

# Synthesis, spectral characterization of Schiff base Cu(II) novel complexes derived

## Abstract

Cu (II) Schiff base complexes of the type  $[HLCuX_2]$  where X = Cl, OAc have been synthesized by condensation of acetylacetone and Thio-carbohydrazide (2:2) in the presence of divalent metal salt in methanolic medium. The complexes have been characterized with the help of elemental analysis, conductance measurements, magnetic measurements and their structural configuration have been determined by various spectroscopic (electronic, IR,  $^1H$  NMR,  $^{13}C$  NMR, GCMS) techniques. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers are octahedral.

**Keywords :** Metal complexes, Spectroscopic study. Thio-carbohydrazide and acetylacetone

## Introduction

Copper is known for its distinctive reddish brown color. Copper is an ancient metal; ornaments, coins, and statues were fashioned from it since ancient times. Copper is notorious for its habit of developing a green oxidation tarnish on exposed surfaces, which is caused by exposure to weathering. If kept away from water and moisture, it will not tarnish. The green tarnish is sometimes known as patina, especially when referring to historic statues and objects where the antique nature is enhanced by tarnish. Macrocyclic and compounds have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, catalysis<sup>1</sup>. It is well known that N and S atoms play a key role in the coordination of metal at the active sites of numerous metallobiomolecules<sup>2</sup>. Metall-organic chemistry is becoming an emerging area of research due to the demand of new metalbased antibacterial and antifungal compounds<sup>3,4</sup>. The aliphatic or aromatic amines can form strong five or six membered chelates rings which are able to produce the metal containing crosslinking agents with required properties<sup>5</sup>. There are a number of important molecules shows biological activities including antibacterial, antifungal<sup>6-9</sup>, antidiabetic<sup>10</sup>, antitumor<sup>11</sup>, antiproliferative<sup>12,13</sup>, anticancer<sup>14,15</sup>, herbicidal<sup>16</sup>, anticorrosion and anti-inflammatory activities<sup>6</sup> Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products. Moreover, Schiff bases are regarded as privileged ligands<sup>17</sup>. Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions<sup>18,19</sup>. The discovery and development of effective antibacterial and antifungal drugs with novel mechanism of action have because an urgent task for infectious diseases research program<sup>20</sup>. Many investigations have proved that binding of a drug to a metalloelements enhances its activity and in some cases, the complex possesses even more healing properties than the parent drug<sup>21</sup>. In the present article, we report the synthesis and characterization of Schiff base derived from acetylacetone and thio-carbohydrazide, and its metal complexes to gain more information about related structural and spectral properties as well as their antimicrobial activities.

## Experimental

### Reagents

The entire chemicals used were of the analytical reagent grade, acetylacetone and thio-carbohydrazide procured from Acros and s.d.-fine, respectively. Metal salts were purchased from Merck.

### Synthesis of Schiff base macrocyclic ligand

### Synthesis of Cu (II) complexes.

A solution of Cu metal salt (1 mmol) in methanol (20 mL) was added to a hot solution (75 °C) of macrocyclic ligand in ethanol (40 mL) and the reaction mixture was refluxed for 10-12h. The complex was precipitated by adding distilled water. The precipitate of the complex was filtered, washed with water, then with hot methanol and finally dried in vacuum desiccator over anhydrous  $CaCl_2$  (yield 40-45%, Fig 1).

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### Analytical and physical measurements

The microanalysis of C, H, and N were estimated by elemental analyzer (Perkin Elmer 2400), at SAIF, CDRI, Lucknow, India and the metal contents of Cu (II) was determined using atomic absorption spectrophotometer Perkin Elmer 5000. (See Table I containing also some physical properties of the prepared compounds). The conductivity was measured on digital conductivity meter (HPG system, G-3001) in DMSO at room temperature. The magnetic susceptibility measurements were carried out on Vibrating Sample Magnetometer (Model PAR 155) at room temperature. Electronic spectra (in DMSO) were recorded on a Hitachi 330 spectrophotometer (5815-32573  $\text{cm}^{-1}$ ). The IR spectra were performed using a FT-IR spectrophotometer Perkin Elmer 1650 in the range 4000–200  $\text{cm}^{-1}$  using Nujol Mull.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (at room temperature) (in DMSO- $d_6$ ) were recorded on a Bruker AVANCE II 300 DRX or average 400 DRX spectrometer with reference to  $\text{Me}_4\text{Si}$  (0.0 ppm). The FAB mass spectra (at room temperature) were recorded on VG-70-S mass spectrometer.

### Results and Discussion

#### Infrared Spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The presence of a single medium band in the region 3250-3330  $\text{cm}^{-1}$  in the complexes may be assigned to N-H stretch<sup>22</sup>. It was noted that a pair of bands corresponding to  $\nu(\text{NH}_2)$  at 3245  $\text{cm}^{-1}$  and 3309  $\text{cm}^{-1}$  are present in the spectra of the thiocarbohydrazide. The value of  $\nu(\text{C}=\text{N})$  stretching vibration is found lower (1520–1560  $\text{cm}^{-1}$ ) than the expected value (1580–1650  $\text{cm}^{-1}$ ). This lower value of  $\nu(\text{C}=\text{N})$  stretching may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom<sup>23</sup> indicating that coordination takes place through nitrogen of (C=N) groups. The bands present in the range 3020–3040  $\text{cm}^{-1}$  may be assigned due to (C–H) stretching vibrations of benzil and naphthalene ring<sup>24</sup>. The C–N stretch in the range 1000-1300  $\text{cm}^{-1}$ . The band near 780  $\text{cm}^{-1}$  in thiocarbohydrazide may be assigned as being due to free  $\nu(\text{C}=\text{S})$ . The band at 3292-3438  $\text{cm}^{-1}$  is due to the presence of OH group in the complexes. This band is also present in the spectra of all the complexes, which indicate that sulphur is not coordinating to the metal atom<sup>25</sup>. The far infrared spectra show bands in the region 420–450  $\text{cm}^{-1}$  corresponding to  $\nu(\text{M}-\text{N})$  vibrations<sup>26</sup>. The presence of bands in all complexes in the region 420–450  $\text{cm}^{-1}$  originates from the (M–N) azomethine vibrational modes and identifies coordination of azomethine nitrogen<sup>27</sup>. The bands present at 290–310  $\text{cm}^{-1}$  may be assigned due to  $\nu(\text{M}-\text{Cl})$  vibrations<sup>28</sup>.

The appearance of two characteristic bands in the ranges 1561–1559  $\text{cm}^{-1}$  and 1370–1367  $\text{cm}^{-1}$  in the case of complexes was attributed to  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ , respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ . The separation value,

$\Delta\nu(\text{COO}^-)$ , between  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ , in these complexes were more than 190  $\text{cm}^{-1}$  (191–193  $\text{cm}^{-1}$ )<sup>29</sup>.

#### $^1\text{H}$ NMR

A survey of literature reveals that the NMR spectroscopy has been proved useful in establishing the structure and nature of many Schiff base ligand and their complexes. The  $^1\text{H}$  NMR spectra of Schiff base ligand (HL) was recorded in  $d_6$ -dimethylsulfoxide (DMFO- $d_6$ ) solution using  $\text{Me}_4\text{Si}$  (TMS) as internal standard. The  $^1\text{H}$  NMR spectra of the ligand shows broad signal at 9.4-12.1 ppm due to the  $-\text{NH}$  [30]. The multiplets in the region 1.12-1.56 ppm may be assigned to aliphatic proton<sup>30</sup>.

$^{13}\text{C}$  NMR of the Schiff base ligand, the signal appeared in the region 113-158 are assigned to aromatic carbon. The signal at 198.3-185.6, 182.8-171.2, 165.4-150.7 and 148.1-15.8 ppm are due to C=S, C=N, C=O and  $\text{CH}_3$  respectively.

#### Magnetic measurements and electronic spectral studies

The electronic spectra of the cobalt (II) complexes (5) and (6) gave two bands at 1200–1051, and 489-433 nm, which could be assigned to the transitions  $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{T}_2\text{g}(\text{F})$  ( $\nu_1$ ) and  $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{T}_2\text{g}(\text{P})$  ( $\nu_3$ ), respectively, suggesting an octahedral geometry around Co(II) ion<sup>33</sup>. The complexes 5 and 6 show magnetic moment values in the range 2.2–2.5 B.M., which is smaller than the calculated value for two Co (II) ions in octahedral geometries and this may be due to antiferromagnetism between the two ion-centers.

#### Conclusion

The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The electronic spectral data is in the favor of octahedral geometry of the complexes.

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#### References

1. Busch, D.H., Science, 1971, **171**, 241.
2. Bagihalli, G.B., Avaji, P.G., Patil, S.A., Badami, P.S., Eur. J. Med. Chem. 2008, **43**, 2639.
3. Scozzafava, A., Supuran, C.T., J. Med. Chem. 2000, **43**, 3677.
4. Rice, S.A., Givskov, M., Steinberg, P., Kjelleberg, S., J. Mol. Microbiol. Biotechnol. 1999, **1**, 23.
5. Kurnoskin, A.V., Polym. Compos. 1993, **14**, 481.
6. Kumar, G., kumar, D., Singh, C.P., Kumar, A., Rana, V.B., J. Serb. Chem. Soc. 2010, **75**, 629.
7. Singh, D.P., Kumar, K., Sharma, C., Eur. J. Med. Chem. 2009, **44**, 3299.
8. Singh, K., Bharwa, M.S., Tyagi, P., Eur. J. Med. Chem. 2007, **42**, 394.
9. Kumar, G., kumar, D., Devi, S., Johari, R., Singh, C.P., Eur. J. Med. Chem. 2010, **45**, 3056.

10. Vanco, J., Marek, J., Travnicek, Z., Racanska, E., Muselik, J., Svajlenova, O., J. Inorg. Biochem. 2008, **102**, 595.
11. Galal, S.A., Hegab, K.H., Kassab, A.S., Rodriguez, M.L., Kervin, S.M., El-Khamry, A.M.A., El-Diwani, H.I., Eur. J. Med. Chem. 2009, **44**, 1500.
12. Chaviara, A.T., Cox, P.J., Repana, K.H., Papi, R.M., Papazisis, K.T., Zambouli, D., Kortsaris, A.H., Kyriakidis, D.A., Bolos, C.A., J. Inorg. Biochem. 2004, **98**, 1271.
13. Illan-Cabeza, N.A., Hueso-Urena, F., Moreno-Carretero, M.N., Martinez-Martos, J.M., Ramirez-Exposito, M.J., J. Inorg. Biochem. 2008, **102**, 647.
14. Desai, S.B., Desai, P.B., Desai, K.R., Heterocycl. Commun. 2001, **7**, 83.
15. Pathak, P., Jolly, V.S., Sharma, K.P., Orient. J. Chem. 2000, **16**, 161.
16. Samadhiya, S., Halve, A., Orient. J. Chem. 2001, **17**, 119.
17. Yoon, T.P., Jacobsen, E.N., Science, 2003, **299**, 1691.
18. Mirkhani, V., Moghadam, M., Tangestaninejad, S., Mohammadpoor-Baltork, I., Rasouli, N., Catal. Commun. 2008, **9**, 219.
19. Chen Y., Ruppel, J.V., Zhang X.P., J. Am. Chem. Soc. 2007, **129**, 12074.
20. Smith, H.J., Simons C., Proteinase and Peptidase Inhibition: Recent Potential Targets for Drug Development, Taylor and Francis, London, 2001.
21. Lippard, S.J., Berg, J.M., Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1999.
22. Bain, G.A., West, D.X., Krejci, J., Martinez, J.V., Ortega, S.H., Toscano, R.A., Polyhedron. 1997, **16**, 855.
23. Lodeiro, C., Basitida, R., Bertolo, E., Macias, A., Rodriguez, R., Transition Met. Chem. 2003, **28**, 388.
24. Mikhailov, O.V., Kazymova, M.R., Shumilova, T.A., Solovieva, S.S., Transition Met. Chem. 2004, **20**, 732.
25. Chandra, S., Thakur, S., Transition Met. Chem. 2004, **29**, 925.
26. Shakir, M., Islam, K.S., Mohamed, A.K., Shagufa M., Hasan, S.S., Transition Met. Chem. 1999, **24**, 577.
27. Rana, V.B., Singh, D.P., Singh, P., Teotia, M.P., Transition Met. Chem. 1982, **7**, 174
28. Khan, T.A., Hasan, S.S., Varkey, S.P., Rather, M.A., Jahan, N., Shakir, M., Transition Met. Chem. 1997, **22**, 4.
29. Boghaei, D.M., Gharagozlou, M., Spectrochem. Acta, 2007 **67A**, 944.
30. Gunthkal, M.S., Goudal, T.R., Patil, S.A., Oriental J. Chem. 2000, **16**, 151.
31. Wood, J.S., Prog. Inorg. Chem. 1971, **16**, 227.
32. Singh, D.P., Rana, V.B., Polyhedron, 1995, **14**, 2901.
33. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.

Table 1,  
Elemental analysis in % and molar conductance ( $\Lambda_m$  in DMSO) in  $\text{Scm}^2\text{mol}^{-1}$  and magnetic moment ( $\mu_{\text{eff}}$ ) in  $\mu_B$  of the Schiff base ligand and its metal complexes

Complex	FW	Colour	C	H	N	M	$\Lambda_m$	$\mu_{\text{eff}}$
			Calculated (Found)	Calculated (Found)	Calculated (Found)	Calculated (Found)		
$\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2$	340.48	yellow	42.33 (42.28)	5.92 (5.91)	32.91 (32.85)			
$[\text{Cu}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{Cl}_2]\text{Cl}$	498.83	Orange	28.89 (28.81)	4.04 (4.12)	22.47 (22.48)	10.42 10.40	59	4.38
$[\text{Cu}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{OAc}_2]\text{OAc}$	569.61	Greenish Yellow	37.96 (37.95)	5.13 (5.14)	19.67 (19.72)	9.13 (9.15)	66	4.68

Fig 1. Synthesis of novel Schiff base complexes.

