



Spectral and Antimicrobial Screening of Cu(II), Ni(II) and Co(II) Coordination Compounds with Nitrogen Oxygen and Sulphur Containing Tridentate Schiff Base

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ABSTRACT

A series of coordination compounds have been prepared with tridentate Schiff base ligands, 2 ethyl-[(hydroxy propyl)]- 3, 1 (4H) quinazoline- 4-semicarbazone [EHPQS] and 2-ethyl-[(hydroxy propyl)]- 3, 1 (4H) quinazoline- 4-thiosemicarbazone [EHPQT]. The obtained complexes were characterized by molar mass, elemental analysis, infrared spectra, electronic spectra, magnetic susceptibility molar conductance analysis and spectral studies show that the Schiff base EHPQS/EHPQT behaves as tridentate chelating agent and coordinated to metal ions via, azomethine nitrogen alcoholic oxygen atom and with either carbonyl or thione sulphur atom of ligand. The electronic spectra and molar susceptibility of the complexes show a distorted octahedral geometry for Cu(II) complexes where as octahedral geometry for Co(II) and Ni(II) metal ions. The Schiff base ligand and their metal complexes have been tested for antimicrobial activities against Gram positive bacteria; *Staphylococci aureus* and Gram negative bacteria *Escherichia coli*.

Key words : EHPQS/EHPQT/Schiff bases/ Co(II), Ni(II) and Cu(II)/ Antimicrobial studies.

INTRODUCTION

Schiff base ligands and their metal complexes exhibit numerous biocidal activities^{1,2}, such as antitumour³, antibiotic⁴ and antiviral⁵. Schiff bases have attracted the interest of many chemists due to their ability to coordinate with various metal ions and also their reactions with microbial DNA and inhibiting tumor growth⁶, which have been reported by several workers in the past. Such

ligands have unusual configuration, structural liability and are sensitive to molecular environment. As a continuation of our interest in the field of the chemistry of, the present communication deals with the synthesis, spectral and antimicrobial studies of Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from condensation of 2-ethyl -[3-(hydroxy propyl)]-3,1(4H) quinazoline -4 one with semicarbazide/thiosemicarbazide hydrochloride.

EXPERIMENTAL

All the used chemicals and reagent used were analytical grade. The solvents were used without any purification, the metal contents were determined using standard procedures¹². IR spectra of ligand and complexes over the region 4000-200 cm^{-1} were recorded on Parkin Elmer's model 577 spectrometer using KBR disc. Molar conductivity of the complexes were measured at room temperature by using systronics conductivity meter model 303 in DMF. Magnetic susceptibility was carried out by Gouy's method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. Electronic spectra over the region 10000-25000 cm^{-1} were recorded by Cary 2390 spectrometer using 10^{-3}M DMF solution of complexes.

Preparation of the ligand EHPQS/EHPQT

A suspension of 2-ethyl-[(hydroxy propyl)]-3, 1(4H) quinazoline-4-one was allowed to react with semicarbazide/thiosemicarbazide hydrochloride dissolved in 10ml ethanolic solution acetate. The mixture was heated on water bath for

4h, after cooling and slow evaporation the compounds, EHPQS/EHPQT as colourless prismatic needles was formed. The compounds were recrystallised with methanol. M.P. $201 \pm 1^\circ\text{C}$ for EHPQ and $209 \pm 1^\circ\text{C}$ for compound EHPQT.

Preparation of the Complexes

The complex of Cu(II), Ni(II) and Co(II) were synthesized by refluxing ethanolic solution of respective metal acetates (0.001M) to the Schiff base ligands (0.002M) EHPQS/EHPQT dissolved in minimum volume of ethanol. Partial removal of the solvent and cooling to room temperature gave coloured complexes which was filtered, washed thoroughly with ethanol and finally dried.

RESULTS AND DISCUSSION

Both the ligands and their complexes are air and moisture free crystalline solids. The complexes are intensively coloured. The complexes are insoluble in common inorganic solvent and only soluble in DMF. The elemental analysis data concur well with the proposed formulae for the ligands and

Table 1 : Colour, Molar mass, Analytical, Magnetic susceptibility, Electronic spectra, molar conductance and Decomposition temperature of the complexes

Compounds (Colour)	Molar Mass	% Analysis found (calculated)				μ_{eff} B. M.	λ_{max} electronic cm^{-1}	DT $^\circ\text{C}$	Ω_m ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$
		M	C	N	H				
EHPQS (Colourless)	274		60.29 (60.96)	27.04 (27.13)	6.14 (6.20)				
EHPQT (Colourless)	290		66.80 (66.97)	25.39 (25.51)	5.77 (5.83)				
$[\text{Co}(\text{EHPQS})_2]$ (Brown)	606.93	9.62 (9.70)	51.22 (51.40)	22.89 (23.06)	5.21 (5.27)	4.85	10200, 15800, 22400	217	7.6
$[\text{Ni}(\text{EHPQS})_2]$ (Red)	606.71	9.58 (9.67)	51.88 (52.08)	22.88 (23.01)	5.21 (5.27)	3.16	12600, 17300, 25400	210	7.1
$[\text{Cu}(\text{EHPQS})_2]$ (Sky Blue)	611.54	10.30 (10.39)	50.83 (51.01)	22.78 (22.89)	5.18 (5.23)	1.84	13500, 18200	218	8.3
$[\text{Co}(\text{EHPQT})_2]$ (Brownish red)	638.93	9.14 (9.22)	48.62 (48.83)	21.80 (21.91)	4.93 (5.00)	4.89	10300, 15400, 22100	222	7.9
$[\text{Ni}(\text{EHPQT})_2]$ (Brick red)	638.71	9.12 (9.19)	48.64 (48.84)	21.79 (21.91)	4.95 (5.01)	3.20	12300, 17500, 25200	202	5.9
$[\text{Cu}(\text{EHPQT})_2]$ (Blue)	643.54	9.80 (9.87)	48.36 (48.48)	21.64 (21.75)	4.93 (4.97)	1.87	13650, 17950	226	5.4

DT = Decomposition Temperature

stoichiometry of the proposed structure of complex $[M(\text{EHPQS}/\text{EHPQT})_2]$.

A broadband observed in ligands, EHPQS/ EHPQT at 3450 cm^{-1} is broadened and has shifted to a lower frequency region at 3400 cm^{-1} on the complexation with metal ion proposing coordination of alcoholic oxygen by deprotonation^{13,14}. IR spectra of the both ligands EHPQS/ EHPQT show a broad band at 3200 cm^{-1} assigned to $\nu_{\text{N-H}}$. This band remains unperturbed on complexation that indicates non-involvement of either terminal or secondary amino group in coordination.

The IR spectra of the ligands EHPQS/ EHPQT show strong band at 1570 cm^{-1} assigned $\nu_{\text{C=N}}$. This band also shifts to lower wave number by $20\text{-}25\text{ cm}^{-1}$ suggesting participation of azomethine linkage with metal ion. The IR Spectra of the ligand EHPQS shows a strong and broad band at 1740

cm^{-1} assigned $\nu_{\text{C=O}}$. This band undergoes red shift on complexation indicating the involvement carbonyl oxygen in coordination. The IR Spectrum of ligand EHPQT show a strong band at 790 cm^{-1} assigned to $\nu_{\text{C=S}}$. This band is shifted to lower frequency region after complex formation indicating linkage of thione sulphur atom to the metal ion. Metal ligand vibration are generally observed in the far IR region and usually give valuable information regarding the bonding of ligand to the metal ion. The appearance of the three bands in the far IR regions at $575\text{-}525$, $475\text{-}435$ and $405\text{-}385\text{ cm}^{-1}$ assigned to $\nu_{\text{M-O}}$, $\nu_{\text{M-S}}$ and $\nu_{\text{M-N}}$ band respectively.

The coordination with azomethine Nitrogen/N atom of NH_3 / pyridine/ α , β and γ -picolines as well coordination of alcoholic oxygen by deprotonation is supported by appearance to above mentioned three bands in the Far IR region. The above argument is further supported by the low value of the molar conductance of the complexes

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

Compounds	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=S}}$
EHPQS	3450 s,b	3260 b	1740 s,b	1570 s,b	
EHPQT	3430 s,b	3260 b		1560 s,b	790 s,b
$[\text{Co}(\text{EHPQS})_2]$	3420 m,b	3260 b	1720 m,b	1555 m,b	
$[\text{Ni}(\text{EHPQS})_2]$	3430 m,b	3260 b	1715 m,b	1550 m,b	
$[\text{Cu}(\text{EHPQS})_2]$	3425 m,b	3260 b	1720 m,b	1550 m,b	
$[\text{Co}(\text{EHPQT})_2]$	3405 m,b	3260 b		1540 m,b	770 m,b
$[\text{Ni}(\text{EHPQT})_2]$	3400 m,b	3260 b		1535 m,b	765 m,b
$[\text{Cu}(\text{EHPQT})_2]$	3400 m,b	3260 b		1535 m,b	765 m,b

S = strong; m = medium; b = broad

Table 3: Antimicrobial activity of Schiff base ligands and their metal complexes

Ligand/ Complexes	<i>S. aureus</i>	<i>E. coli</i>
EHPQS	8	6
EHPQT	9	7
$[\text{Co}(\text{EHPQS})_2]$	15	12
$[\text{Ni}(\text{EHPQS})_2]$	16	12
$[\text{Cu}(\text{EHPQS})_2]$	17	14
$[\text{Co}(\text{EHPQT})_2]$	18	15
$[\text{Ni}(\text{EHPQT})_2]$	20	17
$[\text{Cu}(\text{EHPQT})_2]$	22	19

in the range $5.4\text{-}8.3\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which proposes non-electrolytic nature of the complexes.

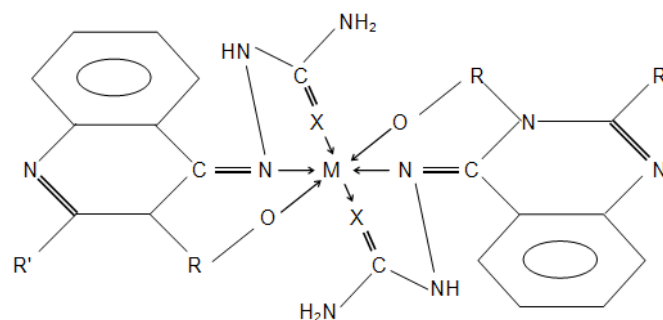
Electronic Spectra and magnetic moments of the complexes

Electronic spectra of the Co(II) complexes exhibits three bands in the region $10200\text{-}10300\text{ cm}^{-1}$, $15400\text{-}15800\text{ cm}^{-1}$ and $22100\text{-}22400\text{ cm}^{-1}$ assigned to the 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^{21,22} geometry for Co(II) complexes which is supported by the magnetic moment value in the range $4.85\text{-}4.89\text{ B.M.}$ The Ni(II) complexes exhibit three absorption bands at 12600

,17500 and 25000 cm^{-1} assignable to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively in an octahedral environment. The proposed octahedral geometry of Ni(II) complexes supported by the magnetic susceptibility value in the range 3.16-3.20 BM. The Cu(II) complexes exhibit two spectral bands in the region 13500-13650 cm^{-1} and 17950-18200 cm^{-1} assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ and C. T. bands respectively which proposed distorted octahedral²⁶ geometry. The magnetic susceptibility value for Cu(II) complexes are found in the range 1.84-1.87 B.M.^{23,24}

Antimicrobial Activity

Ligands EHPQS/ EHPQT and their metal complexes of Co(II), Ni(II) and Cu(II) were evaluated against Gram positive bacteria, staphylococcus aureus and Gram negative bacterial *Escherichia coli*. The susceptibility of certain strains of bacteria the ligand and their metal complexes were evaluated by measuring the size of bacteriostatic diameter through paper disc plate method²⁷. The metal complex shows better inhibition as compared to their ligands. It might be due to complexation of metal ions with Schiff base ligands.



X = oxygen or sulphur; R = n-propyl, R' = ethyl

Fig. 1: $[M(EHPQS)_2]$ / $[M(EHPQT)_2]$

Such metal complexes might be inhibiting the enzyme activity of the bacterial system. Antimicrobial activity data for the ligand and their metal complexes are given in Table-3

CONCLUSIONS

On the basis of analytical and spectral data the tentative structure of the complexes of the type $[M(EHPQS)_2]$ and $[M(EHPQT)_2]$ are proposed to be octahedral in nature. The synthesized Schiff bases, EHPQS/EHPQT acts as uninegative tridentate ligand. The metal ions are coordinated through alcoholic oxygen by deprotonation and azomethine.

The remaining coordination of the metal

ion is satisfied by either carbonyl oxygen of semicarbozone moiety or thione sulphur of thiosemicarbozone moiety. All these observations put out together lead us to propose the complex of Co(II) and Ni(II) to have octahedral geometry whereas geometry of Cu(II) complexes is proposed to be distorted octahedral geometry as shown in Fig.1.

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