

## Study of Some Novel Complexes of Ni(II) and Cu(II) with Schiff Base Ligand Derived from Hydroxamic Acid

Sanjay Kumar, Mahavir Upmanyu, Priyanka

Department of Chemistry, Jagdam College, Chapra, Saran, Bihar, India

Corresponding Author – sanjaykrujain@gmail.com

### ABSTRACT

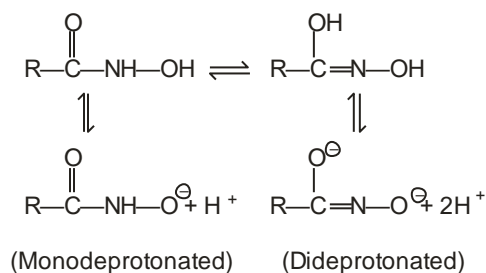
In this paper, we report the synthesis and characterisation of some novel complexes of Ni(II) and Cu(II) with 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid in presence of bases like ammonia, pyridine, phenyl isocyanide, quinoline and  $\pi$ -picoline. The complexes have been characterised on the basis of elemental analyses, molar mass determination, molar conductance and magnetic susceptibility measurements, UV-visible and IR spectroscopic investigations. The complexes have been formulated as  $[M(L)(B)_3]$  where, L=dideprotonated 2-(o-hydroxybenzophenone imino) benzohydroxamic acid ( $LH_2$ ),  $B=NH_3$ , pyridine, phenyl isocyanide, quinoline and  $\pi$ -picoline and  $M=Ni(II)$  and  $Cu(II)$ . The ligand (L) behaves as dianionic tridentate ligand. The complexes have been found to be paramagnetic and non-electrolytic in nature. All the complexes are found to have octahedral geometry as indicated by the values of magnetic moments and the positions of u.v.-visible spectral bands. The nature of metal-ligand bonding has been established on the basis of IR spectral studies.

**Keywords** : Hydroxamic Acid, Chelating Ligand, Spectral Investigation, Magnetic Susceptibility, Molar Conductance, Tridentate

### I. INTRODUCTION

Due to the low toxicity and varieties of biological activities, hydroxamic acids ( $R-CO-NHOH$ ) and their derivatives have been the subject of research for inorganic and bio-inorganic chemists in the recent past. They exhibit antibacterial [1-3], antifungal [4-5], antitumour [6-8], antituberculous [9] and antimalarial [10] properties. They are also known to inhibit enzymes such as urease [11], peroxidase [12] and metalloproteinase [13]. Numerous hydroxamic acid analogues are known to inhibit DNA synthesis by making the enzyme ribonucleotide reductase inactive [14]. Symptoms of asthma and other obstructive airway diseases are treated with cinnamohydroxamic acids which inhibit 5-

lipoyxygenase [15]. Hydroxamic acids display antiradical and antioxidant properties [16]. Siderophores, which are involved in the processes of iron transport from environment to living organisms, are complexes of Fe(III) with naturally occurring hydroxamic acids [17-18]. Hydroxamic acids have diverse applications in analytical, industrial and pharmaceutical fields [19-23]. These applications of hydroxamic acids are due to their ability to form stable chelates with transition metal ions whereby their biological activities are augmented. Hydroxamic acids are deprotonated in two anionic structures where one of them is monodeprotonated while the other is dideprotonated.



Hydroxamic acids act as (O, O) donor ligands which form five membered chelate rings with metal ions. Keeping in view the wide range of applications of hydroxamic acids and their derivatives, novel complexes of Ni(II) and Cu(II) with the ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid in the presence of bases like  $\text{NH}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ , phenyl isocyanide, quinoline and  $\pi$ -picoline have been synthesised and characterised.

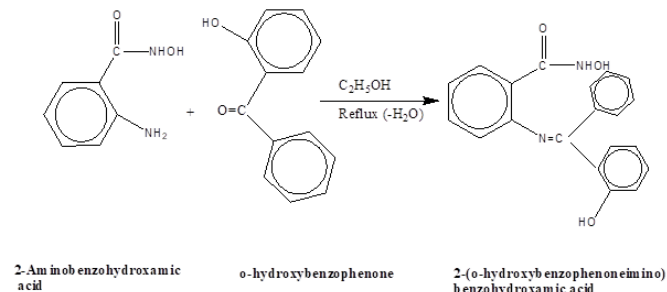
## II. EXPERIMENTAL

### 2.1 Materials and Methods

All chemicals used were of analytical grade purchased from Sigma Aldrich and were used as received without further purification. The microanalysis of C, H and N present in the ligand and complexes was done by elemental analyser Euro EA (Model EA 3000), the magnetic susceptibility of complexes was determined using vibrating sample magnetometer (Model PAR 155). Molar conductance of complexes was determined using digital conductivity meter (HPG System, G-3001). Metals in complexes were estimated by the standard method [24]. The IR spectra of ligand and complexes were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  using Agilent Technologies FT-IR spectrophotometer (Cary 630). Electronic spectra of metal complexes were recorded on Hitachi 300 spectrophotometer. Molar masses of complexes were determined by cryoscopic method.

### 2.2. Synthesis of the ligand

The ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid was prepared by the condensation of o-hydroxy benzophenone with 2-amino benzohydroxamic acid [25-26].



**Procedure:** 0.1 mole (15.2 g) of 2-aminobenzohydroxamic acid was dissolved in minimum volume of ethanol. Further, 0.1 mole (19.8 g) of o-hydroxy benzophenone was dissolved in minimum volume of ethanol. The two ethanolic solutions were mixed slowly with constant stirring. The mixture solution was refluxed in a round bottom flask using water condenser for about 4 hours. After cooling the solution, a pale yellow crystalline solid was separated which was filtered and washed with small amount of acetone and then with ether.

C = 72.28%, H = 4.81%, N = 8.43%, Yield = 70%, M.P =  $136^\circ\text{C}$ .

### 2.3 Synthesis of complexes of Ni(II) and Cu(II) with the ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid in the presence of $\text{NH}_3$ , pyridine, phenyl isocyanide, quinoline and $\pi$ -picoline

**Procedure:** To an ethanolic solution of 0.01 mole  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  /  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was added an ethanolic solution of 0.01 mole (3.32 g) of the ligand ( $\text{LH}_2$ ) slowly with constant stirring. The mixture solution was refluxed with small amount of  $\text{NH}_3$  / pyridine / phenyl isocyanide / quinoline /  $\pi$ -picoline in a round bottom flask using water condenser for about 2 hours. After allowing the solution to stand overnight, a coloured crystalline solid was separated which was

filtered and washed with small amount of acetone. The solid was dried over KOH pellets kept in a desiccator. Melting point of the solid was then recorded. The complexes were found to be insoluble in common organic solvents such as benzene, toluene, methanol, ethanol, chloroform, carbon tetrachloride and ether. However, they were found to be soluble in DMF and DMSO. The yield was approximately 63%.

### III. RESULTS AND DISCUSSION

#### 3.1 Microanalytical data

From microanalytical data (Table-1), the stoichiometries of the newly synthesised complexes have been established. The experimental molar masses of complexes proved beyond doubt their monomeric nature. The microanalytical data and the observed molar masses of complexes are in good agreement with the proposed molecular formula (Table-1) of respective complexes.

Table-1

Sl. No.	Complex compound	Colour	M.P. (°C)	Molar mass found (Calculated)	%Found (% calculated)			
					C	H	N	M
1.	$[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{NH}_3)_3]$	Light Green	195.5	437 (439.7)	54.24 (54.58)	5.28 (5.23)	15.90 (15.92)	13.26 (13.35)
2.	$[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_6\text{H}_5\text{NC})_3]$	Light Green	204.6	693 (697.7)	70.22 (70.51)	4.17 (4.15)	10.06 (10.03)	8.43 (8.41)
3.	$[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_9\text{H}_7\text{N})_3]$	Green	217.2	771 (775.7)	72.52 (72.70)	4.48 (4.51)	9.08 (9.02)	7.62 (7.57)
4.	$[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_5\text{N})_3]$	Green	211.5	622 (625.7)	67.30 (67.12)	4.58 (4.63)	11.23 (11.19)	9.42 (9.38)
5.	$[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_4\text{N}.\text{CH}_3)_3]$	Green	214.2	669 (667.7)	68.34 (68.29)	5.24 (5.17)	10.52 (10.48)	8.82 (8.79)
6.	$[\text{Cu}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{NH}_3)_3]$	Blue	216.5	446 (444.5)	54.15 (53.99)	5.26 (5.17)	15.80 (15.75)	14.32 (14.28)
7.	$[\text{Cu}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_6\text{H}_5\text{NC})_3]$	Light Blue	224.6	705 (702.5)	70.28 (70.04)	4.18 (4.13)	9.93 (9.96)	9.12 (9.04)

8.	$[\text{Cu}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_9\text{H}_7\text{N})_3]$	Yellowish blue	241.5	784 (780.5)	72.38 (72.26)	4.54 (4.48)	8.92 (8.97)	8.22 (8.14)
9.	$[\text{Cu}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_5\text{N})_3]$	Light Green	236.2	633 (630.5)	66.64 (66.61)	4.62 (4.59)	11.24 (11.10)	10.14 (10.01)
10.	$[\text{Cu}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_4\text{N}.\text{CH}_3)_3]$	Blue	239.8	670 (672.5)	66.83 (66.79)	5.26 (5.20)	10.55 (10.41)	9.50 (9.44)

$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3$  = dideprotonated ligand 2-(o-hydroxybenzophenoneimino) benzohydroxamic acid ( $\text{LH}_2$ ).

M=Ni (II), Cu(II)

### 3.2 Molar conductance

The molar conductances of metal complexes were measured in  $10^{-3}\text{M}$  DMF solution at room temperature. The molar conductance values of complexes were found in the range of  $16\text{--}25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating their non-electrolytic nature [27]. All the complexes have therefore been reasonably formulated as in Table -1.

### 3.3 Magnetic susceptibility

The magnetic moment values of Ni(II) complexes have been found to be in the range of 2.92-3.10 BM. The magnetic moment values are indicative of the octahedral configuration of ligands around the central metal ion. The ground term of Ni(II) in octahedral field is  $^3\text{A}_{2g}$  and hence no orbital contribution to magnetic moment is expected. The value in excess of the  $\mu_s$  value (2.83 BM) may be due to first order Zeeman effect. The value of magnetic moment of Cu(II) complexes are found in the range of 1.90-2.00 BM suggesting distorted octahedral geometry.

### 3.4 Electronic spectra

Electronic spectra of complexes of Ni(II) displayed three bands in the region  $13410\text{--}13425 \text{ cm}^{-1}$ ,  $16125\text{--}$

$16315 \text{ cm}^{-1}$  and  $20840\text{--}20930 \text{ cm}^{-1}$  corresponding to transitions,

$^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ ,  $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$  and  $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$

respectively indicating octahedral geometry of complexes [28-29]. The electronic spectra of Cu(II) complexes displayed three adsorption bands in the region  $13175\text{--}13182 \text{ cm}^{-1}$ ,  $16940\text{--}16965 \text{ cm}^{-1}$  and  $23816\text{--}23822 \text{ cm}^{-1}$  which may be assigned to transitions,

$^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ ,  $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$  and  $^2\text{B}_{1g} \rightarrow ^2\text{E}_{1g}$  respectively. The number and range of electronic spectral bands of Cu(II) complexes suggest distorted octahedral geometry for complexes[30-32].

### 3.5 Infrared spectra:

(i) The symmetric N — O stretching vibration at  $1120 \text{ cm}^{-1}$  in IR spectrum of the ligand got shifted to lower frequency region by  $10\text{--}15 \text{ cm}^{-1}$  in complexes suggesting the coordination of the ligand through nitrogen atom of the N–O moiety of hydroxamate group [33].

(ii) The azomethine ( $>\text{C}=\text{N}-$ ) band located at  $1640 \text{ cm}^{-1}$  in the spectrum of the ligand got red shifted by  $15\text{--}20 \text{ cm}^{-1}$  in the spectra of complexes indicating the coordination of the ligand through nitrogen atom of the azomethine group to metal ions [34-35].

(iii) The strong and sharp band due to  $\nu_{\text{NH}} + \nu_{\text{OH}}$  modes in the range of  $3230\text{--}3250\text{ cm}^{-1}$  in the spectrum of the ligand disappeared and a new broad and unsymmetrical band appeared in the range  $3420\text{--}3460\text{ cm}^{-1}$  in the spectra of complexes indicating the presence of at least one free  $\text{—OH}$  group in complexes.

(iv) The band at  $1450\text{ cm}^{-1}$  in the spectrum of the ligand due to  $\nu_{\text{C-O}}$  of the phenolic group got shifted to lower frequency region to  $1180\text{--}1190\text{ cm}^{-1}$  in the spectra of complexes indicating the deprotonation of phenolic-OH and participation of its oxygen atom in coordination to the metal ion [36].

Formation of metal-ligand bond is further confirmed by the appearance of medium intensity bands in the region  $474\text{--}478\text{ cm}^{-1}$  and  $522\text{--}536\text{ cm}^{-1}$  in the spectra of complexes assignable to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$  modes of vibrations respectively [37].

(v) Ammine complexes display a doublet band at  $3320\text{ cm}^{-1}$  and  $3410\text{ cm}^{-1}$  due to symmetric and antisymmetric modes of  $\nu_{\text{NH}}$  vibrations respectively indicating the presence of ammonia molecules in coordination sphere.

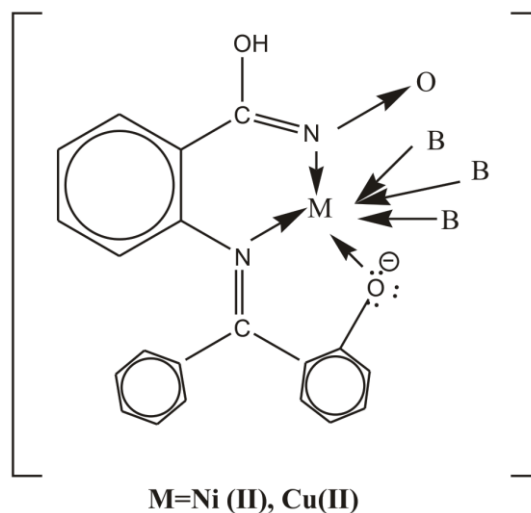
(vi) Phenyl isocyanide complexes display IR bands in the region  $2210\text{--}2220\text{ cm}^{-1}$  which may be assigned to  $\nu_{\text{CIN}}$  mode of vibration.

(vii) Appearance of a new band in IR spectrum of quinoline complexes at  $1030\text{ cm}^{-1}$  due to the breathing mode of vibration of quinoline ring [38] indicating the participation of quinoline molecule in coordination to the metal ion through its nitrogen atom.

(viii) Appearance of a new band at  $1483\text{ cm}^{-1}$  in IR spectrum of the pyridine complex assignable to breathing mode of pyridine ring vibration of coordinated pyridine through the nitrogen atom. A similar band is obtained in the IR spectrum of  $\pi$ -

picoline complex indicating the presence of  $\pi$ -picoline molecule in coordination sphere.

On the basis of the elemental analyses, determination of molar masses, molar conductance and magnetic susceptibility measurements, UV and IR spectral investigations, the following octahedral structure for Ni (II) complexes and distorted octahedral structure for Cu(II) complexes have been established.



#### IV. CONCLUSION

The ligand 2-(o-hydroxybenzophenoimino)benzohydroxamic acid ( $\text{LH}_2$ ) undergoes dideprotonation during complex formation behaving as dianionic tridentate chelating ligand. The newly synthesised complexes are found to be monomeric with general molecular formula  $[\text{M}(\text{L})(\text{B})_3]$ , where L = dideprotonated ligand  $\text{LH}_2$ , B =  $\text{NH}_3$ , phenyl isocyanide, quinoline, pyridine and  $\pi$ -picoline and M = Ni(II) and Cu(II). All the complexes are paramagnetic and have octahedral geometry. Complexes are found to be non-electrolytic in nature.

#### V. Acknowledgement

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## VI. REFERENCES

1. H. Jahangirian, J. Harson, S. Silong, N.Z. Yusof, K. Shameli, S. Eissazadeh, R. R. Moghaddam, B. Mahdavi, M. Jafarzade : J. Med. Plants Res., 5(19), 4826, 2011.
2. H.Agarwal, O. P. Agarwal, R.Karnawat, I.K.Sharma, P.S.verma: Int. J. Appl. Biol. & Pharm. Tech, 1(3), 1293, 2010.
3. A.O. Aliyu, J.N. Wabueze: Int. J. Physical Sci., 2(7), 167, 2008.
4. S.Sonika, S.Neeraj : Der Chemica Sinica, 4(3), 108, 2013
5. M.J. Miller: Chem. Rev., 89, 1563, 1989.
6. H.L. Elford, G.L. Wampler, B.V. Riet : Cancer Res., 39, 844, 1979.
7. Naqeebullah, F.Yang, M.C. Kok, K.M. Lo, F.R. Nor, C.O. Theng: Molecules, 18, 8696, 2013.
8. D. Pal, S.Saha : J. Adv. Pharm. Tech. Res., 3(2), 92, 2012.
9. C.J. Marmion, T. Murphy, J. R. Docherty, K.B. Nolan: Chem. Commun, 1153-115, 2000.
10. D. Veale, J. Carmichael, B.M. Cantwell, H.L.Elford, R. Blackic, D.J.Kerr, S.B. Kaye, A.L. Harris,: Br. J. Cancer, 58(1), 70, 1988.
11. M. Arnold, D.A. Brown, O.Deeg, W.Errington, W. Haase, K.Herlihy, T.J. Kemp, H. Nimir, R. Wemer: Inorg. Chem., 37, 2920, 1998.
12. S.S.C. Tam, D.H. S. Lee, E.Y. Wang, D.G. Munroe, C.Y.Lau: J. Biol. Chem., 270, 13948, 1995.
13. I. Botos, L. Scapozza, D. Zhang, L.A. Liotta, E.F. Meyer: Proc. Nat. Acad. Sci., 93, 2749, 1996.
14. I.K. Larsen, B.M. Sjøberg, L. Thelander: Eur.J. Biochem., 125, 75, 1982.
15. J.P. Demers, V.M. William: U.S. Patent Appl. Pat. No. 4, 820, 828, 1989.
16. M.Z. Koncic, M. Barbaric, V. Perkovic, B.Zoric: Molecules, 16(8), 6232, 2011.
17. A. M. A. Gary, A.L. Crumbliss: Metal Ions in Biological Systems, Marcel Dekker, New York, 35, 239, 1998.
18. J.B. Neilands: J. Biol. Chem., 270, 26723, 1995.
19. G. Borland, G. Murphy, A. Ager: J. Bio-Chem, 274, 2810, 1999.
20. K.M. Bttomley, W.H. Johnson, D.S. Waltor: J. Enzy. Inhibition, 13(2), 79, 1998.
21. K.W. Vogel, D.G. Druckhammer: J Am. Chem. Soc., 120, 3275, 1998.
22. K.K.Ghosh, P. Tamrakar: Indian J. Chem., 40(A), 524, 2001.
23. B.A. Holmen, M.I. Tejedor, W.H. Casey: Langmuir, 13, 2197, 1997.
24. J. Mendham, R.C. Denney, J.D.Barns, M. Thomas, B. Sivasankar: Vogel's Test book of Quantitative Chemical Analysis, Sixth Edition, Pearson Education Ltd. 411-412, 200.
25. E. Sonn, C.M. Harris: Coord. Chem. Rev. 4, 391, 1989.
26. M. Mohapatra, C.D. Kailash: Indian J. Chem, 29A, 342, 1990.
27. N. Raman, J. Josheph, A. Senthil Kumara Velan, C. Pothiraj: The Korean Society of Mycology, 34(4), 214, 2006.
28. R. Poppalardo: Phill, Mag., 4, 219, 1959.
29. ABP Lever: Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
30. ABP Lever, E. Montovani: Inorg. Chem., 10, 817, 1971.
31. R.L. Carlin: Trans. Met. Chem., 4, 211, 1968.
32. R.K. Patel, R.N. Patel: J. Ind. Chem. Soc., 67, 238, 1990.
33. Bhawani Shankar, Rashmi Tomar, Rakesh Kumar, Madhu Godhara, Vijay Kumar Sharma: J. Chem. Pharm. Res., 6(5), 925, 2014.
34. M. Hazra, T. Dolai, A. Pandey, S.K. Dey, A. Patra: Bioinorg. Chem. Appl., Doi: 10.1155/2014/104086.
35. C. Cenol, Z. Hayvali, H. Dal, T. Hokelek: J. Mol. Struct., 997, 53, 2011.

36. A.H. Azza, L. Wolfgang: *Spectrochimica Acta Part A*, 95, 596, 2012.
37. N. Raman, T. Baskaran, A. Selvan, R. Jeyamurugan: *J. Iran. Chem. Res.*, 1, 129, 2008.
38. A.E. Ozel, Y. Buyukmurat, S. Akyuz: *J. Mol. Struct.*, 565-566, 455, 2001.

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