



## Synthesis, Spectral and Biocidal Studies of Co(II), Ni(II) and Cu(II) Complexes of Hydrazone

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### ABSTRACT

The present work is concerned with synthesis and study on metal complexes of Co(II), Ni(II) and Cu(II) with bidentate Schiff base ligand, 2-methyl -[3(hydroxyl butyl)]- 3, 1(4H) quinazoline -4- Hydrazone (MHBQH). The complexes have the general formulae  $[(ML)_2 X_2]$ , Where M=Co(II), Ni(II) and Cu(II); L=MHBQH and X=NH<sub>3</sub>, pyridine,  $\alpha$ ,  $\beta$  and  $\gamma$  picolines. The structure of the ligand, mode of bonding and overall geometry of the complexes were determined through, Infrared, electronic spectral studies of elemental analyses, molar mass, magnetic susceptibility and molar conductance. These studies revealed octahedral complexes for Co(II) and Ni(II) and distorted octahedral geometry for Cu(II) complexes. Biocidal activity of the ligands and its metal complexes against several organisms, *Escherichia coli* and *Staphylococcus aureus* are reported. Compounds exhibited the high effect of activity.

**Key words:** MHBQH/ Co(II), Ni(II) and Cu(II)/ Complexes/ Biocidal screening/ Chelate effect.

### INTRODUCTION

The chemistry of Schiff base ligands exhibit a wide range of potentially important biocidal properties<sup>1-2</sup>. Schiff bases are important class of chelating ligands obtained by condensation of aldehydes or ketones with primary amine. They are promising molecules in coordination chemistry because of their remarkable pharmacological importance such as antiparasital, antitumor and antifungal.<sup>3-8</sup> Hydrazones are important in the development of coordination chemistry of a number of metal ions, particularly, the transition metals<sup>9</sup>.

Schiff bases are fairly good biological agent and exhibit excellent importance in biochemistry and medicine. It is established from the survey of literature that the biocidal activity of Schiff base ligand enhanced many fold when it form coordination compound with metal ions. In respect of importance of Schiff base ligands and their metal complexes and in continuation of our earlier work in this field, in this communication it reports the synthesis, characterization and biocidal screening of Co(II), Ni(II) and Cu(II) complexes with Schiff bases ligand 2 - methyl - 1 - (hydroxyl butyl)]- 3, 1 (4H) – quinazoline - 4-Hydrazone (MHBQH).

## EXPERIMENTAL

All the chemicals and reagents used were analytical grade. The solvents were used without any purification. The metal contents were determined using standard method<sup>17</sup>. IR spectra of the ligand and complexes were recorded on Perkin-Elmer model 577 spectrophotometer using KBr disc. Molar conductance of the complexes were measured by using Systronics conductivity meter model-303 in DMF. Electronic Spectra of the complexes were recorded in the region 10,000-25000  $\text{cm}^{-1}$  by Cary 2390 spectrophotometer using  $10^{-3}$  DMF solution of the complexes. Magnetic susceptibility of the complexes was carried out by Gouy's method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard.

### Preparation of the ligand,(MHBQH)

Equimolar (0.001m) ethanolic solution of 2-methyl - [3 - (hydroxyl butyl)] - 3, 1 (4H) quinazoline - 4 - one and Hydrazine hydrate (0.001m) was refluxed for 4h in round bottom flask. During the reflux a microcrystalline colourless compound was separated, which was isolated by filtration and dried in air and finally purified by crystallising in ethanol. Yield-65% m.p.-192 $\pm$ 0C.

### Preparation of the complexes

All the metal complexes of Schiff bases were prepared by the following method. The complexes of Co(II), Ni(II) and Cu(II) were prepared by reacting ethanolic solution (0.001m) of respective metal acetate to schiff base, MHBQH(0.002m) dissolved in minimum volume of ethanol. The reaction mixture was refluxed on a water bath for 4h. The solution was then cooled and treated with liquor ammonia/ pyridine/  $\alpha$ -,  $\beta$ - and  $\gamma$ - picolines with each of metal separately and the procedure in each case of similar nature with slight variation of timing of reflux. The reaction mixture was again refluxed for 3h. Partial removal of the solvent and cooling to room temperature gave solid coloured complexes which were filtered, washed thoroughly with ethanol and finally dried. Yield-65%-70%.

## RESULTS AND DISCUSSION

The important infrared frequencies of the ligand and its complexes along with their tentative assignment are given in Table-2. The broadband

between 3415  $\text{cm}^{-1}$  assigned<sup>18-19</sup> to  $\nu_{\text{O-H}}$ . This band has been broadened and its position has shifted to a lower frequency region 3385  $\text{cm}^{-1}$  on complexation that suggests the coordination with alcoholic oxygen with metal ion after deprotonation. The linkage with oxygen is further confirmed by the appearance of the band in the far infrared region at 545-520  $\text{cm}^{-1}$  assigned to  $\nu_{\text{M-O}}$ <sup>20,21</sup> in the complexes. The IR spectrum of the ligand exhibits a broad band at 3180  $\text{cm}^{-1}$  assigned<sup>19,22</sup>  $\nu_{\text{N-H}}$  vibrations. This band remains unaffected on complexation that indicates, non-involvement of primary or secondary amino group in the coordination. A medium intensity band at 1580  $\text{cm}^{-1}$  assigned<sup>19,23</sup> to  $\nu_{\text{C=O}}$  of azomethine is shifted to lower frequencies 1560  $\text{cm}^{-1}$  upon complexation of azomethine nitrogen with metal ion. The linkage with N is further confirmed by the appearance of a band in the far ir region at 425-450  $\text{cm}^{-1}$  in the complexes assigned<sup>19,22</sup> to  $\nu_{\text{M-O}}$ . The remaining coordination sites are occupied by N-atom of ammonia, pyridine,  $\alpha$ ,  $\beta$  and  $\gamma$ - picolines. The Spectra of pyridine as well as picoline adducts shows an additional band near 650 $\text{cm}^{-1}$ , assigned to pyridine and picoline molecule which is supported<sup>24</sup> by the literature. The above observations strongly support the coordination of the ligand as uninegative bidentate ON donor sequence. The remaining coordination sites is satisfied by N-atom of neutral molecule such as ammonia, pyridine,  $\alpha$ ,  $\beta$  and  $\gamma$ - Picolines which also supported by low value of molar conductance of the complexes that lie in the range 4.1-6.9 Oh  $\text{m}^{-1}\text{cm}^2\text{mol}^{-1}$  which indicate non-electrolytic<sup>25</sup> nature of the complexes.

### Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of the complexes in DMF were recorded over the region 10,000-25,000 $\text{cm}^{-1}$ . The Co(II) complexes exhibit three electronic spectra bands, 9300, 14500 and 21500, assignable to transitions,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  respectively indicate an octahedral<sup>25,26</sup> geometry. The proposed geometry is further supported<sup>27,28</sup> by high  $\mu_{\text{eff}}$  value in the range 4.84-4.97B.M. The Ni(II) complexes display three electronic bands in the regions, 13000, 17400 and 23000; assignable 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  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  respectively indicating an octahedral<sup>26,29</sup> geometry for Ni(II) complexes. The proposed octahedral geometry of

Table 1: Physical characteristics of ligand MHBQH and its Co(II), Ni(II) and Cu(II) complexes

Compounds (Colour)	Molar Mass	M	% Analysis found (calculated)	N	H	$\lambda_{\text{max}}$ electronic $\text{cm}^{-1}$	DT $^{\circ}\text{C}$	$\mu_{\text{eff}}$ B. M.	$\Omega_{\text{m}}$ $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
MHBQH (Colourless)	246	9.96 (10.07)	63.29 (63.41)	22.68 (22.76)	6.89 (6.91)				
[Co(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] (Brown)	584.93	9.93 (10.07)	53.12 (53.33)	19.08 (19.04)	5.74 (5.81)	9300, 14700, 21300	210	4.84	4.3
[Co(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ] (Brown)	708.93	8.22 (8.31)	43.81 (44.00)	15.65 (15.79)	4.71 (4.79)	9350, 14780, 21340	204	4.87	4.7
[Co(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ] (Brownish red)	738.93	7.90 (7.97)	42.11 (42.22)	15.04 (15.15)	4.50 (4.60)	9400, 14730, 21380	203	4.90	4.2
[Co(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ] (Brownish red)	738.93	7.91 (7.97)	42.04 (42.22)	15.07 (15.15)	4.53 (4.60)	9380, 14760, 21390	207	4.92	9.1
[Co(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ] (Brownish red)	738.93	7.92 (7.97)	42.04 (42.22)	15.03 (15.15)	4.54 (4.60)	9380, 14680, 21410	220	4.97	4.9
[Ni(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] (Green)	584.71	9.93 (10.04)	53.14 (53.35)	19.07 (19.15)	5.75 (5.81)	13100, 17330, 23300	190	3.17	5.6
[Ni(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ] (Green)	708.71	8.20 (8.28)	43.85 (44.02)	15.68 (15.80)	4.73 (4.79)	13140, 17300, 23280	193	3.15	5.3
[Ni(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ] (Green)	738.71	7.87 (7.94)	42.06 (42.23)	15.04 (15.16)	4.54 (4.60)	13200, 17340, 23240	199	3.11	4.8
[Ni(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ] (Yellowish green)	738.71	7.88 (7.94)	42.10 (42.23)	15.09 (15.16)	4.53 (4.60)	13170, 17380, 23220	206	3.12	5.7
[Ni(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ] (Yellowish green)	738.71	7.86 (7.94)	42.08 (42.23)	15.09 (15.16)	4.53 (4.60)	13210, 17510, 23000	206	3.12	5.7
[Cu(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] (Blue)	589.54	10.69 (10.77)	52.78 (52.92)	18.86 (18.99)	5.71 (5.76)	11700, 18300	224	1.89	6.3
[Cu(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ] (Blue)	713.54	8.82 (8.90)	43.60 (43.72)	15.58 (15.69)	4.70 (4.76)	11900, 18240	227	1.87	6.9
[Cu(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ] (Sky blue)	743.54	8.48 (8.54)	44.67 (41.96)	14.96 (15.06)	4.53 (4.57)	11740, 18280	230	1.86	6.8
[Cu(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ] (Sky blue)	743.54	8.46 (8.54)	41.72 (41.96)	14.93 (15.06)	4.52 (4.57)	11780, 18220	228	1.93	6.2
[Cu(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ] (Sky blue)	743.54	8.47 (8.54)	41.84 (41.96)	14.97 (15.06)	4.50 (4.57)	11830, 18200	217	1.96	6.4

DT = Decomposition Temperature

Table 2: IR spectral bands (cm<sup>-2</sup>) of ligand MHBQH and its metal complexes

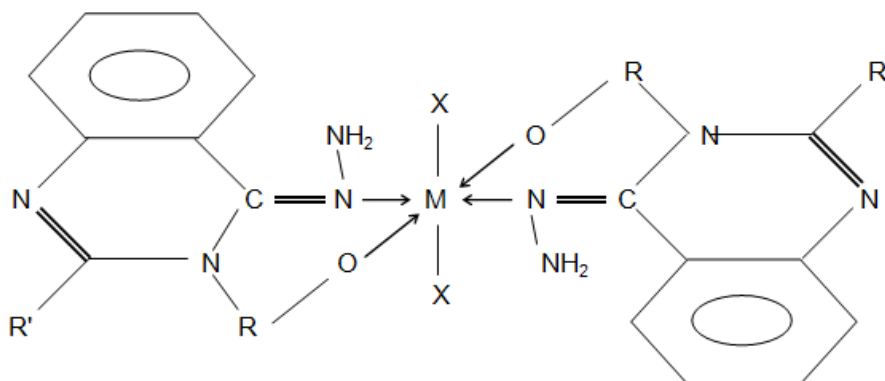
Compounds	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
MHBQH	3400 s,b	3180 s,b	1480 s,b		
[Co(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3380 m,b	3160 m,b	1455 m,b	525 m	465 m
[Co(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	520 m	465 m
[Co(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	525 m	460 m
[Co(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ]	3380 m,b	3155 m,b	1455 m,b	530 m	465 m
[Co(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ]	3380 m,b	3155 m,b	1450 m,b	535 m	465 m
[Ni(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3350 m,b	3155 m,b	1460 m,b	540 m	440 m
[Ni(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ]	3380 m,b	3150 m,b	1460 m,b	540 m	450 m
[Ni(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ]	3380 m,b	3155 m,b	1460 m,b	545 m	445 m
[Ni(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ]	3370 m,b	3155 m,b	1455 m,b	540 m	440 m
[Ni(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	540 m	445 m
[Cu(MHBQH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	500 m	435 m
[Cu(MHBQH) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> ]	3380 m,b	3150 m,b	1460 m,b	510 m	435 m
[Cu(MHBQH) <sub>2</sub> ( $\alpha$ -pic) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	505 m	430 m
[Cu(MHBQH) <sub>2</sub> ( $\beta$ -pic) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	515 m	430 m
[Cu(MHBQH) <sub>2</sub> ( $\gamma$ -pic) <sub>2</sub> ]	3375 m,b	3155 m,b	1455 m,b	500 m	435 m

S = strong; m = medium; b = broad

Ni(II) complexes is also supported by  $m_{\text{eff}}$  value in the range 3.11-3.17 BM respectively. The electronic spectra of all the Cu(II) complexes exhibit two spectral bands in the regions 12000cm<sup>-1</sup> and 18000 cm<sup>-1</sup> indicating octahedral<sup>26,30</sup> geometry for Cu(II) complexes. These bands may be assigned to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> and charge transfer bands. The magnetic susceptibility<sup>27,28</sup> value of Co(II) complexes lie in the range 1.86-1.96 B.M.

#### Biocidal Measurement

Antimicrobial activity of the ligand and their metal complexes of Co(II), Ni(II) and Cu(II) were evaluated against the *Escherichia coli* and *Staphylococcus aureus*. Metal complexes show better inhibition as compared to the ligand due to chelate effect. The susceptibilities were evaluated by measuring the size of bacteriostatic diameter through paper disc diffusion technique.<sup>31</sup> The result exhibits that the antibacterial activities of the complexes were found to be in the order of Cu(II) > Ni(II) > Co(II).



M = Co(II), Ni(II) and Cu(II); X = NH<sub>3</sub>, pyridine/  $\alpha$ -picoline,  $\beta$ -picoline and  $\gamma$ -picoline; R = Butyl, R' = methyl

Fig. 1: [M(MHBQH)<sub>2</sub> X<sub>2</sub>]

**CONCLUSIONS**

IR spectra data and other experimental observations suggest ONN coordination of the ligand with metal ion and as such ligand and ligand behave as uninegative tridentate manner. The proposed structure of complexes of Co(II), Ni(II) and Cu(II) are depicted in Fig-I. Antibacterial data suggest that ligand and their metal complexes have potential antibacterial activity. Further investigation is required to explore such ligand for the industrial use.

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