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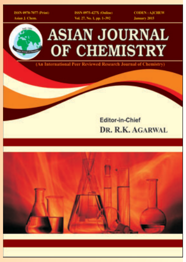

Synthesis and Antifungal Potential of Co(II), Ni(II) and Cu(II) Chelates with Nitrogen, Oxygen and Sulphur Containing Schiff Bases

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In the present article a series of complex of the type ML_2 where M = Co(II), Ni(II) and Cu(II), L = 2-butyl-[3-hydroxy propyl)-3,1-(4*H*)-quinazoline semicarbazone/thiosemicarbozone have been synthesized. Their structures were confirmed by means of molar mass, elemental analyses, infrared spectra, electronic spectra, magnetic susceptibility and conductivity measurement. All the compounds were screened against species of plant pathogenic fungi using disc diffusion technique. It was observed on comparison with reference to fungicides, the complexes were found to be more effective than ligands,

Keywords: Schiff base, Transition metal, Complexes, Antiungal studies.

INTRODUCTION

Quinazoline derivatives are used in several biocidal activities such as agriculture[1], antimicrobial[2-5], antiviral[6], antitumour[7], analgesic[8] and anticancer[9]. It is established from the survey of literature that the biocidal activity of any compound enhanced many folds when coordinated with suitable metal ions. In continuation of our recent work[10-14] in Schiff base metal complexes, in the present work we have synthesized Co(II), Ni(II) and Cu(II) complexes with quinazoline based Schiff bases 2-butyl-[3-(hydroxyl propyl)]-3,1-(4*H*)-quinazoline semicarbazone (BHQS) and 2-butyl-[3-(hydroxyl propyl)]-3,1-(4*H*)-quinazoline thiosemicarbazone (BHQT).

EXPERIMENTAL

All the chemicals used in the study were of analytical grade. The estimation of metal contents were carried out by the standard methods[15]. The molar conductance of the coordination compounds in DMF were carried out on systronics conductivity meter model 303. The IR spectra were recorded in KBr (4000-200 cm^{-1}) on Perkin-Elmer spectrophotometer. The electronic spectra were recorded on Cary-2390 spectrophotometer in 10000-25000 cm^{-1} range. The magnetic susceptibility of the complexes were measured on Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant.

Synthesis of ligands: The ligand BHQS/BHQT were synthesized by the condensation with 2-butyl-[3-(hydroxy propyl)]-3,1(4*H*)-quinazoline semicarbazide/ thiosemicarbazide hydrochloride in 1:1 molar ratio. The resulting mixture was refluxed for 3 h and then allowed to stand overnight at room temperature. The product were crystallized from the same solvent and dried in oven.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) were prepared by reacting ethanolic solution of the ligand BHQS/BHQT with ethanolic solution of the corresponding metal acetate in a molar ratio 2:1. The resulting mixture was refluxed on water bath for 3 h. The solid coloured complexes, which was separated on cooling were filtered, washed with ethanol and dried in oven. Yield in all cases are about 80 % (Table-1).

RESULTS AND DISCUSSION

The IR spectra of the ligand and complexes were recorded in KBr and the prominent absorption bands are given in Table-2. The infrared spectrum of the free ligands BHQS/BHQT exhibited a broad medium band of intensity around 3400 cm^{-1} is broadned and has shifted to a lower frequency region at 3370 cm^{-1} on the complexation with metal ions, proposes coordination of alcoholic oxygen by deprotonation[16,17]. The IR spectra of the ligand BHQS/BHQT exhibit a strong and broad

TABLE-1
ANALYTICAL AND PHYSICAL MEASUREMENT OF SCHIFF BASES AND THEIR METAL COMPLEXES

Compounds	Molar	% Analysis found (calculated)				λ_{max}	μ_{eff}	Ωm ohm^{-1}	DT
(colour)	mass	M	C	N	H	Electronic (cm^{-1})	(B.M.)	(cm^{2} mol^{-1})	(°C)
BHQS	317	(60.56)	60.42	21.83	7.18	-	-	-	-
Colourless			(60.56)	(22.08)	(7.25)				
BHQT	333	-	54.50	20.89	6.81	-	-	-	-
Colourless			(54.65)	(21.02)	(6.90)				
[Co(BHQS)$_2$]	692.93	8.41	55.28	20.06	6.57	9800, 16200	4.87	136.4	203
Brown		(8.50)	(55.41)	(21.02)	(6.63)	23300			
[Co(BHQT)$_2$]	724.93	8.04	52.83	19.77	6.28	10300, 15700	5.02	128.3	201
Brown		(8.12)	(52.97)	(19.3)	(6.34)	22600			
[Ni(BHQS)$_2$]	692.71	8.39	55.24	20.06	6.58	10600, 15800	3.17	122.8	196
Green		(8.47)	(55.43)	(20.21)	(6.64)	24600			
[Ni(BHQT)$_2$]	724.71	8.01	52.83	19.14	6.28	11900, 16400	3.26	118.3	204
Green		(8.10)	(52.98)	(19.13)	(6.34)	24560			
[Cu(BHQS)$_2$]	697.54	49.02	54.90	19.90	6.53	13900, 18400	1.94	117.3	211
Blue		(9.10)	(55.05)	(20.07)	(6.59)				
[Cu(BHQT)$_2$]	729.54	8.62	52.50	19.04	6.23	13300, 19600	1.86	119.4	213
Blue		(8.10)	(52.63)	(19.19)	(6.30)				

DT = Decomposition temperature

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF LIGAND BHQS/BHQT AND ITS METAL COMPLEXES OF Co(II), Ni(II) AND Cu(II)

Compounds	$\nu_{O\text{-}H}$	$\nu_{C=O}$	$\nu_{C=S}$	$\nu_{C=N}$	$\nu_{M\text{-}O}$	$\nu_{M\text{-}N}$	$\nu_{M\text{-}S}$
BHQS	3400	1660		1470			
BHQT	3395		780	1475			
[Co(BHQS)$_2$]	3375	1635		1450	525	400	
[Co(BHQT)$_2$]	3370		755	1455		410	455
[Ni(BHQS)$_2$]	3375	1635		1450	540	405	
[Ni(BHQT$_2$]	3370		755	1455		400	480
[Cu(BHQS)$_2$]	3375	1635		1450	505	395	
[Cu(BHQT)$_2$]	3370		755	1455		405	460

band at 1470 cm^{-1} assigned to $\nu_{C=N}$. This band shifted to lower wave numbers on complexation which suggests involvement of azomethine N in bonding with metal ions. The linkage with azomethine nitrogen is further supported by the appearance of a far IR band at 410-395 cm^{-1} assigned[18-20] to $\nu_{M\text{-}N}$. The next IR spectrum of the ligand BHQS exhibits a strong and broad band at 1660 cm^{-1} assigned to $\nu_{C=O}$. This band undergoes red shift on complexation that propose coordination of carbonyl oxygen with metal ion. The linkage with oxygen atom is supported by the appearance of a new band at 540-505 cm^{-1} in the complexes[19-21]. The IR spectrum of the ligand BHQT exhibits a strong band at 780 cm^{-1} assigned[22] to $\nu_{C=S}$. This band is shifted to lower frequency region in the complexes which proposes the linkage at thione sulphur atom to metal ion. The linkage with sulphur atom with metal ion is further supported by the appearance of a new far infrared region at 480-455 cm^{-1} in the complexes assigned[19,20,22] to $\nu_{M\text{-}S}$.

Electronic spectra and magnetic moment of the complexes: Electronic spectra of the Co(II) complexes exhibit three bands in the region, 10300-9800, 16200-15700 and 23300-22600 cm^{-1} assigned to transitions, $^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, $^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and $^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$, respectively. These bands propose an octahedral[23-25] geometry for Co(II) complexes. The proposed geometry is further supported[26,27] by the magnetic susceptibility value of Co(II) complexes in the range 4.87-5.02 BM.

The electronic spectra of Ni(II) complexes exhibit three spectral bands in the regions, 11900-10600, 16400-15800 cm^{-1} followed by a strong intense band in the vicinity of 24600 cm^{-1} assigned to the transitions, $^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, $^{3}T_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and $^{3}T_{2g}(F) \rightarrow {}^{3}A_{2g}(P)$, respectively. These spectral bands propose octahedral geometry[25,28] for Ni(II) complexes. The proposed octahedral geometry of Ni(II) complexes is further supported[26,27] by the magnetic moment value in the range of 3.17-3.26 BM. The electronic spectra of Cu(II) complexes exhibit two spectral bands in the regions, 13300-13900 and 19600-18400 cm^{-1} assigned to the transitions; $^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transfer bands suggesting[29] octahedral geometry for a Cu(II) complexes. The magnetic moment value for Cu(II) complexes lie in the range 1.86-1.94 BM.

Conductivity measurements: Conductivities of the complexes of Co(II), Ni(II) and Cu(II) were measured in the solvent DMF and all the complexes were found to be electrolytic[30] in nature of 1:2 type and conductivity values are in the range 117.3-136.4 ohm^{-1}cm^{2}mol^{-1}.

Antifungal studies: The ligand BHQS and BHQT and their metal complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antifungal activity against the test fungi, *Aspergillus flavus, Aspergillus niger* and *Rhizoctonia bataticola* by disc diffusion technique using DMF as solvent as concentration of 50 mg. The activity of complexes were found to be in the order: Cu(II) > Ni(II) > Co(II) (Table-3). It is established from the literature that the metal complexes show enhanced antifungal activity than free ligands. The chelation theory accounts for the increased activity of the metal comp-

TABLE-3
ANTIFUNGAL SCREENING DATA OF THE LIGANDS AND COMPLEXES

Serial number	Ligands and complexes	*Aspergillus flavus*	*Aspergillus niger*	*Rhizoctonia bataticola*
1	BHQS	15	22	32
2	BHQT	17	25	38
3	$[Co(BHQS)_2]$	29	36	47
4	$[Co(BHQT)_2]$	31	42	53
5	$[Ni(BHQS)_2]$	37	48	61
6	$[Ni(BHQT)_2]$	39	51	66
7	$[Cu(BHQS)_2]$	42	56	72
8	$[Cu(BHQT)_2]$	45	69	82

lexes[31-34]. The chelation reduces the polarity of the metal atom mainly due to the partial sharing of its positive charge with the donor groups and possible π-electron delocalization within the whole chelation ring. The chelation ring increases the lipophilic nature of the central atom which subsequently favours its permeation activity of the complexes. This can also be explained on the basis of their high solubility, fineness of the particles, size of the metal ion and the presence of bulker organic moieties.

Conclusion

On the basis of above studies, it is concluded that the ligands BTQS/ BTQT act in a tridentate manner and coordination is proposed through azomethine N, carbonyl oxygen/thione sulphur and oxygen atom of alcoholic group after deprotonation. The geometry of the Co(II), Ni(II) and Cu(II) complexes are proposed to be octahedral in nature as shown in Fig. 1.

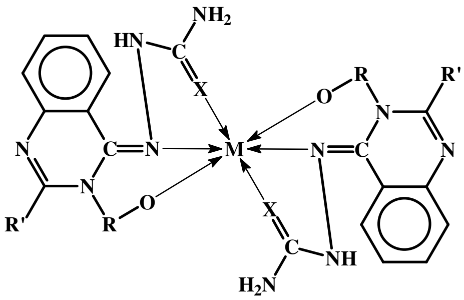

Fig. 1. [M(BHQS)$_2$] and [M(BHQT)$_2$]; M = Co(II), Ni(II) and Cu(II); X = Oxygen or Sulphur; R = *n*-propyl, R' = ethyl

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