



Structural and Spectroscopic Aspects of Schiff Base Metal Complexes of Cobalt(II), Nickel(II) and Copper(II)

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ABSTRACT

The complexes of Co(II), Ni(II) and Cu(II) with Schiff base 2-butyl thioquinazoline 4(3H) thiosemicarbazone were synthesized. The general formulae of the complexes are of the type $\{M(L)_2X_2\}$, L=2 – butyl thioquinazoline 4(3H) thiosemicarbazone; x = Cl⁻, Br⁻, I⁻ and NO₃⁻. Elemental analyses and spectral (IR, electronic) studies of the synthesized complexes suggest the presence of octahedral, environment around the central metal ion. These complexes were also subjected to study their antimicrobial screening against, Gram positive bacteria *Candida albicans* and gram negative bacteria *Escherichia coli* by disc diffusion technique.

Key words : Schiff bases/ BTQT / Complex / Co(II), Ni(II) and Cu(II)/ antimicrobial screening.

INTRODUCTION

Thiosemicarbazone used as suitable ligand due to variable bonding abilities and several biocidal importance such as inhibitory action antiviral, antibacterial and anti-fungal activity¹⁻⁹. Based on the above biocidal importance of thiosemicarbazone and in continuation of our earlier recent work¹⁰⁻²³ on the synthesis and characterization of Schiff base metal complexes with nitrogen and sulphur containing

Schiff base, we report here the synthesis and antimicrobial evaluation of complexes of Co(II), Ni(II) and Cu(II) with the ligand, 2 butyl-thioquinazoline 4(3H) thiosemicarbazone.

EXPERIMENTAL

The chemical and reagent were used as obtained from commercial supplies without further purification. The analysis of carbon, hydrogen and

nitrogen as well as metal ions were performed using standard procedure²⁴. IR spectra were recorded in KBr pellets in 4000-200 cm^{-1} region on Perkin Elmer-577 spectrophotometer. Electronic spectra were recorded on Cary-2390 spectrophotometer in the 10000-25000 cm^{-1} . Magnetic susceptibility of the complexes were done on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. Molar conductivity of the Complexes were done at room temperature on Systronics conductivity meter model 303 using DMF as a solvent. Antimicrobial activity of the ligand and the complexes was carried out against *E. coli* and *S. aureus* by disc diffusion method.

Preparation of the ligand

A solution of thiosemicarbazide (0.01 mol) in 25 ml in ethanol was added to 2-butyl thioquinazoline 4(3H) one (0.01 m) dissolved in ethanol (25 ml) with occasional stirring. The reaction mixture was heated under reflux on a water bath for 4 h. After reducing the solvent volume to Ca . 30 ml and cooling to room temperature, the colourless solid obtained was filtered, washed with ethanol and dried in a oven. Yield-70% m.p.- 316°C \pm 1°C

Synthesis of complexes

The complexes were prepared by reacting appropriate metal halide/nitrate with the ethanolic solution of the ligand in molar ratio 1:2. The resulting mixture was refluxed for 3-4 h. On cooling to room temperature the coloured complexes were precipitated out. It was filtered, washed with hot water, ethanol and finally dried in oven yield 60-65%.

RESULTS AND DISCUSSION

In order to give conclusive evidence about the structure of the metal complexes, the main IR bands of the metal complexes, the main IR bands were compared with those of the free ligands. The IR spectra of the free ligand shows a medium band at 1570 cm^{-1} shifting towards lower wave number is due to the coordination of azomethine nitrogen with metal ion. The proposed linkage with azomethine nitrogen with metal ions are further supported by the appearance of a band in for IR region at 435-460 cm^{-1} in the complexes assigned^{26, 27} to $\nu_{\text{M-N}}$. The $>\text{C}=\text{S}$ band appearing at 840 \mathbf{cm}^{-1} in IR spectrum of ligand is shifted towards lower wave number in the spectra of the complex. This is due to coordination of thione sulphur²⁸ atom to metal ions. The linkage with metal ion with thione sulphur atom is further supported by the appearance of a band in far IR region at 395-410 cm^{-1} assigned^{26,27} to $\nu_{\text{M-S}}$. The Coordination through halogen atoms are indicated by the appearance of a band in far IR region at 315-260 cm^{-1} assigned^{26,27} to $\nu_{\text{M-X}}$ ($\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$). The coordination with halogen is supported by the low molar conductivity of the complexes in the range 8.9-14.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. The band at 1320 cm^{-1} and 1440 cm^{-1} indicates mono-coordinate linkage of nitrate groups with metal ions. Linkage with oxygen atom of nitrate group is support by appearance of a far IR band at 545-515 cm^{-1} assigned to $\nu_{\text{M-O}}$.

On the basis of IR spectral positions it may be proposed that ligand BTQT, acts as neutral

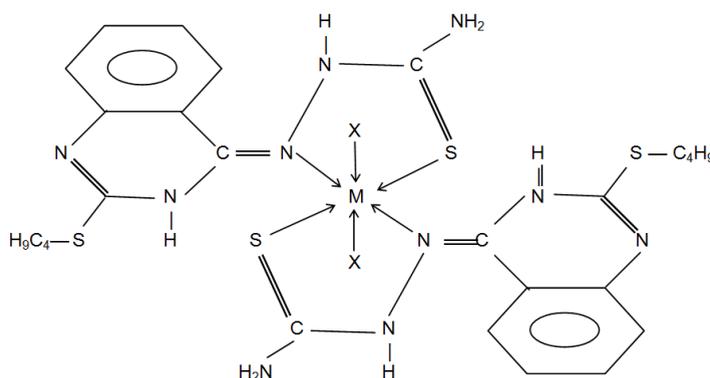


Fig.1 : $[\text{M}(\text{BTQT})_2]$

$\text{M} = \text{Co}(\text{II})$ and $\text{Ni}(\text{II})$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ or NO_3^- .

$\text{M} = \text{Cu}(\text{II})$; $\text{X} = \text{Cl}^-, \text{Br}^-$ or NO_3^- .

Table 1 : Analytical Data of ligand BTQT and its Metal Complexes

Compounds (Colour)	Molar Mass	% Analysis found (calculated)				Ω_m ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} B. M.	DT°C	λ_{max} electronic cm ⁻¹
		M	C	N	H				
BTQT	307		58.64 (50.81)	22.69 (22.80)	5.48 (5.53)				
Colourless [Co(BTQT) ₂ Cl ₂]	743.93	7.83 (7.92)	41.80 (41.93)	18.70 (18.81)	4.51 (4.57)	12.6	4.89	231	10540, 16400 24000
Brown [Co(BTQT) ₂ Br ₂]	832.74	6.94 (7.07)	37.29 (37.46)	16.69 (16.81)	3.96 (4.08)	12.1	4.99	216	10600, 16100 24200
Brown [Co(BTQT) ₂ I ₂]	926.70	6.26 (6.35)	33.54 (33.66)	14.98 (15.10)	3.61 (3.66)	11.3	4.88	219	9900, 16200 23800
Brown [Co(BTQT) ₂ (NO ₃) ₂]	796.93	7.30 (7.39)	39.01 (39.15)	17.44 (17.56)	4.22 (4.26)	11.8	4.86	227	10510, 16800 23900
Brown [Ni(BTQT) ₂ Cl ₂]	743.71	7.80 (7.89)	4.186 (41.95)	18.71 (18.82)	4.50 (4.57)	13.6	3.11	203	12000, 17600 24490
Red [Ni(BTQT) ₂ Br ₂]	832.52	6.96 (7.05)	37.34 (37.47)	16.68 (16.81)	3.98 (4.08)	13.1	3.08	214	12300, 17690 24500
Reddish Brown [Ni(BTQT) ₂ I ₂]	926.50	6.24 (6.33)	33.52 (33.67)	14.97 (15.11)	3.62 (3.66)	14.7	3.12	211	11900, 17800 24610
Reddish Brown [Ni(BTQT) ₂ (NO ₃) ₂]	796.71	7.28 (7.36)	39.04 (39.16)	17.43 (17.57)	4.21 (4.26)	14.3	3.14	207	12100, 18300 24440
Green [Cu(BTQT) ₂ Cl ₂]	748.54	8.39 (8.48)	31.11 (31.27)	18.58 (18.70)	4.49 (4.54)	9.6	1.92	236	13200, 20100
Green [Cu(BTQT) ₂ Br ₂]	837.35	7.42 (7.58)	37.11 (37.26)	16.58 (16.7)	4.01 (4.06)	8.9	1.86	241	13600, 20300
Green [Cu(BTQT) ₂ (NO ₃) ₂]	801.5	7.83 (7.92)	38.70 (38.92)	17.33 (17.46)	4.19 (4.24)	9.3	1.93	237	12900, 19700

DT = Decomposition Temperature

bidentate ligand. Coordination proposes through azomethine nitrogen and thione sulphur to the metal ion. The remaining coordination centers are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ or NO₃⁻.

Magnetic susceptibility electronic spectra

The electronic spectra of the Co(II) complexes exhibit three bands in the region 10600-9900 cm⁻¹ 16800-16100 cm⁻¹ and 24200-23800cm⁻¹ assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) respectively suggesting ²⁹ an octahedral geometry of Co(II) complexes. The proposed geometry is further supported^{30,31} by the magnetic moment value in the range 4.86-4.99 BM.

The electronic spectra of Ni(II) complexes exhibit three bands in the region 11800-12300 cm⁻¹ strong intense band in the vicinity of 24500 cm⁻¹ assignable due to the transitions, ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³A_{2g}(P) respectively. These positions propose²⁹ an octahedral geometry for Ni(II) complexes which is further supported^{30,31} by

the magnetic moment of value of Ni(II) complexes in the range 3.08-3.14 B.M. The electronic spectra of Cu(II) complexes exhibit two spectral bands in the region 12900-13600 cm⁻¹ and 19700-20300 cm⁻¹ assigned to the transitions, ²E_g → ²T_{2g} and charge transfer band. The magnetic moment value of Cu(II) complexes lie in the range of 1.86-1.93 B.M. The above data of electronic spectra suggested an octahedral geometry for Cu(II) complexes.

Molar conductance

Molar conductance of the complexes were measured in DMF at the concentration 10⁻³ and all the complexes were found to be non-electrolytic in nature due to 10 W value of molar conductance in the range 8.9-14.3 ohm⁻¹ cm² mol⁻¹.

Antimicrobial Screening

Antibacterial activity of Schiff base ligand, BTQT and its Cobalt, Nickel and Copper complexes

Table-2 : Infra Red spectral data of the ligand and complexes

Compounds	V _{C=O}	V _{C=N}	V _{M-O}	V _{M-N}	V _{M-X}
BTQT	1570	840			260
[Co(BTQT) ₂ Cl ₂]	1550	810	450	410	
[Co(BTQT) ₂ Br ₂]	1550	820	440	405	270
[Co(BTQT) ₂ I ₂]	1545	805	455	400	280
[Co(BTQT) ₂ (NO ₃) ₂]	1540	810	460	405	
[Ni(BTQT) ₂ Cl ₂]	1550	820	440	395	295
[Ni(BTQT) ₂ Br ₂]	1545	810	435	400	305
[Ni(BTQT) ₂ I ₂]	1540	810	435	405	315
[Ni(BTQT) ₂ (NO ₃) ₂]	1545	820	440	405	
[Cu(BTQT) ₂ Cl ₂]	1550	820	460	400	285
[Cu(BTQT) ₂ Br ₂]	1540	810	455	395	290
[Ni(BTQT) ₂ (NO ₃) ₂]	1540	810	440	395	300

have been tested by disc diffusion technique³³. The Gram positive and Gram negative organism such Gram negative bacterial *E. Coli* and Gram Positive bacteria *Candida albicans* were used to find out the antimicrobial activity. All the complexes showed a remarkable antimicrobial activity against bacteria. From the results it is proposed that the metal complexes are found to have more biocidal activity than the parent ligand.

CONCLUSIONS

The IR spectral studies revealed that the ligand, BTQT acted as a neutral bidentate(NS donor) in all the complexes. The magnetic conductance and electronic spectral studies reveal the complexes were paramagnetic with octahedral geometries. The remaining valency are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ or NO₃⁻. All investigated complexes were non-electrolytic in nature as given in Fig.-1.

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