



## Spectrophotometric Determination of Co(II), Ni(II) and Cu(II) Complexes with Schiff Base Containing Nitrogen and Sulphur Donor Sites

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### ABSTRACT

Coordination compounds of Co(II), Ni(II) and Cu(II) are synthesized by the reaction of 3-propyl-(N-ortho toluene) quinazoline thiosemicarbazone. An attempt has been made to probe the structures, bonding pattern and geometries of their coordination compounds by the molar mass, elemental analyses, infrared spectra, electronic spectra, molar conductance data and decomposition temperature.

**Keywords:** PTQT/ Co(II), Ni(II) and Cu(II) complexes/ Schiff Base.

### INTRODUCTION

The chemistry of transition metal complexes has been rapidly expanding not only because their potential applications, but also due to the intriguing variety of architecture exhibited by these compounds<sup>1-5</sup>. Schiff base derivative incorporating a fluorescent moiety are a useful tool for optical sensing of metal ions. Thin organic and organometallic films have attracted research interest due to their technologically important optical and electronic properties. These materials exhibit luminescence, they are used as conductors, semiconductors and organic light emitting diodes (OLED)<sup>6-7</sup>. A considerable interest has been shown to biologically active transition metal complexes, largely due to their ability to interact with DNA<sup>8</sup>. The

complexes which can bind or cleave DNA at specific sites, may play an important role in genomic research and in photodynamic therapy against cancer<sup>9</sup>. It is well known that some coordination compounds can inhibit the multiplication of cancer cells by binding and damaging DNA<sup>10</sup>.

Motivated from the above mentioned biochemical significance of Schiff base and their transition metal complexes with nitrogen and sulphur containing Schiff bases and in continuation of our earlier research work<sup>11-20</sup> in this field we are hereby reported the synthesis and characterization of coordination compounds of Co(II), Ni(II) and Cu(II) with Schiff base ligand. 3-propyl-(N-ortho-toluene) quinazoline thiosemicarbazone (PTQT).

## EXPERIMENTAL

All reagent were analytical grade and used without further purification. The metal contents were analysed by standard procedure<sup>21</sup>. The electronic spectra of the complexes were recorded on Cary-2390 spectrophotometer in the 10000-25000  $\text{cm}^{-1}$ . The infrared spectra of the ligand and metal complexes in the region 200-4000  $\text{cm}^{-1}$  were recorded on Perkin Elmer 577 spectrophotometer. The magnetic susceptibility was measured using Gouy balance using mercury tetrakisothiocyanato cobaltate as a calibrant. The molar conductance was measured by Systronics conductivitymeter model 303 using DMF as a solvent.

Analytical data, electronic spectral data, molar conductance value, magnetic susceptibility value, decomposition temperature and molecular formula of the ligand as well as their complexes are recorded in Table.1 and the salient features of IR bands are recorded in Table-2.

### Preparation of the ligand

Ethanolic solution of 3-propyl (N-ortho toluene) quinazoline (0.01m) in ethanol and thiosemicarbazide hydrochloride dissolved in 10% solution of sodium acetate in ethanol. The resulting mixture was refluxed on water bath for 2 h with occasional stirring. The solvent was concentrated to half of its volume and then poured in ice cold water. A solid precipitated out immediately which was filtered, washed with distilled water and cold ethanol.

Recrystallization of crude product from ethanol gave the Schiff Base, PTQT, Yield 70%, m.p.  $183 \pm 1^\circ\text{C}$ .

### Preparation of the complexes

The following general method was adopted for the preparation of the halide complexes of cobalt(II), nickel(II) and copper(II).

The complexes were prepared by reacting metal halides (0.05 g) of the cobalt(II), nickel(II) and copper(II) in ethanol with ethanolic solution of the ligand 3-propyl(N-ortho-toluene) thiosemicarbazone (0.1g). The mixture was then refluxed under stirring condition. The mixture was then refluxed for 3 h.

The product was precipitated out and was collected by filtration followed by washing with cold water. Then the product was dried in oven. Yield 75-80%.

The following general method was adopted for the preparation of nitrate and perchlorate complexes. The complexes were prepared by using metal nitrates/ perchlorate salts of cobalt(II), nickel(II) and copper(II) to a hot ethanolic solution of the ligand 3-propyl (N-ortho toluene) thiosemicarbazone. The mixture was in the molar ratio 1:2. The mixture was then refluxed under stirring condition. The mixture was then refluxed for 4 hours. The product was precipitated out and was collected by filtration followed by washing with cold water. Then the product was dried in oven. Yield 75-80%.

## RESULTS AND DISCUSSION

### Infrared Spectral Study

The IR spectrum of the complexes was compared with those of the free ligand in order to determine the involvement of the coordination sites in the chelation. Analysis by IR results in the absorption spectra in the IR region and registered bands or signals. IR spectra of the ligand, PTQT exhibited the characteristic strong band at 1560  $\text{cm}^{-1}$  assignable<sup>22,24</sup> to azomethine ( $>\text{C}=\text{N}$ ). In the spectra of the complex this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity proposes possible linkage of the azomethine nitrogen with metal ions. The infrared spectra of the ligand shows a strong and broad band at 780  $\text{cm}^{-1}$  assigned<sup>22-25</sup> to  $\nu_{\text{C-S}}$ . After complex formation this band also shows red shift proposes coordination of metal through thione sulphur atom of thiosemicarbazone moiety.

The evidence of bonding ligand, PTQT to metal ion through oxygen atom of either nitrate or perchlorate ion, N-atom of azomethine group and thione sulphur of thiosemicarbazone moiety is supported by the appearance of bands due to  $\nu_{\text{M-O}}$ <sup>22-26</sup> at 540-515  $\text{cm}^{-1}$ ,  $\nu_{\text{M-S}}$ <sup>22-26</sup> at 475-455  $\text{cm}^{-1}$  and  $\nu_{\text{M-N}}$ <sup>22-26</sup> at 435-410  $\text{cm}^{-1}$  respectively. The evidence of metal-halogen coordination is supported by the low molar conductance values<sup>27</sup> of the complexes in the range 4.7-11.3  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  and appearance of a band in the region 325-265  $\text{cm}^{-1}$  assigned<sup>22-26</sup> to  $\nu_{\text{M-X}}$ .

**Table.1: Colour Analytical, magnetic susceptibility, molar conductivity and decomposition temperature of ligand PTQT and its metal complexes**

Compounds (Colour)	% Analysis found (calculated)				$\lambda_{\max}$ electronic $\text{cm}^{-1}$	$\Omega_{\text{m}}$ ohm $^{-1}$ $\text{cm}^2 \text{mol}^{-1}$	$\mu_{\text{eff}}$ B.M.	DT °C
	M	C	N	H				
PTQT (Colourless)		64.81 (64.95)	19.80 (19.94)	5.93 (5.98)				
[Co(PTQT) $_2$ Cl $_2$ ] (Yellow)	6.93 (7.08)	84.21 (84.38)	16.70 (16.82)	4.97 (5.04)	8720, 17200, 20040	6.3	4.83	219
[Co(PTQT) $_2$ Br $_2$ ] (Yellow)	5.73 (5.80)	76.09 (76.24)	15.13 (15.20)	4.48 (4.56)	8700, 17060, 20080	6.1	4.89	209
[Co(PTQT) $_2$ I $_2$ ] (Red)	5.73 (5.80)	69.06 (69.18)	13.68 (13.79)	4.07 (4.13)	8910, 11010, 20100	6.9	4.67	224
[Co(PTQT) $_2$ (NO $_3$ ) $_2$ ] (Red)	6.58 (6.65)	79.14 (79.32)	15.70 (15.82)	4.68 (4.74)	8800, 17040, 20020	7.3	5.02	202
[Co(PTQT) $_2$ (ClO $_4$ ) $_2$ ]	6.04 (6.13)	73.01 (73.13)	14.49 (14.58)	4.30 (4.37)	8860, 17210, 19940	5.9	5.10	211
[Ni(PTQT) $_2$ Cl $_2$ ] (Brown)	6.96 (7.06)	84.22 (84.40)	16.70 (16.82)	4.98 (5.04)	10300, 14400, 24310	5.2	3.06	213
[Ni(PTQT) $_2$ Br $_2$ ] (Brown)	6.29 (6.37)	76.09 (76.26)	15.10 (15.20)	4.50 (4.56)	10260, 14100, 25980	4.9	3.11	207
[Ni(PTQT) $_2$ I $_2$ ]	5.70 (5.78)	69.07 (69.19)	13.69 (13.79)	4.06 (4.13)	10190, 14080, 25100	4.7	3.02	228
[Ni(PTQT) $_2$ (NO $_3$ ) $_2$ ] (Red)	6.57 (6.63)	79.16 (79.34)	15.69 (15.82)	4.68 (4.74)	10220, 14200, 25800	5.2	3.09	216
[Ni(PTQT) $_2$ (ClO $_4$ ) $_2$ ]	6.02 (6.11)	72.99 (73.14)	14.44 (14.58)	4.68 (4.74)	10100, 14160, 24900	4.9	3.01	204
[Cu(PTQT) $_2$ Cl $_2$ ] (Blue)	7.68 (7.59)	83.78 (83.91)	16.65 (16.73)	4.96 (5.02)	14600, 24640	9.2	1.84	221
[Cu(PTQT) $_2$ Br $_2$ ] (Blue)	6.78 (6.86)	75.70 (75.86)	15.04 (15.12)	4.47 (4.53)	14380, 24310	10.8	1.89	217
[Cu(PTQT) $_2$ (NO $_3$ ) $_2$ ] (Blue)	6.05 (7.14)	78.78 (78.91)	15.62 (15.73)	4.68 (4.72)	14510, 24210	10.2	1.86	212
[Cu(PTQT) $_2$ (ClO $_4$ ) $_2$ ]	6.49 (6.58)	72.66 (72.75)	14.39 (14.51)	4.29 (4.35)	14700, 24700	11.3	1.92	203

DT = Decomposition Temperature

**Table. 2: Salient features of IR spectral data (cm<sup>-1</sup>) for ligand PTQT and its metal complexes**

Compounds	V <sub>C=N</sub>	V <sub>C=S</sub>	V <sub>M-O</sub>	V <sub>M-N</sub>	V <sub>M-S</sub>	V <sub>M-X</sub>
PTQT	1560s,b	800 s, b				
[Co(PTQT) <sub>2</sub> Cl <sub>2</sub> ]	1530 m,b	790 m,b		470 m,b	420 m	325 m
[Co(PTQT) <sub>2</sub> Br <sub>2</sub> ]	1535 m,b	780 m,b		470 m	420 m	315 m
[Co(PTQT) <sub>2</sub> I <sub>2</sub> ]	1535 m,b	775 m,b	510 m	470 m	420 m	325 m
[Co(PTQT) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1535 m,b	775 m,b	505 m	465 m	425 m	
[Co(PTQT) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1530 m,b	775 m,b	510 m	465 m	415 m	
[Ni(PTQT) <sub>2</sub> Cl <sub>2</sub> ]	1530 m,b	775 m,b		460 m	415 m	275 m
[Ni(PTQT) <sub>2</sub> Br <sub>2</sub> ]	1535 m,b	780 m,b		470 m	410 m	280 m
[Ni(PTQT) <sub>2</sub> I <sub>2</sub> ]	1530 m,b	780 m,b	515 m	470 m	410 m	280 m
[Ni(PTQT) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1530 m,b	780 m,b	510 m	460 m,b	415 m	
[Ni(PTQT) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1530 m,b	775 m,b		465 m	420 m	
[Cu(PTQT) <sub>2</sub> Cl <sub>2</sub> ]	1530 m,b	780 m,b		465 m	415 m	270 m
[Cu(PTQT) <sub>2</sub> Br <sub>2</sub> ]	1535 m,b	770 m,b	515 m,b	470 m	415 m,b	275 m
[Cu(PTQT) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1525 m,b	770 m,b	520 m,b	470 m	410 m	
[Cu(PTQT) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	1535 m,b	775 m,b	520 m,b	470 m	415 m	

m = medium, s = strong, b = broad

The evidence for nitrate complexes indicated by presence of characteristic medium intensity bands at 1280 and 1120 with separation of 160 cm<sup>-1</sup> due to monodentate linkage of nitrate group. Presence of combination bands at 1680 and 1660 with a separation of 20 cm<sup>-1</sup> confirming the monodentate behavior of the nitrate group<sup>28</sup>. The monodentate behavior of perchlorate complexes were confirmed due to the presence of four IR spectra bands at 1130, 1050, 650 and 620 cm<sup>-1</sup> proposing monodentate behavior of perchlorate in group<sup>29</sup>.

Hence on the basis of above discussion on IR spectra data, it proposes that the ligand PTQT acts in a neutral bidentate manner. The remaining coordination positions of metal ions are satisfied 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>.

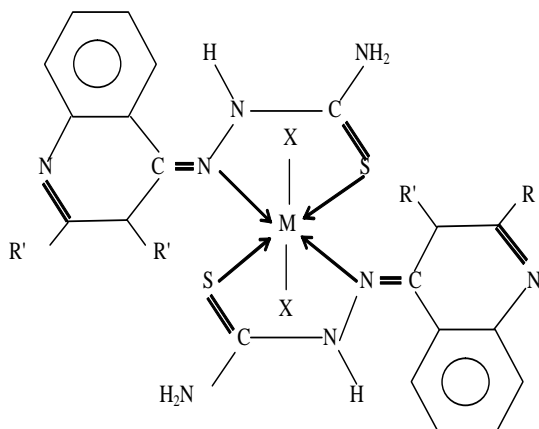
#### Electronic spectra and magnetic susceptibility of the complex :

The cobalt(II) complexes exhibit three spectral bands in the regions at 8800-8900 cm<sup>-1</sup>, 17000-17200 cm<sup>-1</sup> and 19940-20100 cm<sup>-1</sup> assignable to the transitions <sup>4</sup>T<sub>2g</sub>(F) ← <sup>4</sup>T<sub>1g</sub>(F), <sup>4</sup>A<sub>2g</sub>(F) ← <sup>4</sup>T<sub>1g</sub>(F) and <sup>4</sup>T<sub>1g</sub>(P) ← <sup>4</sup>T<sub>1g</sub>(F) respectively which proposes octahedral<sup>30</sup> geometry. The

proposed octahedral geometry of the cobalt(II) complexes is supported<sup>31,32</sup> by high magnetic susceptibility value in the range of 4.67-5.02 BM. The Ni(II) complexes exhibits three spectra bands in the region at 10100-10300, 14080-14400 and 24310-25980 cm<sup>-1</sup> assignable to transitions <sup>3</sup>T<sub>2g</sub>(F) ← <sup>3</sup>A<sub>2g</sub>(F), <sup>3</sup>T<sub>1g</sub>(F) ← <sup>3</sup>A<sub>2g</sub>(F) and <sup>3</sup>T<sub>1g</sub>(P) ← <sup>3</sup>A<sub>2g</sub>(F) respectively which proposed octahedral<sup>30</sup> geometry for Ni(II) complexes. The proposed octahedral geometry of Ni(II) complexes is further supported<sup>31,32</sup> by magnetic susceptibility value of all the Ni(II) complexes in the range 3.01-3.11 BM. The Cu(II) complexes display two ligand field bands in the position 14300-14700 cm<sup>-1</sup> and 24210-24700 cm<sup>-1</sup> assignable to the transition <sup>2</sup>T<sub>2g</sub> ← <sup>2</sup>E<sub>g</sub> and charge transfer band, respectively. The electronic spectra of all the Cu(II) complexes suggesting octahedral<sup>30</sup> geometry around central metal ion. The magnetic moment value of Cu(II) complexes are lie in the range of 1.84-1.92 BM.

#### Molar conductivity measurement :

Molar conductance data of the complexes were measured in the solvent DMF and all the complexes were found to be non electrolytic in nature. The molar conductance value<sup>27</sup> of the complexes are lies in range 4.7-11.3 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.



**Fig.1**  $[M(PTQT)_2X_2]$   $M = \text{Co(II)}, \text{Ni(II)}$  and  $\text{Cu(II)}$ ;  $R =$  propyl  $R' = o\text{-toluidine}$ ;  $X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{and } \text{ClO}_4^-$

## CONCLUSION

Based on the above physico-chemical and spectroscopic studies it is proposed that the ligand PTQT acts in a bidentate manner and coordination is proposed through azomethine N and thione S of thiosemicarbazone moiety. The remaining coordination centre of metal ions are satisfied by negative ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ .

The proposed geometry of the  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cu(II)}$  are shown as Fig.1.

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