



## Synthesis and Characterization of Cu(II), Ni(II) and Co(II) Coordination Compounds with Nitrogen and Oxygen Containing Schiff Base

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### ABSTRACT

Octahedral complexes has been designed and synthesized by a 2-propyl-thioquinoxaline 4(3H) semicarbazone (PTQS) with Co(II), Ni(II) and Cu(II) metal ions. The complexes was characterized by molar mass, elemental analyses, IR electronic spectra, Molar conductivity and magnetic susceptibility assistance. On the above studies it was confirming that metal ions was coordinated with Carbonyl oxygen and azomethine nitrogen atom of semicarbazone moiety. The remaining valency of metal ions are satisfied by negative ions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and No<sub>3</sub><sup>-</sup> ions.

**Keywords:-** PTQS/Semicarbazone/ Co(II), Ni(II) and Cu(II)/ Octahedral complex.

### INTRODUCTION

In the last decade, there have been numerous attempts to produce transition metal complexes containing nitrogen and sulphur donor Schiff base ligands. Schiff bases and their metal complexes exhibited biological activity as antiviral<sup>1</sup>, antibiotics<sup>2</sup> and anti-tumour agents<sup>3</sup> due to presence of their specific moiety. The direct use of transition metal salts as antimicrobial agent cannot be recommended as they are very toxic to host human being. It has been proved from the survey of literature that the biologically active compound show greater

activity when administered as metal complexes than as a free organic compounds. Semicarbazones are used as ligands in coordination chemistry and are biologically active compounds.

Their complexation with different metal enhances the bioactivity of these molecules. These metal based complexes have attracted considerable interest in chemical and biological studies due to their potentially beneficial biocidal activity which may be attributed to formation of their chelates with metal ions<sup>5-10</sup>. Such promising biological potentials of Schiff base and its metal complexes as well as in

continuation of our earlier research work<sup>11-13</sup> in this field we have prompted us synthesized complexes of Co(II), Ni(II) and Cu(II) with Schiff base ligand, 2-propyl-thioquinazolin 4(3H) semicarbazone.

## EXPERIMENTAL

All reagents, were of analytical reagent grade. The metal contents of all the complexes were analysed using standard procedure<sup>14</sup>. The infrared spectra of the ligand and metal complexes in the regions 200-4000  $\text{cm}^{-1}$  were recorded on Perking Elmer -577 spectrophotometer. The electronic spectra were recorded on Cary-2390 spectrophotometer in the 10000-25000  $\text{cm}^{-1}$  and magnetic susceptibility was measured using Gouy balance using mercury tetrathiothiocyanate cobaltate as a calibrant. The molar conductivity was measured on Systronics Conductivity Meter model 303 using DMF as a solvent.

### Preparation of the Ligand

A mixture of 2-propyl thioquinazoline 4(3H) one (5m mol) and semicarbazide hydrochloride (5m mol) was refluxed for 1 h. After cooling, the mixture was poured into distilled water (200 ml) white precipitate were filtered and recrystallised from ethanol. m.p.;  $311 \pm 1^\circ\text{C}$ .

### Synthesis of Metal Complexes

The complexes were prepared by reacting respective halide/nitrate of Co(II), Cu(II) and Ni(II) in ethanoic medium with the ethanolic solution of the ligand, 2-propyl thioquinazoline 4(3H) Semicarbazone in molar ratio 1:2. The resulting reaction mixture was refluxed on water bath for 3-4h. The procedure carried out in each case was similar with slight variation of timing of reflux. On cooling solid coloured complexes separated out which were filtered, washed with ethanol, dried and recrystallised.

## RESULTS AND DISCUSSION

### Infrared Spectra

The mode of band formation in complexation between ligand and metal ions can be effectively determined by the Infrared spectral data (Table-2). The IR spectrum of the ligand PTQS exhibit strong and broad band at  $3200 \text{ cm}^{-1}$  assigned <sup>15</sup> to  $\nu_{\text{N-H}}$ . In

the spectra of the complexes, this band is unaffected which indicates non-involvement of either primary amino or secondary amino group in the coordination. IR spectrum of the ligand exhibit strong and broad band at  $1640 \text{ cm}^{-1}$  assigned<sup>16</sup> to  $\nu_{\text{C=O}}$ . In the spectra of the complexes, this band has shifted to a lower frequency region with slightly reduced intensity, The shift of the band and change in intensity proposes co-ordination of the carbonyl oxygen with metal ions. This is further confirmed on the basis of occurrence of a far IR region band of the complexes at  $540\text{-}510 \text{ cm}^{-1}$  assigned to  $\nu_{\text{M-O}}$ . The absorption bands around  $1460 \text{ cm}^{-1}$  are designated to the azomethine group<sup>18</sup>. In the complexes, the frequencies of azomethine groups appear mostly towards the lower region. The linkage of azomethine nitrogen with metal ion is further supported by the appearance of another far IR band at  $440\text{-}405 \text{ cm}^{-1}$  assigned<sup>19</sup> to  $\nu_{\text{M-N}}$ . The above IR spectra data indicates that ligand coordinate to the metal through the carbonyl oxygen and azomethine nitrogen. The evidence of metal halogen linkage is confirmed by the appearance of a band in the region  $320\text{-}270 \text{ cm}^{-1}$  assigned<sup>20</sup> to  $\nu_{\text{M-X}}$  (X=Cl, Br and I) The evidence of metal halogen linkage is further confirmed by the low value of molar conductance of the complexes on the range  $1.8\text{-}7.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Nitrate complexes show bands in the region  $1340\text{-}1375 \text{ cm}^{-1}$  and  $800\text{-}825 \text{ cm}^{-1}$  due to ionic nitrate and bands at  $1025\text{-}1040 \text{ cm}^{-1}$  can be assigned to coordinated nitrate group<sup>21</sup>. Appearance of bands at  $1360\text{-}1440 \text{ cm}^{-1}$  confirms the monodentate coordination mode of the nitrate group<sup>22</sup>.

### Electronic Spectra and Magnetic Susceptibility of the Complex

The electronic<sup>23</sup> spectra of all the complexes have been recorded in the region  $10000\text{-}25000 \text{ cm}^{-1}$ . The electronic spectral and magnetic susceptibility<sup>24,25</sup> data (Table-2) suggest octahedral geometry of the complexes.

### Conductivity measurement

Molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range  $1.8\text{-}7.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in DMF proposes their non-electrolytic<sup>26</sup> nature. The molar conductance values also supported the structure assigned on the basis of physiochemical and spectroscopic measurements.

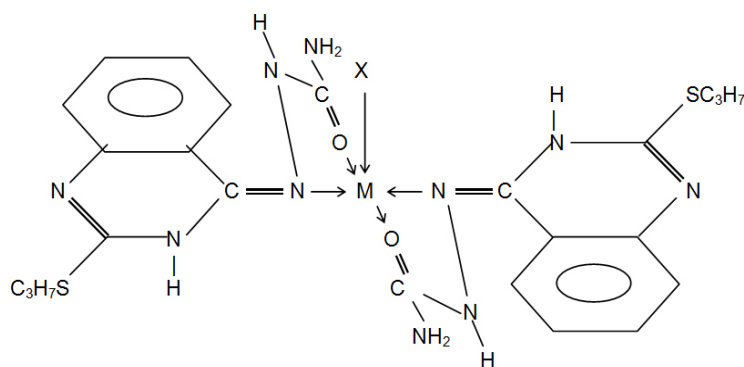
Table 1: Analytical, electronic and molar conductance measurements

Compounds (Colour)	Molar Mass	% Analysis found (calculated)				$\mu_{\text{eff}}$ B. M.	$\Omega_{\text{m}}$ ohm $^{-1}$ cm $^2$ mol $^{-1}$	DT °C	$\lambda_{\text{max}}$ electronic cm $^{-1}$
		M	C	N	H				
PTQS	278		51.62 (51.79)	25.04 (25.17)	5.69 (5.75)				
Colourless [Co(PTQS) $_2$ Cl $_2$ ]	685.93	8.50 (8.59)	40.79 (41.98)	20.28 (20.41)	4.61 (4.66)	5.1	3.3	1.89	20800
Brown [Co(PTQS) $_2$ Br $_2$ ]	774.75	7.51 (7.60)	36.98 (37.17)	17.96 (18.07)	4.07 (4.13)	4.96	3.1	193	20730
Brown [Co(PTQS) $_2$ I $_2$ ]	868.73	6.70 (6.78)	32.97 (33.15)	16.02 (16.11)	3.64 (3.68)	4.92	2.6	198	21080
Brown [Co(PTQS) $_2$ (NO $_3$ ) $_2$ ]	738.93		7.89	38.71	18.82	4.29	4.99	1.8	201
20300 Brown [Ni(PTQS) $_2$ Cl $_2$ ]	685.71	7.97 (8.50)	38.97 (41.83)	18.94 (20.28)	4.33 (4.60)	3.04	4.7	204	11600, 15400, 23100
Yellowish red [Ni(PTQS) $_2$ Br $_2$ ]	774.53	7.49 (7.58)	36.96 (37.18)	17.98 (18.07)	4.08 (4.13)	3.08	4.9	211	11200, 15100, 23600
Yellowish red [Ni(PTQS) $_2$ I $_2$ ]	868.51	6.69 (6.75)	32.94 (33.16)	15.97 (16.11)	3.60 (3.68)	3.02	5.3	217	11480, 15300, 22800
Yellowish red [Ni(PTQS) $_2$ (NO $_3$ ) $_2$ ]	738.71	7.87 (7.94)	38.70 (38.98)	18.80 (18.95)	4.28 (4.33)	3.11	6.8	223	12060, 15600, 23100
Yellowish red [Cu(PTQS) $_2$ Cl $_2$ ]	690.54	9.13 (9.20)	41.52 (41.70)	20.14 (20.27)	4.58 (4.63)	1.98	7.3	179	13080, 18900
Yellowish red [Cu(PTQS) $_2$ Br $_2$ ]	779.36	8.08 (8.15)	36.89 (36.95)	17.85 (17.96)	4.06 (4.10)	1.93	7.7	186	13400, 18200
Yellowish red [Cu(PTQS) $_2$ (NO $_3$ ) $_2$ ]	743.54		8.48	38.60	18.71	4.25	1.89	7.9	189
13560, 16660 Yellowish red		8.54	38.73	18.82	4.30				

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

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{M-O}$	$\nu_{M-N}$	$\nu_{M-X}$
PTQS	1640 s,b	1480 s,b			
[Co(PTQS) <sub>2</sub> Cl <sub>2</sub> ]	1620 m,b	1460 m,b	535 m	425 m	285 m
[Co(PTQS) <sub>2</sub> Br <sub>2</sub> ]	1615 m,b	1455 m,b	540 m	420 m	295 m
[Co(PTQS) <sub>2</sub> I <sub>2</sub> ]	1610 m,b	1450 m,b	535 m	435 m	305 m
[Co(PTQS) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1620 m,b	1455 m,b	530 m	440 m	310 m
[Ni(PTQS) <sub>2</sub> Cl <sub>2</sub> ]	1610 m,b	1455 m,b	535 m	430 m	275 m
[Ni(PTQS) <sub>2</sub> Br <sub>2</sub> ]	1620 m,b	1455 m,b	540 m	440 m	280 m
[Ni(PTQS) <sub>2</sub> I <sub>2</sub> ]	1620 m,b	1455 m,b	525 m	410 m	275 m
[Ni(PTQS) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1610 m,b	1450 m,b	510 m	420 m	280 m
[Cu(PTQS) <sub>2</sub> Cl <sub>2</sub> ]	1610 m,b	1455 m,b	520 m	415 m	270 m
[Cu(PTQS) <sub>2</sub> Br <sub>2</sub> ]	1610 m,b	1460 m,b	525 m	410 m	280 m
[Cu(PTQS) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1610 m,b	1460 m,b	530 m	405 m	300 m
[Ni(PTQS) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1620 m,b	1450 m,b	530 m	425 m	320 m

s = strong; m = medium; b = broad



M = Co(II), Ni(II); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and NO<sub>3</sub><sup>-</sup>

M = Cu(II); X = Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>

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

### CONCLUSIONS

Thus on the basis above studies it is concluded that the ligand PTQS acts in a bidentate manner and coordination is proposed through azomethine N and carbonyl oxygen of

Semicarbazone moiety. The remaining centre of the metal ion is satisfied by negative ions such as Cl, Br, I or NO<sub>3</sub>. The geometry of the Co(II), Cu(II) and Ni(II) complexes are proposed to be octahedral in nature as shown in Fig 1.

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