

## Physico-chemical and Antifungal Investigation of Metal Complexes of Co(II), Ni(II) and Cu(II) with Schiff Base

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In this paper, the synthesis of Co(II), Ni(II) and Cu(II) complexes with 2-phenyl[3-(hydroxyl propyl)]-3,1-(4H)-quinazolin-4-one semicarbazone/thiosemicarbazone (PHQS/PHQTS) is reported. Structural characterization has been done on the basis of elemental analysis, IR, electronic spectra, magnetic susceptibility, molar conductance data. Complexes have been proposed to be octahedral in geometry. The ligand as well as complexes were screened for their antifungal studies.

**Key Words:** Metal(II) complexes, Antifungal activity, Semicarbazone, Thiosemicarbazone.

### INTRODUCTION

Schiff bases and their metal complexes have gained importance for the past several years because of their application as models in biochemical, biological, analytical and antimicrobial<sup>1-4</sup> system such as antilepral<sup>5</sup>, anti-tubercular<sup>6</sup> activities. Keeping the above fact in mind and our previous work<sup>7-12</sup> on Schiff base metal complexes in the present paper, the complexes of Co(II), Ni(II) and Cu(II) with 2-phenyl[3-(hydroxyl propyl)]-3,1-(4H)-quinazolin-4-one semicarbazone/thiosemicarbazone (PHQS/PHQTS) are reported. The ligands PHQS/PHQTS along with metal complexes were also tested for their antifungal activity.

### EXPERIMENTAL

All the chemicals were BDH reagents. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. The electronic spectra recorded on a Shimadzu 160 A spectrophotometer. Magnetic susceptibility measured by a Guoy balance using mercury tetrathiothiocyanato cobaltate as a calibrant. Molar conductance data were made on systronics conductivity meter model 303 using DMF as a solvent. The metal contents were determined using standard<sup>13</sup> procedures. The biological experiment for determining antifungal activity of ligand as well as their metal complexes were done by filter paper disc method<sup>14</sup>.

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**Preparation of the ligand PHQS/PHQTS:** 2-phenyl-[3-(hydroxy propyl)]-3,1(4H) quinazolin-4-one was prepared by modifying the earlier reported method<sup>15</sup>. Ethanolic solution of 2-phenyl-[3-(hydroxy propyl)]-3,1(4H) quinazolin-4-one was allowed to react with semicarbazide/thiosemicarbazide hydrochloride dissolved in 10 mL ethanolic solution of sodium acetate. The resulting mixtures were heated on water bath for 2-3 h with frequent shaking. After cooling, the precipitate was collected, washed with ether, treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with water and crystallized twice from ethanol to furnish 2-phenyl-[3-(hydroxy propyl)]-3,1(4H)-quinazolin-4-one semicarbazone/thiosemicarbazone as colourless prismatic needles, m.p.  $236 \pm 1$  °C for ligand 2-phenyl-[3-(hydroxy propyl)]-3,1(4H)-quinazolin-4-one semicarbazone (PHQS) and  $242 \pm 1$  °C for ligand PHQTS. Yield *ca.* 70 %.

**Preparation of the complexes:** The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting ethanolic solutions of metal acetate of Co(II), Ni(II) and Cu(II) in ethanolic medium with ethanolic solutions the ligands PHQS/PHQTS and the procedure carried out in each case was of similar nature with a slight variation of refluxing time. The coloured complexes obtained in each case were, cooled, filtered and washed with ethanol several times to remove any excess of the metal acetate and/or ligand. Finally, the complexes were washed with anhydrous diethyl ether and dried in oven. Yield *ca.* 60-65 %.

## RESULTS AND DISCUSSION

The analytical data, colour, decomposition temperature, electronic spectra, magnetic susceptibility as well as molar conductance data are recorded in Table-1.

The infrared spectra of the ligand as well as coordination compounds have been measured in the region  $4000-200$   $\text{cm}^{-1}$  and are recorded in the Table-2. Literature survey<sup>16</sup> establish the fact that semicarbazone/thiosemicarbazone ligands can coordinate through oxygen/sulphur atoms of either semicarbazone/thiosemicarbazone moiety. The IR spectra of the both ligands PHQS/PHQTS shows a broad band at  $3200$   $\text{cm}^{-1}$  which can be assigned<sup>17</sup> to  $\nu(\text{N-H})$  vibrations. This band remains unperturbed on complexation proposes non involvement of either terminal or secondary amino groups in the coordination with metal ions. A broad band observed in ligands PHQS/PHQTS at  $3400$   $\text{cm}^{-1}$ . This band has been broadened and its position has shifted to a lower frequency region at  $3360$   $\text{cm}^{-1}$  after complexation proposes<sup>18</sup> coordination of alcoholic oxygen atom by deprotonation.

TABLE-1  
ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA,  
DECOMPOSITION TEMPERATURE, MOLAR CONDUCTANCE DATA OF  
Co(II), Ni(II) AND Cu(II) COMPLEXES WITH LIGAND PHQS AND PHQTS

| Compd./colour  | Elemental analysis:<br>Found (Calcd.) % |                  |                |                  | $\mu_{\text{eff}}$<br>(BM) | $\Lambda_m$<br>(ohm <sup>-1</sup><br>cm <sup>2</sup> mol <sup>-1</sup> ) | $\lambda_{\text{max}}$<br>electronic<br>(cm <sup>-1</sup> ) | Decom-<br>position<br>temp.<br>(°C) |
|--|---|------------------|----------------|------------------|----------------------------|--|---|-------------------------------------|
|  | M                                       | C                | H              | N                |                            |  |   |                                     |
| PHQS<br>Colourless   | –                                       | 62.80<br>(62.76) | 5.81<br>(5.84) | 21.67<br>(21.53) | –                          | –  | –   | –                                   |
| PHQTS<br>Colourless  | –                                       | 60.67<br>(59.82) | 5.51<br>(5.57) | 20.54<br>(20.52) | –                          | –  | –   | –                                   |
| [Co(PHQ <sub>2</sub> ) <sub>2</sub> ]<br>Red               | 8.39<br>(8.33)                          | 57.60<br>(57.71) | 5.02<br>(5.09) | 19.71<br>(19.80) | 5.12                       | 17.3   | 10100, 16200,<br>23000                                      | 260                                 |
| [Co(PHQ <sub>2</sub> TS) <sub>2</sub> ]<br>Orange          | 8.03<br>(7.93)                          | 55.43<br>(55.21) | 4.70<br>(4.87) | 18.86<br>(18.94) | 4.91                       | 16.6   | 10300, 16400,<br>23100                                      | 235                                 |
| [Ni(PHQ <sub>2</sub> ) <sub>2</sub> ]<br>Brown             | 8.37<br>(8.30)                          | 57.86<br>(57.73) | 4.93<br>(5.09) | 19.72<br>(19.81) | 3.26                       | 13.4   | 12000, 17300,<br>24100                                      | 275                                 |
| [Ni(PHQ <sub>2</sub> TS) <sub>2</sub> ]<br>Deep brown      | 8.09<br>(7.94)                          | 55.37<br>(55.23) | 4.82<br>(4.87) | 18.86<br>(18.95) | 3.17                       | 12.8   | 12100, 17000,<br>24100                                      | 277                                 |
| [Cu(PHQ <sub>2</sub> ) <sub>2</sub> ]<br>Blue              | 8.33<br>(8.25)                          | 57.49<br>(57.34) | 4.93<br>(5.05) | 19.74<br>(19.67) | 1.84                       | 14.8   | 13700, 18000  | 310                                 |
| [Cu(PHQ <sub>2</sub> TS) <sub>2</sub> ]<br>Yellowish green | 8.46<br>(8.54)                          | 54.69<br>(54.87) | 4.80<br>(4.84) | 18.51<br>(18.42) | 1.90                       | 15.1   | 13000, 17400  | 289                                 |

TABLE-2  
KEY IR SPECTRAL DATA (cm<sup>-1</sup>) OF LIGAND PHQS/PHQTS AND  
THEIR METAL COMPLEXES

| Compd.                                  | $\nu(\text{N-H})$ | $\nu(\text{O-H})$ | $\nu(\text{C=O})$ | $\nu(\text{C=N})$ | $\nu(\text{C=S})$ | $\nu(\text{M-O})$ | $\nu(\text{M-S})$ | $\nu(\text{M-N})$ |
|---|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| PHQS                                    | 3200 s            | 3400 s,b          | 1660 s,b          | 1505 s,b          |                   |                   |                   |                   |
| PHQTS                                   | 3220 s            | 3420 s,b          | 1665 s,b          | 1500 s,b          | 800 s             |                   |                   |                   |
| [Co(PHQ <sub>2</sub> ) <sub>2</sub> ]   | 3200 s            | 3365 m,b          | 1695 s,b          | 1475 m,b          |                   | 540 m             |                   | 410 m             |
| [Co(PHQ <sub>2</sub> TS) <sub>2</sub> ] | 3220 s            | 3390 m,b          | 1700 s,b          | 1470 m,b          | 770 m,b           | 520 m             | 435 m             | 415 m             |
| [Ni(PHQ <sub>2</sub> ) <sub>2</sub> ]   | 3200 s            | 3370 m,b          | 1690 s,b          | 1480 m,b          |                   | 530 m             |                   | 430 m             |
| [Ni(PHQ <sub>2</sub> TS) <sub>2</sub> ] | 3220 s            | 3395 m,b          | 1700 s,b          | 1465 m,b          | 780 m,b           | 525 m             | 470 m             | 425 m             |
| [Cu(PHQ <sub>2</sub> ) <sub>2</sub> ]   | 3200 s            | 3370 m,b          | 1690 s,b          | 1475 m,b          |                   | 535 m             |                   | 420 m             |
| [Cu(PHQ <sub>2</sub> TS) <sub>2</sub> ] | 3220 s            | 3400 m,b          | 1695 s,b          | 1470 m,b          | 775 m,b           | 530 m             | 450 m             | 410 m             |

IR spectra of the Schiff base PHQS exhibit strong and broad band at 1665 cm<sup>-1</sup> which may be assignable<sup>19</sup> to  $\nu(\text{C=O})$ . In the spectra of the complex this band suffers upward shift at 1700 cm<sup>-1</sup> and appearance of a band at 555-520 cm<sup>-1</sup> in the complex may be assignable<sup>20</sup> to  $\nu(\text{M-O})$  confirm the coordination of carbonyl oxygen atom to the metal ion as well as linkage of alcoholic oxygen to the metal ion.

A red shift in  $\nu(\text{C}=\text{N})$  band ( $1500\text{ cm}^{-1}$ ) in the spectra of free ligands PHQS/PHQTS to lower value  $1470\text{ cm}^{-1}$  in their complexes is consistent<sup>21</sup> with coordination of the azomethine nitrogen to the central metal ion. The linkage through N is further confirmed by the appearance of a new band in the far infrared region at  $430\text{--}400\text{ cm}^{-1}$  in the complexes may be assigned to  $\nu(\text{M}\text{--}\text{N})$ <sup>22</sup>.

The spectrum of the ligand PHQTS shows a sharp and strong band at  $800\text{ cm}^{-1}$ , which may be assigned<sup>23</sup> to  $\nu(\text{C}=\text{S})$ . This band suffers downward shift at  $780\text{--}770\text{ cm}^{-1}$  proposes linkage through thione sulphur atom of thiosemicarbazone moiety. The linkage through S atom of thione group is further confirmed by the appearance of a band in the far IR region at  $470\text{--}450\text{ cm}^{-1}$  in the complexes which may be assigned<sup>24</sup>  $\nu(\text{M}\text{--}\text{S})$ . The above observations proposes that the ligand PHQS/PHQTS were behaves as a binegative tridentate manner and bonded to the metal ions through alcoholic oxygen, azomethine N atom and oxygen/sulphur atoms of either semicarbazone/thiosemicarbazone moiety<sup>25</sup>.

**Electronic spectra and magnetic moment data:** The electronic spectra of Co(II) complexes exhibit three broad bands recorded in the regions at  $10000$ ,  $16000$  and  $23000\text{ cm}^{-1}$  which may be assigned  ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ,  ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ , respectively which proposes an octahedral<sup>25</sup> geometry of the complexes. The proposed geometry of Co(II) complexes is further supported<sup>26</sup> by the magnetic moment value of the Co(II) complexes in the region  $4.91\text{--}5.12\text{ BM}$ . The electronic spectra of all the Ni(II) complexes exhibits three spectral bands in the regions  $12000$ ,  $17000$  and at  $24000\text{ cm}^{-1}$  which may be assigned due to the transitions,  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ ,  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$  and  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ , respectively. The above mentioned range of electronic spectra proposes octahedral<sup>25</sup> geometry of the Ni(II) complexes which is further supported<sup>26</sup> by magnetic moment value in the range of  $3.17\text{--}3.26\text{ BM}$ . The electronic spectra of Cu(II) complexes exhibits two spectral bands in the regions,  $13700\text{--}13000$ ,  $18000\text{--}17400\text{ cm}^{-1}$  which may be assignable to the transitions  ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$  and CT band which proposes octahedral<sup>24</sup> geometry of Cu(II) complexes. The magnetic values of Cu(II) complexes lie in the range of  $1.84\text{--}1.90\text{ BM}$ .

**Antifungal activity:** The antifungal activity of the ligands PHQS and PHQTS as well their metal ccomplexes were done against two fungi, *Apergillus flavus* and *Pinicillium expansum* by paper disc plate method<sup>14</sup> at concentration levels of  $2.0$  and  $0.2\%$  (w/v) in DMF. Standard PDA medium was used. Filter paper discs of diameter  $12\text{ mm}$  were used and the diameters of zones of inhibition formed around each disc after incubating for a period of  $72\text{ h}$  at  $25\text{--}30^\circ\text{C}$  were recorded in Table-3. Results were compared with fungicides, Dithane Z-78. On comparison with reference to fungicide, the complexes were found to more effective than ligands, PHQS and PHQTS.

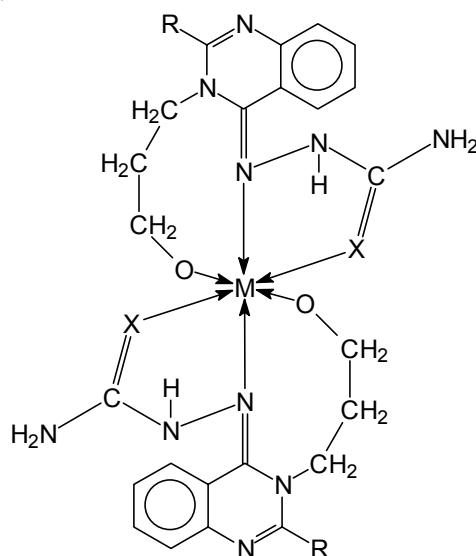
TABLE-3  
ANTIFUNGAL ACTIVITY OF PHQS/ PHQTS AND THEIR METAL COMPLEXES

| Compounds                 | Zone of inhibition of 1000 ppm (%) |                            |
|---------------------------|------------------------------------|----------------------------|
|                           | <i>Penicillium expansum</i>        | <i>Aspergillus flavous</i> |
| PHQS                      | 74                                 | 56                         |
| PHQTS                     | 84                                 | 67                         |
| [Co(PHQS) <sub>2</sub> ]  | 86                                 | 74                         |
| [Co(PHQTS) <sub>2</sub> ] | 97                                 | 83                         |
| [Ni(PHQS) <sub>2</sub> ]  | 93                                 | 61                         |
| [Ni(PHQTS) <sub>2</sub> ] | 100                                | 100                        |
| [Cu(PHQS) <sub>2</sub> ]  | 87                                 | 70                         |
| [Cu(PHQTS) <sub>2</sub> ] | 100                                | 100                        |

**Conductivity measurements:** Conductivity measurements made on systronics conductivity meter model 303 using dimethyl formamide as a solvent. The molar conductance value found to be in the range of 12.6-17.3  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  proposes the complexes to be non electrolyte<sup>27</sup> in nature.

### Conclusion

On the basis of spectra data (IR and electronic) elemental analysis, molar conductance data, magnetic susceptibility data the complexes of Co(II), Ni(II) and Cu(II) with ligands PHQS/PHQTS can be presumed to have an octahedral geometry as shown in Fig. 1.



[M(PHQS)<sub>2</sub>] and [M(PHQTS)<sub>2</sub>]; M = Co(II), Ni(II) and Cu(II)  
X = oxygen or sulphur; R = phenyl

Fig. 1

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