

## Synthesis, structural and antifungal investigation of Co(II), Ni(II) and Cu(II) complexes with hydrazone based Schiff base

ANUKUL PRASAD and B.K. RAI

\*Department of Chemistry, M.M. Das Mahila college, Srisia, Muzaffarpur (India).  
Department of Chemistry L.N. T. College, BRA Bihar University, Muzaffarpur (India).

(Received: April 12, 2009; Accepted: June 04, 2009)

### ARSTRACT

Chelates of 1,2-dimethyl-1,4 dihydro-4-oxo-quinazoline (DDOQH) with Co(II), Ni(II) and Cu(II) have been synthesized and characterized on the basis of elemental analysis, IR spectra, magnetic susceptibility, electronic spectra and molar conductance data. On the basis of above observations chelates were proposed to be octahedral geometry with composition  $\{M(DDOQH)_2X_2\}$  where m= Co(II) Ni(II) and Cu(II), X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>. The ligand DDOQH acts in a bidentate manner and coordination proposed to the metal ion through azomethine N and amino N atom of quinazoline derivatives. The remaining coordination sites are occupied by negative ions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>. The ligand as well as metal complexes have been tested for antifungal study against two fungi *Aspergillus flavus* and *Penicillium expansum*.

**Key words:** DDOQH/Co(II), Ni(II) and Cu(II) schiff base/complexes antifungal activity.

### INTRODUCTION

Hydrazone derivative are considered to be an important class of chemical compounds used extensively for the treatment of several diseases<sup>1-3</sup>. Nitrogen containing aromatic hydrazones have been widely used as analytical reagent<sup>4-5</sup>, and corrosion inhibitors<sup>6</sup> and antimicrobial and therapeutic reagents. Keeping the above facts in mind and in continuation of our earlier work<sup>9-11</sup> on hydrazone based schiff base complexes. now we report synthesis and characterization now we report synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with 1,2 dimethyl 1-4 dihydro-4 oxoquinazoline hydrazone. The ligand as well as metal complexes have been tested for antifungal activity.

### EXPERIMENTAL

All the used chemicals were of B.D.H. quality except 1, 2 dimethyl-1 4-dihydro-4

oxoquinazoline which was synthesized by earlier reported<sup>12-14</sup> method.

### Preparation of the ligand

Ethanol solution of 1,2 dimethyl 1,4-dihydro-4-oxo quinazoline (0.01m) was treated with hydrazine hydrate (0.01 m) dissolved in ethanol. The resulting mixture was refluxed on water bath for 3h, then a yellow solid began to separate after allowing the solution to stand for some time. The compound was then cooled, filtered washed with aqueous ethanol, dried and crystallised with ethanol to furnish yellow crystalline solid. yield 60-65%, m.p. -169±1°C.

### Preparation of the complexes

Ethanol solution of 1,2 dimethyl 1-4-dihydro-4-oxo quinazoline hydrazone was treated with ethanolic solution of respective metal halide/nitrate/ perchlorate in the molar ratio. 2:1. The resulting reaction mixture was heated on waterbath for 2h. The preparation procedure for all the complexes was of almost similar nature with a slight

variation of timing of reflux. The solid coloured complexes obtained in each case were filtered and washed with ethanol several times to remove any excess of the ligand. Finally the complexes were washed with anhydrous diethyl ether and dried in oven, yield 60-65%.

The ligand as well as metal complexes were analysed by standard method<sup>14</sup>. The electronic spectra were recorded on shimadzu 160A spectrophotometer. Magnetic moment were measured by Guoy balance using mercury tetrathiocyanato cobaltate as a calibrant. The IR spectra were recorded on Perkin Elmer 577 spectrophotometer using KBr pallets. Molar conductance were done on systronics conductivity meter using DMF. Analytical data, colour, magnetic susceptibility, electronic spectra and decomposition temperature are recorded in Table 1 and Salient features of IR spectral bands are recorded in Table 2.

## RESULTS AND DISCUSSION

The IR spectra of the ligand exhibits strong and broad bands at 3200  $\text{cm}^{-1}$  which can be assigned<sup>15-16</sup> to  $\nu_{\text{N-H}}$  vibrations. In the spectra of the

complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggesting coordination of secondary amino N atom of quonazoline ring with metal ion.

The IR spectra of the ligand exhibits strong and broad bands of medium intensity at 1560  $\text{cm}^{-1}$ , which may be assigned<sup>15,17-18</sup>  $\nu_{\text{C=N}}$ . In the spectra of the complexes this band shows red shift with change in intensity. The shift of the band and change in intensity proposed coordination of the azomethine nitrogen with metal ion. The coordination with azomethine N atom is further supported by the appearance of a far ir band in the region 425-400  $\text{cm}^{-1}$  may be assigned<sup>15,17,19</sup> to  $\nu_{\text{M-N}}$ . The coordination through metal halogen is indicated by the appearance of a band in the region 320-265  $\text{cm}^{-1}$  which may be assigned<sup>15,17,19</sup> to  $\nu_{\text{M-X}}$  ( $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ). The evidence of metal halogen is further supported by the low value of molar conductance of the complexes in the range 3.2-5-9.  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .

On the basis of above ir spectral band assignments it is proposed that ligand DDOQH acts as neutral bidentate manner and coordination proposed through azomethine nitrogen and secondary amino group of quinazoline.

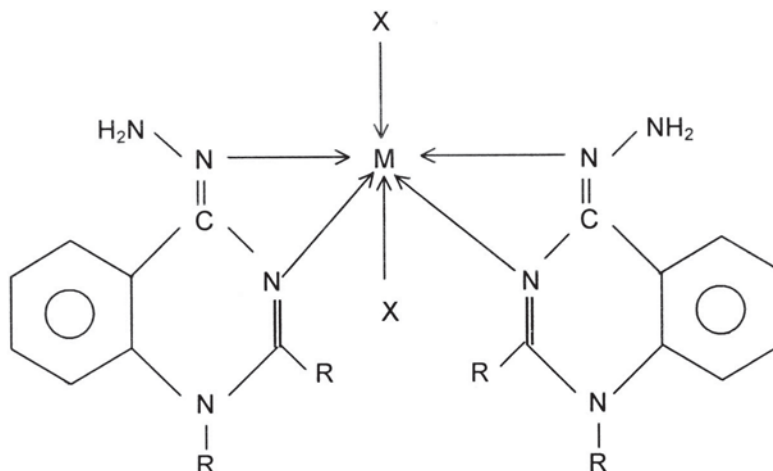


Fig. 1:  $[\text{M}(\text{DDOQH})_2\text{X}_2]$ ; M Co (II) and Ni (II); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>; R =Methyl

**Table 1: Analytical, colour, magnetic, susceptibility, electronic spectra, decomposition temperature and conductivity measurement data of the complexes  $[M(DDOQH)_2]_x$**

Compounds	% analysis found (calculated)				$\mu_{\text{eff}}$ B.M.	$\Omega m$ $\text{ohm}^2 \text{cm}^2$	$\lambda_{\text{max}}$ electronic $\text{cm}^{-1}$	Decomposition Temperature
	M	C	N	H				
DDOQH (Light Yellow)		63.96 (63.82)	29.63 (29.78)	6.41 (6.38)				
$[\text{Co}(\text{DDOQH})_2\text{C}_2]$ (Brown)	11.72 (11.64)	47.31 (47.43)	21.97 (22.13)	4.69 (4.74)	4.96	5.1	8000,13700, 19300	234
$[\text{Co}(\text{DDOQH})_2\text{Br}_2]$ (Dark Brown)	8.51 (8.56)	34.8 (34.88)	16.42 (16.28)	3.56 (3.48)	4.89	5.9	8060,13660, 19340	239
$[\text{Co}(\text{DDOQH})_2]$ (Dark Brown)	10.02 (9.90)	40.43 (40.35)	18.74 (18.83)	3.97 (4.03)	5.01	5.6	8020,13550, 19260	341
$[\text{Co}(\text{DDOQH})_2(\text{NO}_3)_2]$ (Reddish brown)	10.62 (10.54)	43.11 (42.93)	19.92 (20.03)	4.21 (4.29)	5.06	5.4	8300,13780, 19320	246
$[\text{Co}(\text{DDOQH})_2(\text{ClO}_4)_2]$ (Reddish brown)	9.36 (9.29)	38.08 (37.85)	17.77 (17.66)	3.86 (3.78)	4.83	5.5	8500,13780, 19380	252
$[\text{Ni}(\text{DDOQH})_2(\text{Cl})_2]$ (Green)	11.69 (11.60)	47.32 (47.45)	22.28 (22.14)	4.88 (4.74)	3.14	4.6	11040,16200, 19700	269
$[\text{Ni}(\text{DDOQH})_2(\text{Br}_2)_2]$ (Green)	9.96 (9.87)	40.47 (40.36)	18.11 (18.83)	3.96 (4.03)	3.11	4.3	11000,16300, 19900	301
$[\text{Ni}(\text{DDOQH})_2]$ (Yellowish green)	8.40 (8.53)	34.79 (34.90)	16.40 (16.28)	3.52 (3.48)	3.23	4.1	11080,16100, 20000	303
$[\text{Ni}(\text{DDOQH})_2(\text{NO}_3)_2]$ (Greenish yellow)	10.61 (10.50)	43.08 (42.95)	19.89 (20.04)	4.20 (4.29)	3.19	4.2	11200,16200, 20060	313
$[\text{Ni}(\text{DDOQH})_2(\text{ClO}_4)_2]$ (Yellowish green)	9.34 (9.26)	38.11 (37.87)	17.79 (17.67)	3.84 (3.78)	3.21	4.5	11260,16300, 20080	318
$[\text{Cu}(\text{DDOH})_2\text{Cl}_2]$ (Blue)	12.61 (12.44)	47.16 (47.00)	22.10 (21.93)	4.78 (4.70)	1.86	3.2	15300,18700	273
$[\text{Cu}(\text{DDOQH})_2\text{Br}_2]$ (Blue)	10.76 (10.59)	39.91 (40.04)	18.71 (18.68)	3.92 (4.00)	1.81	3.6	15300,18640	289
$[\text{Cu}(\text{DDOQH})_2(\text{NO}_3)_2]$ (Blue)	11.21 (11.27)	42.39 (42.56)	20.04 (19.87)	4.19 (4.25)	1.93	3.8	15600,18500	279
$[\text{Cu}(\text{DDOQH})_2(\text{ClO}_4)_2]$ (Dark blue)	10.08 (9.95)	37.69 (37.56)	17.69 (17.54)	3.83 (3.75)	1.91	3.7	15500,18680	280

**Table 2: IR spectral bands of ligand DDOQH and its metal complexes**

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
DDOQH	3200 s,b,	1560 s,b		
[Co(DDOQH) <sub>2</sub> C <sub>2</sub> ]	3180 m,b	1535 m,b	415 m	265m
[Co(DDOQH) <sub>2</sub> Br <sub>2</sub> ]	3175 m,b	1535 m,b	410 m	270m
[Co(DDOQH) <sub>2</sub> I <sub>2</sub> ]	3180 m,b	1540 m,b	405 m	275m
[Co(DDOQH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3175 m,b	1540 m,b	415 m	
[Co(DDOQH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	3175 m,b	1535 m,b	410 m	
[Ni(DDOQH) <sub>2</sub> (Cl <sub>2</sub> ) <sub>2</sub> ]	3180 m,b	1540 m,b	420 m	300 m
[Ni(DDOQH) <sub>2</sub> (Br <sub>2</sub> ) <sub>2</sub> ]	3175 m,b	1535 m,b	415 m	310 m
[Ni(DDOQH) <sub>2</sub> I <sub>2</sub> ]	3175 m,b	1535 m,b	420 m	320 m
[Ni(DDOQH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3180 m,b	1540 m,b	425 m	
[Ni(DDOQH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	3180 m,b	1535 m,b	420 m	
[Cu(DDOQH) <sub>2</sub> Cl <sub>2</sub> ]	3180 m,b	1535 m,b	415 m	
[Cu(DDOQH) <sub>2</sub> Br <sub>2</sub> ]	3175 m,b	1540 m,b	420 m	290 m
[Cu(DDOQH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3170 m,b	1535 m,b	425 m	295 m
[Cu(DDOQH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	3175 m,b	1535 m,b	425 m	

S = strong      m = medium      b = broad

The remaining coordination sites are occupied by anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>.

The electronic<sup>20</sup> and magnetic susceptibility value<sup>21,22</sup> (Table 1) tentatively proposed octahedral geometry for Co(II), Ni(II) and Cu(II) complexes.

#### Molar conductivity value

The molar conductivity of the Co(II) Ni (II) and Cu(II), Ni (II) and measured in the solvent DMF and the complexes were found to be non electrolytic<sup>23</sup> in nature. The molar conductance value of the complexes are lie in the range 3.2-5-9 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

#### Antifungal activity

The ligand DDOQH as well as its metal complexes of Co(II) Ni(II) and Cu(II) complexes have been screened for their antifungal activity against *Aspergillus niger* and *Penicillium expansum*. The susceptibility of fungi towards ligand and its metal complexes was tested using disc plate method<sup>24</sup>. The observed results suggests an enhancement of the antifungal activity of metal complexes in comparison with free ligands which is supported by the literatruue.

#### CONCLUSIONS

On the basis of above mentioned study the complexes were tentatively proposed an octahedral geometry as shown in Fig. 1.

## REFERENCES

1. Garg. H.G. and Sharma, R.A. *J. Med. Chem.*, **14**: 579 (1970).
2. Moshier, R.W. and Singh, P.P. *J. Med. Chem.*, **13**: 1250(1970).
3. Mittal A.K. and Singal O.P. *J. Indian Chem. Soc.*, **58**: 1089 (1981).
4. Katyal: M. and Dutt. Y, *Talanta*, **22**: 151 (1975)
5. Singh; R.B. Jain, P and Singh; R.P. *Talanta*, **29**: 77 (1982)
6. Elmorsi S.A. and Hassanien; A.M. *Corrs. Sci* **41**: 2337 (1999.)
7. Ibrahim, S.A. EL-Gadhami, Khafagi; Z.A. and EL-Gyar, *J. Inorg. Biochem*, **43**: 1 (1991).
9. Rai; B.K. and Raj, Rajeshwar, *Orient., J. Chem* **20**: 493 (2004).
10. Rai; B.K. *J. Ind. Council Chem.* **23**: 13 (2006).
11. Rai B.K. Rai, Rajeshwar, Rana, Swaty and Sahi, Poonam *Asian J. Chem.* **20**: 149, (2008)
12. Chakaravarti, D., Chakarvarti, R.N. and Chakarvarti, SC *J. Am. Chem. Soc.*, **75**: 337 (1953)
13. Rai B.K. and Balunli Akhilesh, *Asian J. Chem.*, **14**, 305 (2002).
14. Vogel, A.L. A Textbook of quantitative Chemical Analysis. Revised by Besett, J. Denny, R.C. Jeffery, J.H. and Mendham, ELBS 5th Edn. London (1996).
15. Silverstein R.M. Spectrometric Identification of organic compounds, 5th Edn. John-wiley, 123, (1991).
16. Cook D., *Can .J. Chem*, **29**: 1961 (2009).
17. Bellamy L.J. The infrared spectra of complex molecules, wiley new york (1959).
18. Nakamoto K., Infrared spectra of Inorganic and Co-ordination compounds, John wiley international, New york (1970).
19. Nakamoto, K., Spectroscopy and structure of metal chelate compounds, john wiley, new york. (1968)
20. Level A.B.P. Inorganic Electronic Spectroscopy Elsevier New York (1968)
21. Carlin R.L. and VAn Dryeveledt, A.I. magnetic properties of transition metal compounds, springer verlag, New york. (1997)
22. Figgis, B.N. Introduction to ligand field, wiley Eastern Ltd, New Delhi 279 (1976).
23. Singh Charanjit, Parwana H.K. Singh Garjednra and Jolly R.S. *Asian J.Chem* : 1(2000)
24. Baur, A.W. Kirby W.M. Sherries J.C. and Turk M, *Am, J. Clin Pathol* **45**: 493, (1966)(.
25. Chanda. S. Singh G, Tyagi, V.P. and Raizada, *Synth React Inorg. Metal Org. Chem*, **31**: 1759 (2001).
26. Chanda, S, Kumar, V and Verma H.S. *J. Saydi Chem. Soc.* **7**: 337 (2003).