

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 2, February 2017

# Studies on the Copper (II) Complexes with Schiff Bases Containing N, O, and N, S Donors Ligands

Anjani Kumar Shukla

Assistant Professor, Dept. of Chemistry, S.N.S College Muzaffarpur Bihar-842001, India

**ABSTRACT:** Transition metal complexes of copper (II) have been synthesized with 1,2-Diphenyl -4-oxoquinazolinosemicarbazone ( $L_1$ ) and 1,2-Diphenyl-4-oxoquinazolinethiosemicarbazone ( $L_2$ ) ligands. Characteristics of complexes has been done on the basis of elemental analysis, magnetic moment data and spectral studies. The ligands behave as bidentate O,N and N,S donor and the complexes possess octahedral geometry.

**KEYWORDS:** Schiff base, Semicarbazone, Thiosemicarbazone, Bidentate.

### I. INTRODUCTION

Schiff bases are polydentate ligands capable of forming very stable complexes with transition metals. The coordination compounds of Schiff bases plays important role in biological, pharmaceutical and industrial fields [1, 2]. Chemotherapeutically thiosemicarbazone have assumed great importance in the recent years as they possess antibacterial, antiviral and antitumor activities [3-6]. During present investigation. Synthesis and characterisation of Cu (II) complexes with pair of semi and thiosemicarbazone ligands 1, 2- Diphenyl -4 oxoquinazolinosemicarbazone and 1,2- Diphenyl 1-4-oxoquinazoline thiosemicarbazone. The characterisation was done with help of elemental analysis, magnetic moment data and spectral studies.

### II. EXPERIMENTALS

The synthesized ligands  $L_1$  (2.31g) and  $L_2$  (2.47g) in ethanol (20ml) was treated with 1.18 g  $CuX_2$  ( $X=Cl^-, Br^-, NO_3^-, ClO_4^-$ ), separately [7-8] and were refluxing in ethanolic solution for 3 hours, crystallized precipitate was obtained, which was filtered and washed for removal of the unreacted ligands. The complexes were insoluble in inorganic and organic solvents also.

### III. RESULTS AND DISCUSSION

The physical characteristics of the complexes and elemental analysis of Cu, C, H, N were presented in table-1 & 2.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 2, February 2017

**Table -1**

**Physical and Analytical data of Cu (II) Complexes (IN %)**

Complexes	Cu	C	H	N	Cl	Br
[Cu (L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	7.35 (7.52)	59.63 (59.67)	4.00 (4.02)	16.54 (16.57)	8.35 (18.07)	-----
[Cu (L <sub>1</sub> ) <sub>2</sub> Br <sub>2</sub> ]	6.77 (6.90)	5.95 (53.98)	3.16 (3.64)	14.35 (14.99)	-----	17.11 (17.10)
[Cu (L <sub>1</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	7.05 (7.08)	56.11 (56.15)	3.75 (3.78)	18.66 (18.71)	-----	-----
[Cu (L <sub>1</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	6.50 (6.53)	51.78 (51.82)	3.45 (3.49)	14.35 (14.39)	8.11 (8.14)	-----
[Cu (L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	7.21 (7.24)	57.45 (57.49)	3.84 (3.87)	15.92 (15.97)	8.06 (8.10)	-----
[Cu (L <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]	6.55 (6.58)	52.15 (52.19)	3.48 (3.52)	14.45 (14.49)	-----	16.53 (16.57)
[Cu (L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	6.80 (6.38)	54.18 (54.22)	3.61 (3.65)	18.00 (18.07)	-----	-----
[Cu (L <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	6.28 (6.32)	50.12 (50.17)	3.35 (3.38)	13.90 (13.93)	-----	-----

**Table -2**

**Magnetic Moment of Cu (II) complexes**

Complexes	Magnetic Moment (B.M)	Temperature (K)
[Cu (L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	1.92	295
[Cu (L <sub>1</sub> ) <sub>2</sub> Br <sub>2</sub> ]	1.95	295
[Cu (L <sub>1</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1.88	295
[Cu (L <sub>1</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1.94	295
[Cu (L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	1.96	295

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 2, February 2017

[Cu (L <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]	1.90	295
[Cu (L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1.90	295
[Cu (L <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1.87	295

The Cu (II) complexes of type [Cu (L<sub>1</sub>)<sub>2</sub> X<sub>2</sub>] and [Cu (L<sub>2</sub>)<sub>2</sub>X<sub>2</sub>] have magnetic range 1.88 to 1.96 B.M. Which corresponds to one unpaired electron, as all three complexes of Cu (II) complexes may be octahedral, tetrahedral and square planer, no conclusion can be drawn from magnetic moment data. However, electronic spectra proves to be decisive.

### IR spectra:

The ir spectra of all Cu (II) complexes have been recorded in Nujomul or cesium iodide disk during Perkins Elmer 577 modal and given in table-3 &4.

**Table-3**

**Characteristics I.R spectra of the Ligand DOSC and its Cu (II) Complexes (in cm<sup>-1</sup>)**

Compounds	$\nu_{N-H}$	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{M-O}$	$\nu_{M-N}$	$\nu_{M-X}$
C <sub>21</sub> H <sub>17</sub> N <sub>5</sub> O (DOSC)	3220 m,b	1660 s,b	1480 s,m	-----	-----	-----
[Cu (L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	3220 m,b	1700 m,b	1450 m,b	570 m	425 m	315 m
[Cu (L <sub>1</sub> ) <sub>2</sub> Br <sub>2</sub> ]	3220 m,b	1710 m,b	1450 m,b	565 m	420 m	405 m
[Cu (L <sub>1</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3220 m,b	1700 m,b	1455 m,b	555 m	405 m	-----
[Cu (L <sub>1</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	3220 m,b	1705 m,b	1450 m,b	555 m	400 m	-----

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

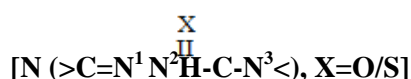
Vol. 6, Issue 2, February 2017

Table-4

Characteristics I.R spectra of the Ligand DOTSC and its Cu (II) Complexes (in cm<sup>-1</sup>)

Compounds	$\nu_{N-H}$	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{M-O}$	$\nu_{M-N}$	$\nu_{M-X}$
C <sub>21</sub> H <sub>17</sub> N <sub>5</sub> S (DOTSC)	3460 m,b	1500 s,b	800 s,m	-----	-----	-----
[Cu (L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	3460 m,b	1465 m,b	770 m,b	480 m	420 m	315 m
[Cu (L <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]	3460 m,b	1470 m,b	775 m,b	475 m	410 m	285 m
[Cu (L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3460 m,b	1475 m,b	780 m,b	470 m	395 m	-----
[Cu (L <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	3460 m,b	1465 m,b	775 m,b	465 m	390 m	-----

Ir of all The complexes are quit complex, structurally important vibrational band such as  $\nu_{N-H}$  stretch,  $\nu_{C=N}$ ,  $\nu_{C=O}$ , and  $\nu_{C=S}$ ,  $\nu_{M-S}$ ,  $\nu_{M-N}$ ,  $\nu_{M-X}$  are discernible and provide unequivocal evidence concerning the nature of bonding of the ligands with metal ions. On the basis of observations it is established that semicarbazone and thiosemicarbazone can coordinated through oxygen or sulphur atom and N<sup>1</sup> of either semicarbazone or thiosemicarbazone moiety.



Their spectra of the ligand DOSC shows a medium and broad peak at 3220 cm<sup>-1</sup> and of ligand DOTSC shows a band at 3560 cm<sup>-1</sup> Which can also be assigned to the  $\nu_{N-H}$  vibrations. The spectra of all complexes shows this band without any change clearly indicated that primary amino group or secondary amino group has not taken part in the coordination with metal ion. The next ir band of structural significance in the spectrum of the ligand DOSC appeared at 1660 cm<sup>-1</sup>. This band is sharp and strong peak may be assigned to  $\nu_{C=O}$  of semicarbazone moiety of quinazoline. The position of this band in all the complexes have been shifted to a higher frequency region at 1700 cm<sup>-1</sup> with slightly reduced intensity. This shift is undoubtedly due to coordination to the oxygen atom of the carbonyl to the metal ion. The coordination through oxygen atom of carbonyl group was further confirmed by the appearance of a band in the far ir region at 580 -520 cm<sup>-1</sup> in the complexes may be assigned to  $\nu_{M-O}$ . The other ir spectra of both the ligands DOSC and DOTSC shows broad band of medium intensity at around 1500 cm<sup>-1</sup> Which can also be assigned to  $\nu_{M=N}$ . In the spectra of the complexes this band shows red shift in the region 1500-1480 cm<sup>-1</sup> clearly indicated coordination of the N atom of azomethine group of semicarbazone or thiosemicarbazone moiety. The coordination through azomethine nitrogen is further confirmed by the appearance of a band in the far ir region at 425-395 cm<sup>-1</sup> in the complexes may be assigned to  $\nu_{M-N}$ . The spectra of ligand DOTSC shows a sharp and strong peak at 800 cm<sup>-1</sup> which may be assigned to  $\nu_{C=S}$  thiosemicarbazone moiety. In the spectra of the complexes this band shows red shift appeared in the region 775-760 cm<sup>-1</sup> clearly indicated about coordination of the sulphur of thiosemicarbazone moiety to the metal ion The

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 2, February 2017

coordination through thione sulphur atom was further confirmed by the appearance of a band in the far ir region at 480-450  $\text{cm}^{-1}$  in the complexes may be assigned to  $\nu_{\text{M-S}}$ .

### Electronic Spectra:

The electronic spectra of all Cu (II) complexes have been recorded using diffuse reflectance techniques taking Barnum sulphate as a standard in the region 11000-25000  $\text{cm}^{-1}$ . The band position are tabulated in table-5.

**Table-5**

**Electronic Spectra of Cu (II) Complexes of the Ligands DOSC and DOTSC Ligands.**

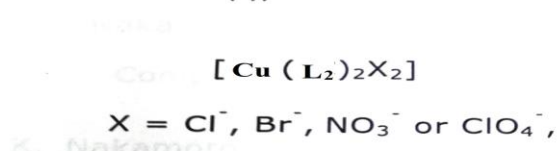
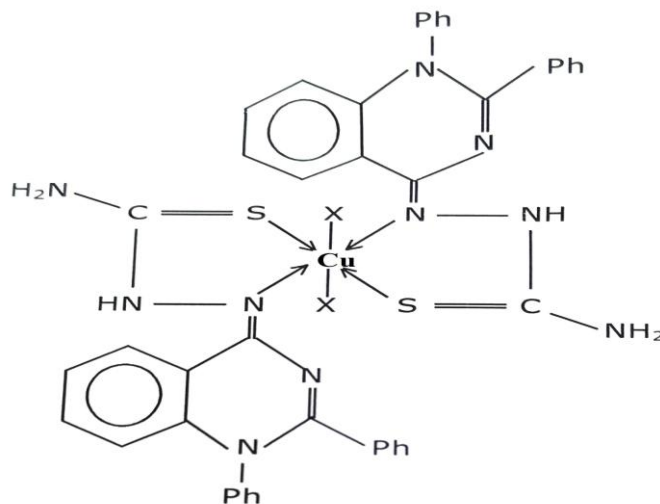
Complexes	Bond Position with assignment in ( $\text{cm}^{-1}$ )
[Cu (L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	12700-17600
[Cu (L <sub>1</sub> ) <sub>2</sub> Br <sub>2</sub> ]	12600-17200
[Cu (L <sub>1</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	12800-17700
[Cu (L <sub>1</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	12300-17700
[Cu (L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	12500-17500
[Cu (L <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]	12700-17300
[Cu (L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	12400-17000
[Cu (L <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	12100-17400

By close examination of table-5, clearly indicated that all complexes of Cu (II) Complexes have been shows two broad band one in the region 12600 – 13600  $\text{cm}^{-1}$  and another in the region 16000 -19000  $\text{cm}^{-1}$ . The electronic spectra of all Cu (II) complexes was clearly indicated that environment around Cu (II) ion was octahedral in all complexes.

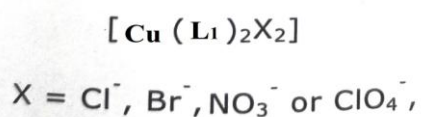
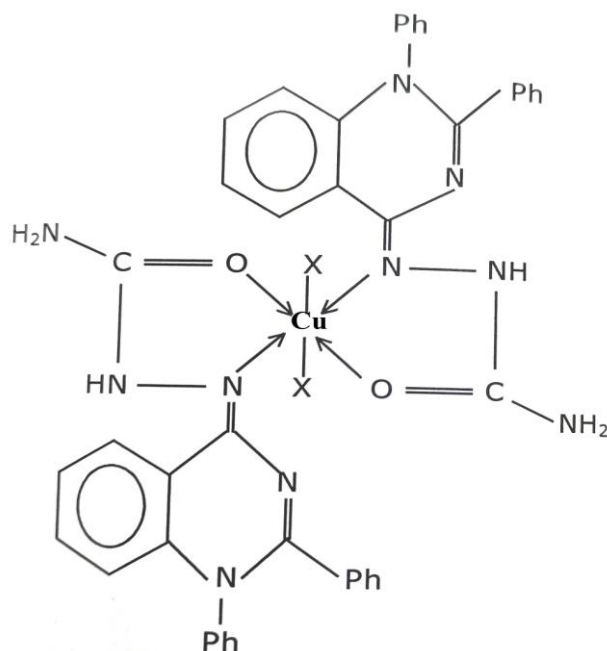
### IV. CONCLUSION

On the basis of elemental analysis, ir spectra, electronic spectra, magnetic moment data, Cu (II) ion was coordinated through N,O of L<sub>1</sub> ligand and N,S atoms of L<sub>2</sub> ligand. Structure complexes were proposed as –

**International Journal of Innovative Research in Science,  
Engineering and Technology**



**Fig-1**



**Fig-2**

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 2, February 2017

## V. ACKNOWLEDGEMENT

The authors are very thankful to Head of university Department of Chemistry, B R A Bihar University Muzaffarpur for providing laboratory facility and valuable suggestions and authors and also thankful to Dr. A.K. Srivastava (Retd) Head of university Department of Chemistry BRA Bihar University Muzaffarpur and Dr. Ramesh Kumar, Professor and Head, Department of Chemistry L.S College Muzaffarpur for valuable suggestions.

## REFERENCES

1. Mannar R Maurya, Ram C Maurya “Coordination chemistry of Schiff base complexes of uranium” Reviews in Inorganic Chemistry, Volume-15, Issue,1-2, Pages,1-108 (1995)
2. Suparna Ghosh, Suman Malik and Bharti Jain “Synthesis, Spectral and Biological Studies of some Transition Metal Complexes Derived from Schiff base of Xipamide Drug” *Mor. J. Chem.* 3 N<sup>o</sup>2 (2015) PP-306-313
3. B.T. Thakur, A. Patel, J. Le. Khadiya, P. Thakur, “Physicochemical studies of symmetrical tetradentateschiff base complexes of chromium(III), cobalt (II), nickel (II), copper (II), zinc(II), oxovanadium(IV) and dioxouranium(VI) derived from 4-acyl pyrazolone and 1,4-diamine” *Indian journal of chemistry*, 35 A (1996) 483.
4. M.R. Maurya, N. Agarwal, S. Khurana, “Synthesis and Characterization of Metal Complexes of Methylene Bridged HexadentateTetraanionic Ligands”*J.Chem.*,39A (2000) 1093
5. Aswar A.S. and Mandlik P.R., Schiff base metal complexes of Cr (III) Mn (III), Fe (III), VO(IV), Zr (IV) and UO<sub>2</sub>(VI), *Polish J. of Chem.*, 77,129, 2003.
6. A. P. Mishra and Monika Soni “Synthesis, Structural, and Biological Studies of Some Schiff Bases and Their Metal Complexes” *Metal-Based Drugs* Volume 2008, Article ID- 875410, 7 pages
7. BoshraM.Awad, Abdel Rehman , S. Ferwanan, Adel M.A Wadallah and Nabil M.EL. Halabi, “Reaction of Nitrilimines with Keto-Alkoxy-carbony-Hydrazones: Synthesis of Substituted 1,2,4-Triazoles and Hetrocyclic Spiro Compounds” *Asian journal of chemistry* ,14 (2002) 1235
8. A.K Srivastava, Anjani Kumar Shukla, Nidhi Srivastava , “Synthesis and Characterisation of Copper (II) Complexes N,S Donor Ligands” *J. Chemtracks* Vol -21 (2019 ) PP-1-4
9. VimalChoudhary, Anju Sharam , Shobha Sharma , “Synthesis Characacterisation and Biological Properties of Mn (II), Co (II), Ni (II) and Cu (II), Chelates of some Schiff Bases Containing N-S-O and N-O-O Moiety” *Asian journal of chemistry*, 14 (2002) 1299.
10. A.P.Mishra , R K Mishra, S P Srivastava,“Structural and antimicrobial studies of coordination compounds of VO (II), Co (II), Ni (II) and Cu (II) with some Schiff bases involving 2-amino-chlorophenol” *Journal of the Serbian Chemical Society*, 74 (5) (2009), pp-523-535, J S C S , 3852