones and Their Metal Complexes. *Mini-Reviews in Medicinal Chemistry*. 2004 Jan 1;4(1):31–9. Available from: <http://dx.doi.org/10.2174/1389557043487484>
4. Sridhar SK, Pandeya SN, Stables JP, Ramesh A. Anticonvulsant activity of hydrazones, Schiff and Mannich bases of isatin derivatives. *European Journal of Pharmaceutical Sciences*. 2002 Aug;16(3):129–32. Available from: [http://dx.doi.org/10.1016/s0928-0987\(02\)00077-5](http://dx.doi.org/10.1016/s0928-0987(02)00077-5).
5. Yogeewari P, Ragavendran JV, Sriram D, Nageswari Y, Kavya R, Sreevatsan N, et al. Discovery of 4-Aminobutyric Acid Derivatives Possessing Anticonvulsant and Antinociceptive Activities: A Hybrid Pharmacophore Approach. *Journal of Medicinal Chemistry*. 2007 May;50(10):2459–67. Available from: <http://dx.doi.org/10.1021/jm061431g>.
6. Reena TA, Seena EB, PrathapachandraKurup MR. Synthesis and spectral studies of cadmium(II) complexes derived from di-2-pyridyl ketone and N4-phenylsemicarbazide: First structural report of a cadmium(II) complex of semicarbazone. *Polyhedron*. 2008 Apr;27(6):1825–31. Available from: <http://dx.doi.org/10.1016/j.poly.2008.02.020>.
7. Casas JS, García-Tasende MS, Sordo J. Main group metal complexes of semicarbazones and thiosemicarbazones. A structural review. *Coordination Chemistry Reviews*. 2000 Nov;209(1):197–261. Available from: [http://dx.doi.org/10.1016/s0010-8545\(00\)00363-5](http://dx.doi.org/10.1016/s0010-8545(00)00363-5).
8. Collen, S.A.J. Everaerts, F.M.;Huf, F.A. Characterisation of ${}^{60}\text{Co}$ -Gamma Radiations Induced Radical Products of Antipyrine by means of High Performance Liquid Chromatography. *Mass Spectrometry, Capillary Zone Electrophoresis, Micellar Electrokinetic Capillary Chromatography and Nuclear Magnetic Resonance Spectrometry*. *J. Chromatogr. A* 1997, 788, 95-103.

9. Singh VP, Katiyar A, Singh S. Synthesis, characterization of some transition metal(II) complexes of acetone p-amino acetophenonesalicyloylhydrazone and their anti microbial activity. *BioMetals*. 2008 Feb 28;21(4):491–501. Available from: <http://dx.doi.org/10.1007/s10534-008-9136-9>.
10. West, D.X.;Carbson, C.S. Galloway, C.P.; Liberta, A.E.; Daniel, C.R. Transition Metal Complexes of Thiosemicarbazones derived from 2-acetylpyridine, Part 6, The Chemical and Antifungal Properties of 2-acetylpyridine ⁴N-diethyl and ⁴N dipropyl thiosemicarbazones and their Cu(II) complexes, *Transition Met. Chem.* 1990,15,91.
11. Joseph M, Suni V, PrathapachandraKurup MR, Nethaji M, Kishore A, Bhat SG. Structural, spectral and antimicrobial studies of copper(II) complexes of 2-benzoylpyridine N(4)-cyclohexylthiosemicarbazone. *Polyhedron*. 2004 Dec;23(18):3069–80. Available from: <http://dx.doi.org/10.1016/j.poly.2004.09.026>.
12. Sulekh Chandra and Monika Tyagi. Ni(II), Pd(II), Pt(II), complexes with ligand containing thiosemicarbazone and semicarbazone moiety: Synthesis, Characterisation and Biological Investigation, *J. Serb. Chem. Soc.* 73(7)(2008)727-734.
13. Chandra S.,;Sangeetika, Rathi, A magnetic and Spectral Studies on Copper(II) Complexes of N-O and N-S donor ligands. *J. Saudi Chem. Soc.* 2001,5(2),175.
14. Bailey RA, Kozak SL, Michelsen TW, Mills WN. Infrared spectra of complexes of the thiocyanate and related ions. *Coordination Chemistry Reviews*. 1971 Aug;6(4):407–45. Available from: [http://dx.doi.org/10.1016/s0010-8545\(00\)80015-6](http://dx.doi.org/10.1016/s0010-8545(00)80015-6).
15. Hester RE, Grossman WEL. Vibrational Analysis of Bidentate Nitrate and Carbonate Complexes. *Inorg Chem*. 1966 Aug;5(8):1308–12. Available from: <http://dx.doi.org/10.1021/ic50042a002>.
16. S. Chandra, L.K. Gupta, *Spectrochim, Acta A* 60(2004)2411; S. Chandra, L.K. Gupta, *J. Indian Chem. Soc.* 82(2005)454.
17. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam. 1984
18. Chandra S, Jain D, Sharma AK, Sharma P. Coordination Modes of a Schiff Base Pentadentate Derivative of 4-Aminoantipyrine with Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies. *Molecules*. 2009 Jan 1;14(1):174–90. Available from: <http://dx.doi.org/10.3390/molecules14010174>.
19. Jezowska-Trzebiatowska B, Lisowski J, Vogt A, Chmielewski P. Synthesis and characterization of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with N-salicydene-o-hydroxymethylaniline. *Polyhedron*. 1988 Jan;7(5):337–43. Available from: [http://dx.doi.org/10.1016/s0277-5387\(00\)80480-5](http://dx.doi.org/10.1016/s0277-5387(00)80480-5).
20. B.J. Hathway, D.E. Billing, *Coord. Chem. Rev.*5(1970)143.
21. A.A.G. Tomilson, B.J. Hathway, D.E. Willing, P.J. Nicholis, *J. Inorg. Nucl. Chem.* 39(1977)417.