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Antimicrobial Activity of Co(II), Ni(II) and Cu(II) Coordination Compounds with Nitrogen, Oxygen Containing Schiff Base

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ABSTRACT

A series of complexes of the type [M(EHPQH)$_2$X$_2$] where M = Co(II), Ni(II) and Cu(II), EHPQH=2-ethyl, [3(hydroxypropyl)]-3, 1 4H quinazoline -4-hydrazone, X= Cl$^-$, Br$^-$, I$^-$ and No-$_3^-$. The geometry of the complexes have been elucidated in the light of molar mass, elemental analysis, IR, electronic Spectra, molar conductance and magnetic susceptibility. The measured molar conductance value indicates that the complexes are non-electrolytic in nature. The above observation indicates that Schiff bases EHPQH behave as bidentate ligand and coordination proposes through azomethine N and oxygen atom of alcoholic group of ligand. The remaining coordination sites are satisfied by negative ion such as Ci$^-$, Br$^-$, I$^-$ and NB$^-$. The geometry of the Co(II) and Ni(II) were proposed to be octahedral in geometry whereas Cu(II) complexes were proposed to be distorted octahedral. The Schiff bases and its complexes have been evaluated for their antibacterial activity. The complexes show enhanced antibacterial activity than ligand.

Key words: Schiff base/ EHPQH/ Co(II), Ni(II), Cu(II)/ Complexes

INTRODUCTION

Metal complexes of Schiff bases have played a significant role in the area of coordination compounds. The ligational behaviour of Schiff base towards the central metal ions provide versatility and extra stability of compound making a greater choice of flexibility.

The chelating ability of analytical and biocidal application of Schiff bases have attracted remarkable attention[1-6]. In continuation of these series of investigation[7-16], attempts have been made to synthesize the new Schiff base conmmplexes with nitrogen, and oxygen containing Schiff bases. In fact the biocidal activities of Schiff bases have been reported to be enhanced significantly after formation of complex compounds with metal ions. Therefore, herein we report the synthesis, characterization and antimicrobial evaluation of properties of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand, 2 ethyl [(hydroxyl propyl)]-3, 1(4H) quinazoline-4-hydrazone.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade except 2-ethyl-[(hydroxyl propyl)]-3,1-(4H) quinazoline, which was prepared by modifying the literature procedure[17].

Synthesis of Ligand EHPQH

The synthesis of 2-ethyl-[3-(hydroxyl propyl)]-3, 1(4H) quinazoline- 4-one-4 hydrazone involves three steps. The first step is the synthesis of 2-methyl-3, 1(4H) benzoxazin-4-one-by reacting anthranilic acid (1.37g) with acetyl chloride. In the second step of the reaction, 2-ethyl-3, 1-(4H) benzoxazine-4-0ne is treated with monopropyl amine to furnish 2-ethyl-[3(hydroxy propyl)]-3, 1-(4H) quinazoline -4-one. In the final step the ligand, EHPQH was synthesized by applying following procedure

Ethanolic solution of 2-ethyl-[3(hydroxyl propyl)]-3, 1-(4H) quinazoline -4-one was allowed to react with ethanolic solution of hydrazine hydrate in the molar ratio 1:1. The mixtures were heated on water bath for 3-4h with frequent shaking. After cooling, the precipitate was collected, washed with ether, treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with waster and recrytallised twice from ethanol to furnish 2-ethyl-[3-hydroxyl propyl)], 3, 1-(4H) quinazoline-4-hydrazone as colourless prismatic needles mp.-203± ^{0}C, Yield-70%.

Preparation of the complexes

All the metal complexes of schiff bases were prepared by the following method.

The complexes of Co(II), Ni(II) and Cu(II) were synthesized by adding ethanolic solution of respective metal acetates (0.001m) to Schiff bases (0.002m) dissolved in minimum volume of ethanol. The reation mixture was refluxed on a water bath for 3h. The solution was then cooled and treated with liquor ammonia/ pyridine/ α, β, or γ- picoline with each of metal separately and the procedure was carried out in each case of of similar nature with slight variation of timing of refluxing. The reaction mixture was again refluxed for two hours. Partial removal of the solvent and cooling to room temperature gave solid coloured complexes which were filtered washed thoroughly with ethanol and finally dried.

The metal complex were determined using standard procedure[18]. IR Spectra of ligand and complexes were recorded in the region 4000-200cm^{-1} on Perkin Elmer model-577 spectrophotometer using KBr disc. Molar conductivity of the complexes was measured at room temperature by using systronics conductivity meter model 303 in DMF. Electronic spectra were recorded in the region 10,000-25000 cm^{-1} by Cary-2390 spectrophotometer using 10^{-3} M DMF solution of the complexes. Magnetic susceptibility measurements were done by Gouys's method at room temperature using $Hg[Co(NCS)_4]$ as standard.

RESULTS AND DISCUSSION

The IR spectrum of the ligand EHPQH exhibits strong and broad band at 3200cm^{-1} assigned[19,20] to $\nu_{(N-H)}$ vibrations. The band remains unaffected on complexation, indicating non-participation of primary or secondary amino group in coordination. The ligand exhibits a sharp and broad band at 3430 cm^{-1} assigned[20,21] to $\nu_{(O-H)}$. This band has shifted to lower wave number after formation by about 3035 cm^{-1}, that indicates linkage of metal ions with oxygen of hydroxyl group after deprotonation. The linkage with oxygen is further supported by the appearance of a band in the far IR region at 535-510 cm^{-1}, assigned to $\nu_{(M-O)}$ in the complexes. The IR spectrum of the ligand show strong and broad band at 1530 cm^{-1} assigned to $\nu_{(C=N)}$. This band also shifts to lower waves number by 2030 cm^{-1} suggesting participation of azomethine linkage with metal ion. The linkage with azomethine is further supported by the appearance of a band in the far IR region at 440-425 cm^{-1} assigned to $\nu_{(M-N}$[22,25] complexes.

Spectroscopic studies of metal complexes proposes that ligand, EHPQH behaves as bidentate, coordinating through the nitrogen of azomethine group, oxygen of hydroxyl group after deprotonation. The remaining coordination number of metals are satisfied N atom of neural molecules, NH_3, puridine, α, β, or γ -picolines.

Electronic spectra and magnetic susceptibility of the complexes

The Co(II) complexes exhibits bands at 9500, 14800 and 22400 cm^{-1} may be assigned to the transitions, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$

Table 1: Analytical and physical measurement of the complexes with the ligand EHPQH

Compounds (Colour)	Molar mass	% Analysis found (calculated)				Ω_m ohm^{-1} cm^2 mol^{-1}	DT ^{o}C	μ_{eff} B.M.	λ_{max} electronic cm^{-1}
		M	C	N	H				
EHPQH Colourless	246		63.28 (63.41)	22.65 (22.76)	6.85 (6.91)				
[Co(EHPQH)$_2$(NH$_3$)$_2$] Brown	584.93	9.94 (10.07)	53.14 (53.33)	19.07 (19.14)	5.75 (5.81)	5.31	209	4.89	9700, 14800, 22600
[Co(EHPQH)$_2$(C$_6$H$_5$N)$_2$] Brown	708.93	8.24 (8.31)	43.83 (44.00)	15.67 (15.79)	4.72 (4.79)	5.36	194	4.83	9670, 14860, 22640
[Co(EHPQH)$_2$(α-pic)$_2$] Yellowish brown	738.93	7.91 (7.97)	42.10 (42.22)	15.06 (15.15)	4.52 (4.60)	5.41	197	4.78	9620, 14880, 22610
[Co(EHPQH)$_2$(β-pic)$_2$] Yellowish brown	738.93	7.92 (7.97)	42.07 (42.22)	15.04 (15.15)	4.54 (4.60)	5.54	191	5.05	9640, 14510, 22660
[Co(EHPQH)$_2$(γ-pic)$_2$] Yellowish brown	738.93	7.90 (7.97)	42.07 (42.22)	15.01 (15.15)	5.53 (4.60)	5.46	201	5.10	9720, 14830, 22690
[Nii(EHPQH)$_2$(NH$_3$)$_2$] Red	584.71	9.96 (10.04)	53.16 (53.35)	19.06 (19.15)	5.76 (5.81)	6.81	212	3.16	11600, 16900
[Ni(EHPQH)$_2$(C$_6$H$_5$N)$_2$] Dark brown	708.71	8.22 (8.28)	43.87 (44.02)	15.69 (15.80)	4.70 (4.79)	6.85	218	3.11	11530, 17100, 25380
[Ni(EHPQH)$_2$(α-pic)$_2$] Orange	738.71	7.88 (7.94)	42.09 (42.23)	15.07 (15.16)	4.53 (4.60)	6.73	222	3.20	11400, 17060, 25300
[Ni(EHPQH)$_2$(β-pic)$_2$] Orange	738.71	7.89 (7.94)	42.11 (42.23)	15.08 (15.16)	4.51 (4.60)	6.67	208	3.24	11460, 17080, 25410
[Ni(EHPQH)$_2$(γ-pic)$_2$] Orange	738.71	7.87 (7.94)	42.12 (42.23)	15.03 (15.16)	4.54 (4.60)	6.70	206	3.19	116900, 17200, 25430
[Cu(EHPQH)$_2$(NH$_3$)$_2$] Blue	589.54	10.68 (10.77)	52.80 (52.92)	18.88 (18.99)	5.69 (5.76)	4.93	199	1.90	18380, 24430
[Cu(EHPQH)$_2$(C$_6$H$_5$N)$_2$] Blue	713.54	8.81 (8.90)	43.59 (43.72)	15.58 (15.69)	4.69 (4.76)	4.80	190	1.94	18340, 24370
[Cu(EHPQH)$_2$(α-pic)$_2$] Greenish blue	743.54	8.47 (8.54)	41.84 (41.96)	14.97 (15.06)	4.51 (4.57)	497	213	1.86	18300, 24400
[Cu(EHPQH)$_2$(β-pic)$_2$] Greenish blue	743.54	8.46 (8.54)	41.80 (41.96)	14.98 (15.06)	4.50 (4.57)	5.12	209	1.89	18310, 24600
[Cu(EHPQH)$_2$(γ-pic)$_2$] Greenish blue	743.54	8.48 (8.54)	41.82 (41.96)	14.95 (15.06)	4.49 (4.57)	5.29	224	1.92	18370, 24900

DT = Decomposition Temperature

Table 2: IR spectral band (in cm^2) of the ligand EHPQH and its complexes

Compounds	ν_{O-H}	ν_{N-H}	$\nu_{C=N-H}$	ν_{M-O}	ν_{M-N}
EHPQH	3430 s,b	3200 s,b	1530 s,b		
$[Co(EHPQH)_2(NH_3)_2]$	3405 m,b	3200 m,b	1505 m,b	510 m	435 m
$[Co(EHPQH)_2(C_6H_5N)_2]$	3400 m,b	3200 m,b	1500 m,b	510 m	430 m
$[Co(EHPQH)_2(\alpha\text{-pic})_2]$	3400 m,b	3200 m,b	1500 m,b	515 m	440 m
$[Co(EHPQH)_2(\beta\text{-pic})_2]$	3400 m,b	3200 m,b	1510 m,b	515 m	425 m
$[Co(EHPQH)_2(\gamma\text{-pic})_2]$	3400 m,b	3200 m,b	1505 m,b	510 m	430 m
$[Nii(EHPQH)_2(NH_3)_2]$	3400 m,b	3200 m,b	1505 m,b	510 m	435 m
$[Ni(EHPQH)_2(C_6H_5N)_2]$	3400 m,b	3200 m,b	1500 m,b	525 m	440 m
$[Ni(EHPQH)_2(\alpha\text{-pic})_2]$	3400 m,b	3200 m,b	1500 m,b	520 m	430 m
$[Ni(EHPQH)_2(\beta\text{-pic})_2]$	3400 m,b	3200 m,b	1510 m,b	530 m	435 m
$[Ni(EHPQH)_2(\gamma\text{-pic})_2]$	3400 m,b	3200 m,b	1510 m,b	535 m	430 m
$[Cu(EHPQH)_2(NH_3)_2]$	3400 m,b	3200 m,b	1510 m,b	515 m	440 m
$[Cu(EHPQH)_2(C_6H_5N)_2]$	3400 m,b	3200 m,b	1510 m,b	520 m	435 m
$[Cu(EHPQH)_2(\alpha\text{-pic})_2]$	3400 m,b	3200 m,b	1510 m,b	520 m	425 m
$[Cu(EHPQH)_2(\beta\text{-pic})_2]$	3400 m,b	3200 m,b	1510 m,b	525 m	435 m
$[Cu(EHPQH)_2(\gamma\text{-pic})_2]$	3400 m,b	3200 m,b	1505 m,b	515 m	440 m

m = medium, s = strong, b = broad

Table 3: Antimicrobial activity of Schiff base ligands EHPQH and their Co(II), Ni(II) and Cu(II) complexes

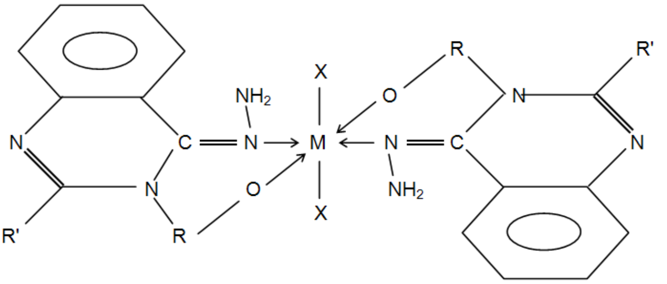
Ligand/ Complexes	Diameter of the zone	
	Bacillus **subtilis**	***Staphylococcus*** **aureus**
EHPQH	9	7
$[Co(EHPQH)_2(NH_3)_2]$	11	10
$[Co(EHPQH)_2(C_6H_5N)_2]$	13	12
$[Co(EHPQH)_2(\alpha\text{-pic})_2]$	12	14
$[Nii(EHPQH)_2(NH_3)_2]$	18	16
$[Ni(EHPQH)_2(C_6H_5N)_2]$	15	13
$[Ni(EHPQH)_2(\alpha\text{-pic})_2]$	16	17
$[Cu(EHPQH)_2(NH_3)_2]$	21	18
$[Cu(EHPQH)_2(C_6H_5N)_2]$	20	17
$[Cu(EHPQH)_2(\alpha\text{-pic})_2]$	23	19

and $^4T_{1g}(E) \rightarrow {}^4T_{1g}(P)$; which indicates an octahedrol arrangement around Co(II) metal ion. The Proposed geometry is further confirmed[27,28] by high melting value in the range 4.78-5.10BM, For all the Co(II) complexes. The Ni(II) complexes exhibits bands at 11400, 16900 and 25300cm^{-1} assigned to the transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ level respectively which indicate an octahedral[26,29] geometry around Ni(II) metal ion. The proposed geometry of all Ni(II) complexes is further supported[27,28] by μ_{eff} value in the range 3.11-3.24 B.M. The Cu(II) complexes exhibits bands at 18300-18900 and 24300-24900 cm^{-1} assigned to the transitions, $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band. The electronic spectra of all Cu(II) complexes suggest an distorted octahedral geometry for all Cu(II) complexes. The Cu(II) complexes exhibits melt value in the range of 1.86-1.94 B.M.

The observed molar conductance (λm = 4.80-6.85 $\Omega^{-1}cm^2mol^{-1}$) of all the complexes in 10^{-3} molar DMF solution is given in Table 1 which suggest the non-electrolytic nature of complexes.

Antimicrobial Activity

The antimicrobial activity of ligands and their Co(II), Ni(II) and Cu(II) complexes were assayed against bacteria *Bacillus subtilis* and *Staphylococcus aureus* using disc diffusion technique[32]. It was observed on comparison with reference to antibiotic, complexes were found to be more effective than ligand. The higher activity of metal complexes may be attributed to the metal ions which has effect on the normal cell membrane. The polar and non-polar properties of the metal complexes make them suitable for permeation to the tissues and cell. Variation in hydrophiliaty decreases the solubility and permeability, making more bioavailability of the compound. It was observed (Table 3) that in comparison to Co(II) and Ni(II) complexes the Cu(II) is more bioactive. This behaviour of Cu(II) complexes may be due to the effect of copper metal ion in the normal cell process.



M = Co(II), Ni(II) and Cu(II); X = NH_3, C_6H_5, α-picoline, β-picoline and γ-picoline; R = n-propyl, R' = Ethyl

Fig.1: [$M(EHPQH)_2 X_2$]

CONCLUSION

The analytical and physiochemical observations of the ligand EHPQH and its complexes propose that synthesized Schiff base acts as uninegative bidentate ligand. The metal ions are coordinated through alcoholic oxygen after deprotonation and with azomethine nitrogen. The remaining coordination centres of metal ions are proposed to be satisfied by nitrogen atom of neutral molecules such as ammonia/pyridine/ α-picoline/ β-picoline and γ-picoline. The geometry of Co(II) and Ni(II) complexes are proposed to be octahedral whereas the geometry for Cu(II) complexes is distorted octahedral in nature as shown in Fig-1.

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