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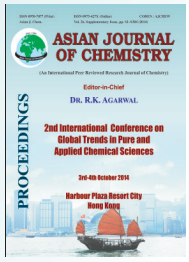

Complexation and Antimicrobial Study of Cobalt(II), Nickel(II) and Copper(II) Metal Ions with Nitrogen and Oxygen Containing Schiff Base

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Transition metal complexes of the composition $[M(BHQH)_2X_2]$; where M = Co(II), Ni(II) and Cu(II); BHQH = 2-butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline-4-hydrazone, X = NH_3, pyridine, α, β, γ-picolines have been prepared. The complexes have been characterized by molar mass, elemental analyses, molar conductance, magnetic moment, electronic, I.R. spectral studies. On the basis of above studies the ligand (BHQH) is suggested to acts in a bidentate manner and coordination takes place through azomethine nitrogen and oxygen atom of hydroxyl group after deprotonation. The remaining coordination sites are occupied by neutral molecules such as NH_3, pyradine, α, β, γ picolines. The Co(II), Ni(II) complexes have proposes octahedral geometry whereas, Cu(II) complexes were proposed to have distorted octahedral geometry. *in vitro* the synthesized compounds were screened against *E. coli* by disc diffusion method.

Keywords: Schiff base, Co(II), Ni(II) and Cu(II) complexes, Antimicrobial study.

INTRODUCTION

Hydrazones derived from the condensation reactions of hydrazides with aldehydes or ketones show excellent biological properties such as antimalarial[1], antimicrobial[2,3] and anticancer[4] activities. In recent years, there has been an enhanced interest in synthesis and characterization of such complexes due to their interesting properties and they have been increasingly used in medicine[5], antivirus[6] as well as promising properties for analytical applications[7,8]. Keeping in view of the importance and the above mentioned effects in mind and in continuation of our recent studies[9-14] on Schiff base Chelates of biological significance, the present work deals with synthesis and characterization of complexes of Co(II), Cu(II) and Ni(II) with Schiff base, 2-butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline-4-hydrazone.

EXPERIMENTAL

All the reagents and chemicals herein used were of analytical grade. The metal contents of all the complexes were estimated using standard procedures[15]. The IR spectra of the ligand and their metal complexes (Table-2) were recorded on Cary-2390 spectrophotometer. Magnetic susceptibility were measured on Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. Molar conductivity were recorded on systronics conductivity meter model 303 using DMF as a solvent.

Synthesis of the ligand: 2-Butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline (0.01 m) was treated with ethanolic solution of hydrazine hydrate (0.001 m). The resulting mixture was heated on water bath for 3 h with frequent shaking. After cooling the precipitate it was collected, washed with ether treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with water and crystallized twice from ethanol to furnish 2-butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline-4-hydrazone (BHQH) as colourless prismatic needles, m.p. -203 ± 1 °C; yield 65 %.

Preparation of the complexes: The complexes were prepared by mixing the appropriate molar quantities of the ligand and the metal salts using the following procedures. The complexes of Co(II), Ni(II) and Cu(II) were prepared by reacting an ethanolic solutions of corresponding metal acetate with ethanolic solution of ligand 2-butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline-4-hydrazone in molar ratio 1:2. The resulting reaction mixture was refluxed on water bath for 2-3 h. The solution was then cooled and treated with liquid ammonia/pyridine/ α, β or γ-picoline with each of metal separately and the procedure carried out in each case of similar nature with slight variation of timing of refluxing. The reaction mixture was again refluxed for 2 h. Partial removal of the solvent and cooling to room temperature gave solid coloured coordination compounds which were filtered, washed thoroughly with ethanol and finally dried in oven. The physico-chemical data of the synthesied complexes and ligand is given in Table-1.

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

Compounds (colour)	Molar mass	% Analysis found (calculated)				μ_{eff} (B.M.)	λ_{max} (cm^{-1})	Ω_m (ohm^{-1} cm^2 mol^{-1})	DT (°C)
		M	C	N	H				
BHQH	274	–	65.69	20.43	7.94	–	–	–	–
Colourless			(65389)	(20.52)	(8.02)				
$[Co(BHQH)_2(NH_3)_2]$	640.93	9.06	56.04	17.36	6.80	4.99	12890, 21530	7.6	232
Yellow		(9.15)	(56.16)	(17.47)	(6.86)				
$[Co(BHQH)_2(C_6H_5N)_2]$	788.93	7.37	45.48	14.05	5.51	5.04	12940, 21700	6.9	216
Yellow		(7.46)	(45.63)	(14.19)	(5.57)				
$[Co(BHQH)_2(\alpha\text{-pic})_2]$	792.93	7.36	45.22	14.01	5.49	5.12	12660, 21300	7.3	223
Yellowish red		(7.43)	(45.40)	(14.12)	(5.54)				
$[Co(BHQH)_2(\beta\text{-pic})_2]$	792.93	7.32	45.21	14.02	5.48	5.06	13100, 21400	6.6	206
Yellowish red		(7.43)	(45.40)	(14.12)	(5.54)				
$[Co(BHQH)_2(\gamma\text{-pic})_2]$	792.93	7.31	45.18	13.99	5.47	5.08	13200, 21800	6.2	219
Yellowish red		(7.43)	(45.40)	(14.12)	(5.54)				
$[Ni(BHQH)_2(NH_3)_2]$	640.71	9.07	56.03	17.33	6.81	3.09	10600, 16400,	7.8	193
Orange		(9.16)	(56.18)	(17.48)	(6.86)		24800		
$[Ni(BHQH)_2(C_6H_5N)_2]$	788.71	7.35	45.50	14.0	5.50	3.04	10900, 16300,	6.6	186
Orange		(7.44)	(45.64)	(14.20)	(5.57)		24200		
$[Ni(BHQH)_2(\alpha\text{-pic})_2]$	797.01	7.32	45.28	13.99	5.50	3.11	10700, 15940,	8.3	191
Reddish orange		(7.40)	(45.41)	(14.12)	(5.55)		24240		
$[Ni(BHQH)_2(\beta\text{-pic})_2]$	792.71	7.31	45.26	13.98	5.49	3.15	10400, 16200,	6.9	182
Reddish orange		(7.40	(45.41)	(14.12)	(5.55)		24100		
$[Ni(BHQH)_2(\gamma\text{-pic})_2]$	792.71	7.30	45.28	13.99	5.48	3.12	10550, 15800,	8.1	186
Reddish orange		(7.40)	(45.41)	(14.12)	(5.55)		24900		
$[Cu(BHQH)_2(NH_3)_2]$	645.54	9.78	55.59	17.20	6.75	1.99	12600, 16100	4.3	236
Brown		(9.84)	(55.76)	(17.34)	(6.81)				
$[Cu(BHQH)_2(C_6H_5N)_2]$	793.54	7.03	45.22	14.01	5.48	1.94	12200, 15900	4.1	222
Brown		(7.15)	(45.36)	(14.11)	(5.54)				
$[Cu(BHQH)_2(\alpha\text{-pic})_2]$	797.54	9.58	45.01	13.90	5.11	1.89	12900, 16400	3.9	228
Deep brown		(9.66)	(45.13)	(14.04)	(5.16)				
$[Cu(BHQH)_2(\beta\text{-pic})_2]$	797.54	9.59	44.98	13.77	5.11	1.88	11300, 16200	3.2	238
Deep brown		(9.66)	(45.13)	(14.04)	(5.16)				
$[Cu(BHQH)_2(\gamma\text{-pic})_2]$	797.54	9.58	44.97	13.28	5.09	1.93	12800, 16600	4.9	212
Deep brown		(9.66)	(45.13)	(14.04)	(5.16)				

DT = Decomposition temperature

RESULTS AND DISCUSSION

The important IR spectral data for ligand and its corresponding Co(II), Ni(II) and Cu(II) complexes are given in Table-2.

The IR spectra of the complexes show strong and broad band at 3460 cm^{-1} assigned[16] to ν(O-H) which has a shift at 20-30 cm^{-1} to lower wave number. This indicates coordination of oxygen atom of hydroxyl group after deprotonation. The coordination with oxygen atom is further supported by the appearance of a far IR band at 520-505 cm^{-1} in the complexes assignable[17] to ν(M-O). The IR spectra of the ligand exhibit strong and broad band at 1480 cm^{-1} assigned[18] to ν(C=N). The band is shifted to lower wave number after complex formation, which proposes coordination of metal ion with azomethine

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

Compounds	ν(O-N)	ν(C=N)	ν(M-O)	ν(M-N)
BHQH	3460 s,b	1480 s,b		
$[Co(BHQH)_2(NH_3)_2]$	3430 m,b	1460 m,b	510 m	410 m
$[Co(BHQH)_2(C_6H_5N)_2]$	3430 m,b	1455 m,b	510 m	410 m
$[Co(BHQH)_2(\alpha\text{-pic})_2]$	3430 m,b	1455 m,b	515 m	405 m
$[Co(BHQH)_2(\beta\text{-pic})_2]$	3435 m,b	1455 m,b	510 m	405 m
$[Co(BHQH)_2(\gamma\text{-pic})_2]$	3430 m,b	1455 m,b	510 m	400 m
$[Ni(BHQH)_2(NH_3)_2]$	3430 m,b	1460 m,b	505 m	395 m
$[Ni(BHQH)_2(C_6H_5N)_2]$	3430 m,b	1455 m,b	505 m	395 m
$[Ni(BHQH)_2(\alpha\text{-pic})_2]$	3435 m,b	1455 m,b	505 m	395 m
$[Ni(BHQH)_2(\beta\text{-pic})_2]$	3430 m,b	1460 m,b	505 m	400 m
$[Ni(BHQH)_2(\gamma\text{-pic})_2]$	3435 m,b	1455 m,b	515 m	400 m
$[Cu(BHQH)_2(NH_3)_2]$	3430 m,b	1455 m,b	510 m	415 m
$[Cu(BHQH)_2(C_6H_5N)_2]$	3435 m,b	1460 m,b	505 m	415 m
$[Cu(BHQH)_2(\alpha\text{-pic})_2]$	3430 m,b	1460 m,b	515 m	420 m
$[Cu(BHQH)_2(\beta\text{-pic})_2]$	3430 m,b	1460 m,b	520 m	425 m
$[Cu(BHQH)_2(\gamma\text{-pic})_2]$	3435 m,b	1460 m,b	520 m	425 m

nitrogen. The appearance of a band in far IR region at 425-395 cm^{-1} in the complexes assignable[17] to ν(M-N). The remaining coordination centres are satisfied by neutral molecules such as NH_3, pyridine, α, β or γ-picoline. The spectra of pyridine and picolines adducts show additional band 650 cm^{-1} assigned to pyridine and picoline rings.

Electronic spectra and magnetic susceptibility of the complexes: The Co(II) complexes exhibit two spectral bands in the region at 13200-12600 and 21800-21300 cm^{-1} assigned to the transitions, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. Proposing octahedral[18,19] geometry. The proposed geometry of Co(II) complexes are further supported[20] by the high magnetic susceptibility value in the range 4.9-5.12 BM. The Ni(II) complexes display three spectral bands in the regions 10400-11000, 16400-15800 and 24900-24100 cm^{-1} assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively, suggested octahedral geometry[21] for Ni(II) complexes. The proposed geometry of Ni(II) complexes is further supported by magnetic susceptibility value in the range 3.04-3.15 BM[22]. The Cu(II) complexes exhibit two spectral bands in the regions, 11700-12200 cm^{-1} and 16600-15900 cm^{-1} assigned to the transitions, $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band suggested distorted octahedral geometry for the Cu(II) complexes. The magnetic susceptibility value of Co(II) complexes lies in the range 1.86-1.94 BM.

Molar conductance: Molar conductance value of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 3.2-8.3 ohm^{-1} cm^2 mol^{-1} in the DMF which proposes their non-electrolytic[23] nature. The molar conductance values also supported the structure assigned on the basis of physico-chemical and spectroscopic measurements.

Antimicrobial activity: Ligand BHQH and their Co(II), Ni(II) and Cu(II) complexes were assayed *in vitro* for their ability to inhibit the growth of representative Gram-negative bacteria *Escherichia coli*. The susceptibilities of certain bacteria to the hydrazone ligand and their complexes were evaluated by measuring the size of bacteriostatic diameter through paper disc plate method[24]. The results are given in Table-3. The results exhibits that the ligand BHQH is less active against the Co(II), Ni(II) and Cu(II) complexes due to chelation theory[25], The data indicates antibacterial activity of the complexes were found to greater than ligand.

Conclusion

The synthesized Schiff base 2-butyl-[3-(hydroxy propyl)]-3,1-(4*H*)-quinazoline-4-hydrazone acts as uninegative bidentate ligand. The complexes of Co(II), Ni(II) and Cu(II) have octahedral geometry whereas geometry of Cu(II) complexes is proposed as distorted octahedral geometry the ten tatine structure of the (Fig. 1) is proposed. The antibacterial activity of the complexes were found to be more than ligand.

TABLE-3
ANTIBACTERIAL ACTIVITIES OF LIGAND BHQH AND ITS Co(II), Ni(II) AND Cu(II) COMPLEXES

S. No.	Complexes	Diameter of zone; *E. coli*
1	BHQH	07
2	$[Co(BHQH)_2(NH_3)_2]$	12
3	$[Co(BHQH)_2(C_6H_5N)_2]$	13
4	$[Ni(BHQH)_2(NH_3)_2]$	14
5	$[Ni(BHQH)_2(C_6H_5N)_2]$	16
6	$[Cu(BHQH)_2(NH_3)_2]$	17
7	$[Cu(BHQH)_2(C_6H_5N)_2]$	19

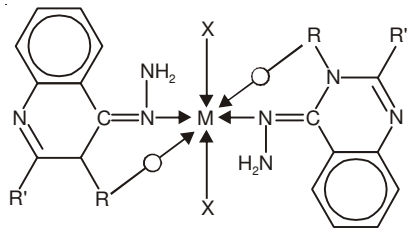

Fig. 1. Proposed structure of $[M(BHQH)_2X_2]T)_2]$; M = Co(II), Ni(II) and Cu(II); X = NH_3, α, β or γ-picoline; R = *n*-propyl, R' = butyl

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