

MODERN SPECTROSCOPIC APPROACH OF COPPER COMPLEXES OF SCHIFF BASE LIGAND

Monika Tyagi^{*1}, Neha Tripathy^{*2}

^{*1}Department of Chemistry, Monad University NH-9, Hapur, India 245304.

^{*2}Department of Chemistry, Mewar University, Gangrar, Chittorgarh, Rajasthan, India, 312901.

ABSTRACT

Cu (II) complexes are synthesized with, pyridine-2-carboxyaldehyde semicarbazone. These complexes have been characterized on the basis of their elemental analysis, molar conductance, magnetic susceptibility and electronic, Nuclear Magnetic Resonance and Mass spectroscopic studies. On the basis of spectral studies ligand acts in a tetradentate manner. Spectroscopic studies have revealed tetragonal geometry for all the complexes and paramagnetic nature with one unpaired electron.

Keywords: Copper (II) complexes, Spectroscopic studies, semicarbazone.

1. INTRODUCTION

Thiosemicarbazones, semicarbazones and their metal complexes have always been matter of attraction for the chemists due to their ability to show variable coordinating ability and to form different kinds of complexes by coordinating through various atoms and showing different kinds of geometry[1], that gives them distinctive capability[2] of trapping metal ions and also donating electron pairs to metal ions.[3] This further makes them special from the point of pharmaceutical properties[4] [5]antimalarial antibacterial[6] anti fungal properties as well as antioxidant activities.[7]The thiosemicarbazones have caused tumor cell death by the bringing about change in the geometry,[8] point of attachment and other conditions.[9] They have also been found to show catalytic activities in various reactions. Researches have also conducted and found positive result for anti-corrosion activities by them against strong acids.[10].As well as the quantum mechanical and computational studies are also being conducted on these kinds of compounds.[11]

The present paper discusses the synthesis and spectroscopic characterization of Copper metal complexes of Chloride, Bromide, Perchlorate and Thiocyanate of Pyridine-2-carboxyaldehyde semicarbazone as ligand.[12]

2. EXPERIMENTAL

Material-All the chemicals used were of analytical grade and procured from Sigma Aldrich and used as received.

Synthesis of ligand

1.115 gm(0.01mole) of semicarbazide hydrochloride, and 0.82 gm(0.01mole) (**Figure 1**) of sodium acetate, separately being dissolved in distilled water and mixed in already reflux heated solution of 0.95 ml (0.01 mole)Pyridine-2-carboxyaldehyde in ethanol with constant and vigorous stirring and maintaining temperature below 25 °C. Off white shining precipitate is filtered out, washed and dried on vacuum [13,14].

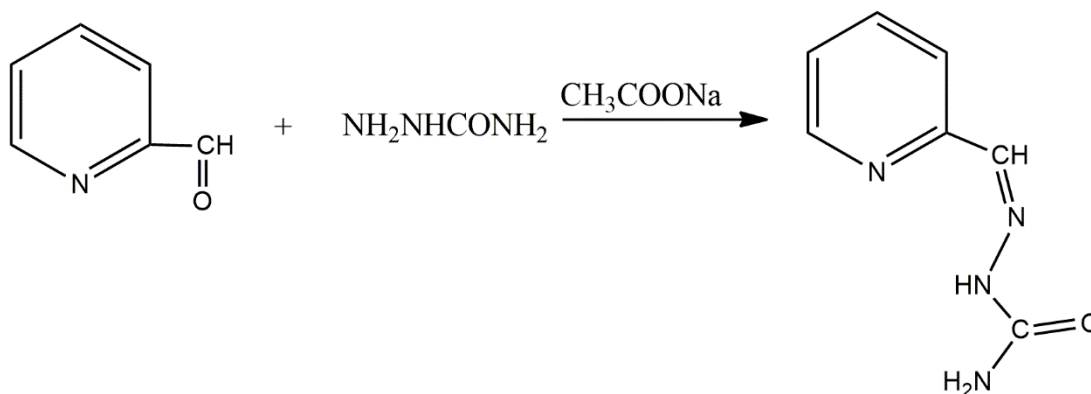


Figure 1: Reaction scheme for ligand

Synthesis Of Complexes

0.002 mole(0.36g)of ligand (2:1) dissolved in minimum amount of hot ethanolic solution is mixed with 0.001 mole heated ethanolic solution of respective metal salts of Copper. The mixture is refluxed for 6-7 hours at a constant temperature. The mixture is cooled on ice bath and left overnight. Precipitate filtered out,washed and dried under

vacuum. Purity of complex was checked with TLC and melting point was determined.

Physical Measurement

C, H and N content were determined by Carlo Erba elemental analyser Magnetic susceptibility has been measured on Gouy Balance, using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. Molar conductance was measured on systronic conductivity meter model 304. Mass spectrum has been recorded on JEOL, JMS, DX 303 mass spectrometer. $^1\text{H-NMR}$ spectra of ligand was recorded on Bruker Advance Ultrashield-500 spectrometer using CDCl_3 as the solvent. IR spectra was recorded on FTIR BX-II spectrophotometer.

3. RESULTS AND DISCUSSION

The IR spectrum of ligand also gives peak at 3445 cm^{-1} , 3200 cm^{-1} corresponding to NH_2 and NH groups, peak at 3046 cm^{-1} corresponding to C-H str, 1659 cm^{-1} corresponding to $\text{C}=\text{O}$ (carbonyl group), 1481 cm^{-1} corresponding to azomethine $\text{CH}=\text{N}$ and at 708 cm^{-1} corresponding to $\text{C}=\text{N}$ (pyridine) bonds. Mass spectrum shows peak at 163 amu corresponding to (M^{+1}) . (Figure 2).

$^1\text{H NMR}$ spectrum with the following peaks can further support the proposed structure. δ 10.53(s, 1H, N(3)H), 8.83(s, 1H, C(6)H), 8.24(s, 1H, N(4)H), 7.53(d, 1H, C(4)H), 8.14(d, 1H, C(1)H), 8.00(t, 1H, C(2)H), 7.84(s, 1H, C(3)H).

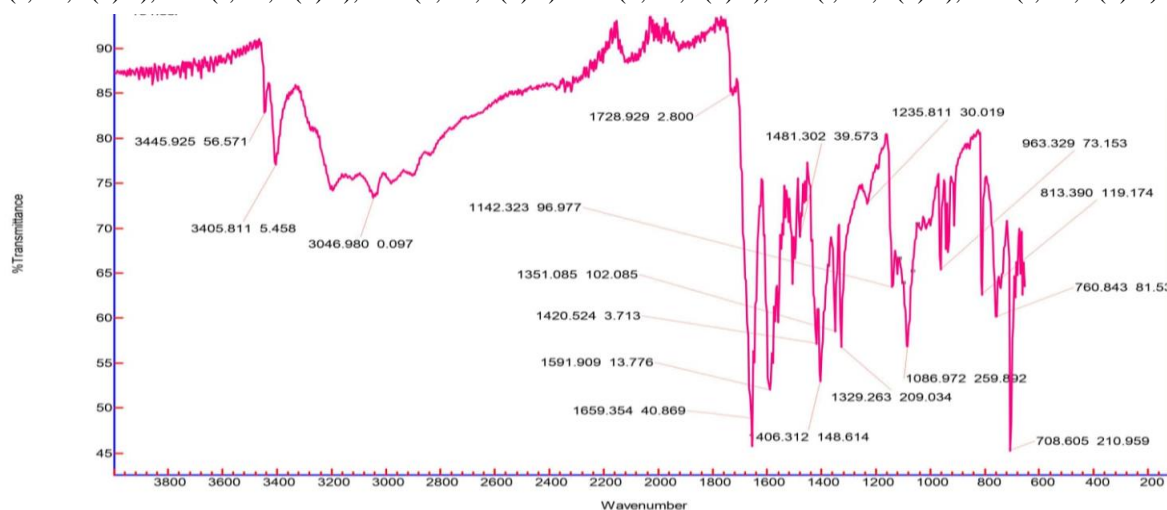


Figure 2 : IR spectrum of Ligand (Pyridine-2-carboxyaldehydesemicarbazone)

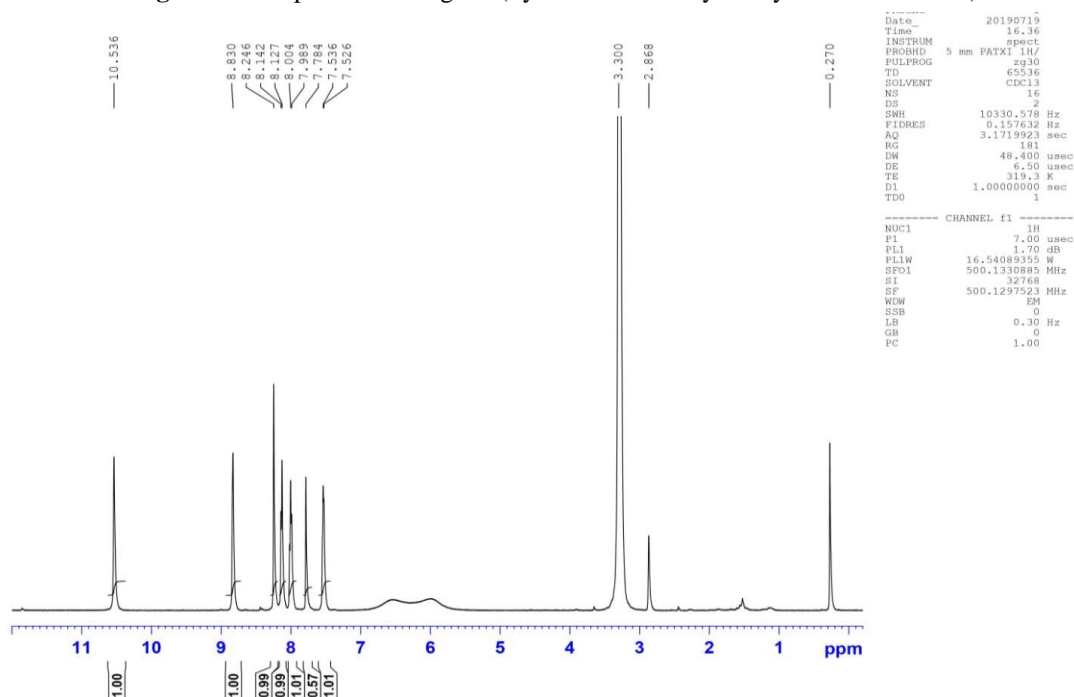


Figure 3 : NMR spectrum of Ligand (Pyridine-2-carboxyaldehydesemicarbazone)

Complexes - The elemental analysis and physical measurement values of the ligand and complexes predicts the formula as mentioned in Table 1. The complexes have been found to be soluble in either DMSO or DMF and sparingly soluble in water and ethanol.

The value of molar conductance of the complexes with ligand 1, in DMSO lie in the range of $5-10 \Omega^{-1}\text{Cm}^2\text{mol}^{-1}$ showing all the complexes to be a non-electrolyte and with ligand 2 lies in the range of $130-185 \Omega^{-1}\text{Cm}^2\text{mol}^{-1}$ showing its 1:2 electrolytic nature.[16]

Interpretation of IR spectra

IR bands provide very important information about the bonding in the complexes. The ligand shows two bands at 3445 cm^{-1} and 3405 cm^{-1} corresponding to NH_2 and NH groups which are not displaced much in the complexes indicating their non involvement in bonding to metal. The bands at 708 cm^{-1} , 1659 cm^{-1} and 1481 cm^{-1} showing downward and upward shift in complexes indicate the involvement of pyridine nitrogen, azomethine nitrogen and carbonyl oxygen respectively in coordination with metal in complexes. Rest of the bands do not show only minimum shift showing the tridentate nature of ligand.[17]

Electronic spectra of complexes

Electronic spectra gives three bands in the region 10110-13121, 16278-18270 and 21830-27630 corresponding to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, supporting the tetragonal geometry for the complexes due to Jahn Teller Distortion. The magnetic moment values lie in the range of 1.89-2.01 B.M., showing their paramagnetic nature with one unpaired electron as expected.[1]

Table 1: Analytical data of ligands and complexes

Sl. No.	Compound	Molecular formula	Molecular weight	Colour	M.P.($^{\circ}\text{C}$)	Yield(%)	Elemental analysis %found(calculated)			
							Cu	C	H	N
1	PASC	$\text{C}_7\text{H}_8\text{N}_4\text{O}$	164	Off white	129	62	-	50.11 (51.21)	4.48 (4.91)	34.0 (34.13)
2	$[\text{Cu}(\text{PASC})_2]\text{Cl}_2$	$\text{CuC}_{14}\text{H}_{16}\text{N}_8\text{O}_2\text{Cl}_2$	463	Creamish green	228	64	13.59 (13.73)	35.98 (36.33)	3.32 (3.48)	24.10 (24.21)
3	$[\text{Cu}(\text{PASC})_2]\text{Br}_2$	$\text{CuC}_{14}\text{H}_{16}\text{N}_8\text{O}_2\text{Br}_2$	551.7	Light brown	234	65	11.20 (11.52)	30.21 (30.48)	2.34 (2.92)	20.12 (20.31)
4	$[\text{Cu}(\text{PASC})_2](\text{SCN})_2$	$\text{CuC}_{16}\text{H}_{16}\text{N}_{10}\text{S}_2\text{O}_2$	508	Brown	232	56	12.26 (12.51)	37.24 (37.83)	2.98 (3.17)	27.52 (27.57)
5	$[\text{Cu}(\text{PASC})_2](\text{ClO}_4)_2$	$\text{CuC}_{14}\text{H}_{16}\text{N}_8\text{Cl}_2\text{O}_{10}$	589	Dark green	241	57	10.58 (10.76)	28.32 (28.46)	2.52 (2.73)	18.61 (18.97)

Table 2: IR spectral data of ligands and complexes

Compounds	N-H (cm^{-1})	C-H (cm^{-1})	C=O (cm^{-1})	CH=N (cm^{-1})	C=N Aromatic (cm^{-1})
PASC	3445,3405	3046	1659	1481	708
$[\text{Cu}(\text{PASC})_2]\text{Cl}_2$	3439	3047	1648	1464	718
$[\text{Cu}(\text{PASC})_2]\text{Br}_2$	3437	3042	1647	1461	720
$[\text{Cu}(\text{PASC})_2](\text{SCN})_2$	3431	3043	1650	1468	722
$[\text{Cu}(\text{PASC})_2](\text{ClO}_4)_2$	3442	3038	1642	1470	727

Table 3: Physical properties of complexes and electronic spectral data

Complexes	Molar conductance $\Omega^{-1}\text{Cm}^2\text{mol}^{-1}$	Magnetic moment μ_{eff} (B.M.)	Electronic spectral data (λ_{max} in cm^{-1})		
[Cu(PASC) ₂] ₂ Cl ₂	185	1.99	11102	18234	23231
[Cu(PASC) ₂] ₂ Br ₂	166	2.01	10137	17560	22270
[Cu(PASC) ₂] ₂ (SCN) ₂	174	1.97	10290	16280	27630
[Cu(PASC) ₂] ₂ (ClO ₄) ₂	130	1.98	11920	16590	23476

4. CONCLUSION

On the basis of elemental analysis data and spectral analysis, the complexes with ligand have been found to possess the formula as shown in Table 1. IR spectral data suggest the tridentate nature of ligand in NNO manner. According to the molar conductance data and electronic spectral studies all the complexes are found to be 1:2 electrolyte having tetragonal geometry and according to the magnetic susceptibility values all the complexes are having Para magnetism with one unpaired electron. Thus, the proposed structures of complexes are depicted in **Figure 4**.

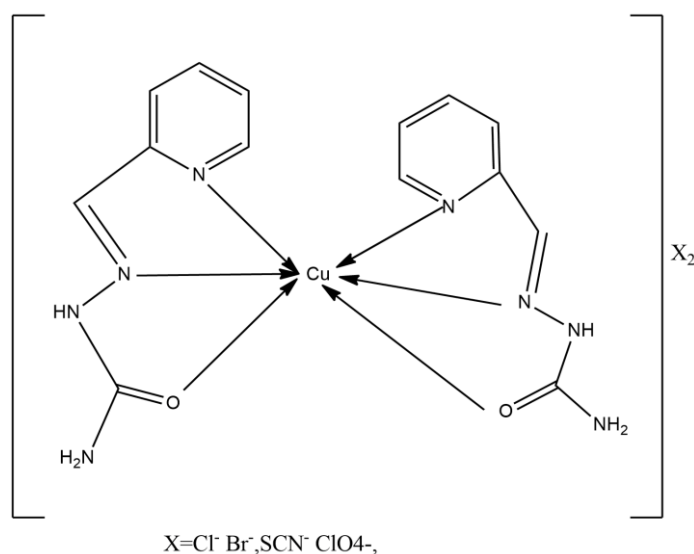


Figure 4 : Proposed structure of complexes with ligand 2(Pyridine-2-carboxyaldehydesemicarbazone)

5. REFERENCES

- [1] C. Surendra Dilip, V. Thangaraj, and A. Paul Raj, "Synthesis, spectroscopic characterisation, biological and DNA cleavage properties of complexes of nicotinamide," *Arab. J. Chem.*, vol. 9, pp. S731–S742, 2016, doi: 10.1016/j.arabjc.2011.07.016.
- [2] A. K. Renfrew, E. S. O'Neill, T. W. Hambley, and E. J. New, "Harnessing the properties of cobalt coordination complexes for biological application," *Coordination Chemistry Reviews*, vol. 375. Elsevier B.V., pp. 221–233, Nov. 15, 2018, doi: 10.1016/j.ccr.2017.11.027.
- [3] W. Hernández et al., "Synthesis, Spectroscopic Characterization, Structural Studies, and in Vitro Antitumor Activities of Pyridine-3-carbaldehyde Thiosemicarbazone Derivatives," *J. Chem.*, vol. 2020, 2020, doi: 10.1155/2020/2960165.
- [4] R. A. C. Souza et al., "Copper(II) complexes based on thiosemicarbazone ligand: Preparation, crystal structure, Hirshfeld surface, energy framework, antiMycobacterium activity, in silico and molecular docking studies," *J. Inorg. Biochem.*, vol. 223, p. 111543, Oct. 2021, doi: 10.1016/J.JINORGBIO.2021.111543.
- [5] K. K. Ilavenil and M. Dhamodharan, "Synthesis, structure and characterisation of Cr(III) and Fe(III) complexes of m-nitro benzaldehyde thio semicarbazone," *J. Chem. Pharm. Sci.*, vol. vol.9, no. 3, pp. 1458–1462, 2016, [Online]. Available: www.jchps.com.
- [6] S. Eğlence-Bakır, "New nickel(II) complexes containing N2O2 donor thiosemicarbazones: Synthesis,

- characterization and antioxidant properties,” *J. Mol. Struct.*, p. 131121, 2021, doi: 10.1016/J.MOLSTRUC.2021.131121.
- [7] W. Hernández et al., “Synthesis, Spectroscopic Characterization, Structural Studies, and In Vitro Antitumor Activities of Pyridine-3-carbaldehyde Thiosemicarbazone Derivatives,” *Hindawi J. Chem.*, vol. 2020, p. 12, 2020, doi: 10.1155/2020/2960165.
- [8] Y. Fu et al., “Calcium release induced by 2-pyridinecarboxaldehyde thiosemicarbazone and its copper complex contributes to tumor cell death,” *Oncol. Rep.*, vol. 37, no. 3, pp. 1662–1670, Mar. 2017, doi: 10.3892/OR.2017.5395.
- [9] B. Xu, W. Yang, Y. Liu, X. Yin, W. Gong, and Y. Chen, “Experimental and theoretical evaluation of two pyridinecarboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution,” *Corros. Sci.*, vol. 78, pp. 260–268, Jan. 2014, doi: 10.1016/J.CORSCI.2013.10.007.
- [10] M. Khalid et al., “An Efficient Synthesis, Spectroscopic Characterization, and Optical Nonlinearity Response of Novel Salicylaldehyde Thiosemicarbazone Derivatives,” *ACS Omega*, vol. 6, no. 24, pp. 16058–16065, Jun. 2021, doi: 10.1021/ACSOMEGA.1C01938.
- [11] W. M. Basyouni, S. Y. Abbas, K. A. M. El-Bayouki, R. M. Daawod, and M. K. Elawady, “Synthesis and antiviral evaluation of 5-(aryloxy)salicylaldehyde thiosemicarbazone derivatives as potent anti-bovine viral diarrhoea virus agents,” <https://doi.org/10.1080/00397911.2021.1925298>, 2021, doi: 10.1080/00397911.2021.1925298.
- [12] S. Chandra, M. Tyagi, and M. S. Refat, “Spectroscopic, thermal and antibacterial studies on Mn(II) and Co(II) complexes derived from thiosemicarbazone,” *J. Serbian Chem. Soc.*, vol. 74, no. 8–9, pp. 907–915, 2009, doi: 10.2298/JSC0909907C.
- [13] M. Tyagi and S. Chandra, “Synthesis, characterization and biocidal properties of platinum metal complexes derived from 2,6-diacetylpyridine (bis thiosemicarbazone),” *Open J. Inorg. Chem.*, vol. 02, no. 03, pp. 41–48, 2012, doi: 10.4236/ojic.2012.23007.
- [14] I. Ali, W. A. Wani, and K. Saleem, “Empirical formulae to molecular structures of metal complexes by molar conductance,” *Synth. React. Inorganic, Met. Nano-Metal Chem.*, vol. 43, no. 9, pp. 1162–1170, 2013, doi: 10.1080/15533174.2012.756898.
- [15] R. K. Agarwal, L. Singh, and D. K. Sharma, “Synthesis, spectral, and biological properties of copper(II) complexes of thiosemicarbazones of Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes,” *Bioinorg. Chem. Appl.*, vol. 2006, 2006, doi: 10.1155/BCA/2006/59509.
- [16] M. El-Behery and H. El-Twigry. Synthesis, magnetic, spectral, and antimicrobial studies of Cu(II), Ni(II) Co(II), Fe(III), and UO₂(II) complexes of a new Schiff base hydrazone derived from 7-chloro-4-hydrazinoquinoline. *Spectrochimica Acta A*, 66, 28-36, 2007.