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Synthesis, Characterization and Antifungal Studies of Some Mixed Ligand Schiff Base Complexes of 2-Phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazolin-4-one Hydrazone of Co(II), Ni(II) and Cu(II)

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The preparation and structural studies of some mixed ligand complexes of Co(II), Ni(II) and Cu(II) with 2-phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazolin-4-one hydrazone (PHQH) have been carried out by elemental analysis, IR, UV spectra, magnetic susceptibility conductivity measurements and thermal study. The complexes has been found to act as bidentate ligand and the coordination occurs both from azomethine nitrogen and oxygen atoms of hydroxyl group. The remaining coordination sites are occupied by nitrogen atoms of ammonia, pyridine, α-picoline, β-picoline and γ-picoline. The geometry of the complexes are proposed to be octahedral. The ligand PHQH as well as metal complexes have been tested for antifungal study against two species *Penicillium expansum* and *Aspergillus flavus*.

Key Words: Co^{2+}, Ni^{2+} and Cu^{2+} Complexes, 2-Phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazoline-4-one hydrazone, Antifungal activity.

INTRODUCTION

There is considerable interest in coordination chemistry of mixed ligand complexes described earlier[1-5]. In continuation of our studies[6-11] on the metal complexes of Schiff base metal complexes, the synthesis and characterization of mixed ligand complexes of Co(II), Ni(II) and Cu(II) with 2-phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazoline-4-one hydrazone (PHQH) are reported.

EXPERIMENTAL

All the chemicals were BDH reagents, IR spectra were recorded on Perkin Elmer 577 spectrophotometer. The electronic spectra recorded on a Shimadzu 160 A spectrophotometer. Magnetic susceptibility measured by a Guoy balance using $Hg[Co(CNS)_4]$ as the calibrant. Conductivity measurements made on systronics conductivity meter model 303 using DMF as a solvent. The metal contents were determined using standard

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procedures[12]. The antifungal experiment of the ligand as well as metal complexes were done by filter paper disc method[13].

Preparation of the ligand: 2-Phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazoline-4-one was prepared by modifying the earlier reported method[14]. Ethanolic solution of 2-phenyl-[3-(hydroxy propyl)]-3,1(4H) quinazolin-4-one was allowed to react with ethanolic solution of hydrazine hydrate in the molar ratio 1:1. The resulting reaction mixtures were 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 recrystallized twice with ethanol to furnish 2-phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazolin-4-one hydrazone (PHQH) as colourless prismatic needles, m.p. 183 ± 1 ºC, yield *ca.* 70 %.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) with ligand PHQH have been formed using corresponding metal acetates in presence of base like, ammonia, pyridine, α, β or γ-picolines with each of metals separately and the procedure carried out in each case was of similar nature with slight variation of refluxing time. Yield *ca.* 60-65 %.

RESULTS AND DISCUSSION

Analytical data, colour, electronic spectra, conductivity measurements, magnetic susceptibility and decomposition temperature are recorded in Table-1.

The key IR spectral data of the Schiff base, 2-phenyl-[3-(hydroxy propyl)]-3,1-(4H)-quinazolin-4-one hydrazone (PHQH) and its metal complex are given in Table-2. The vibrational spectra of the ligand PHQH exhibit a broad band at 3160 cm^{-1} which may be assignable[15] to ν(N–H) vibrations. This band after complexation remains unaffected, proposes non involvement of primary or secondary amino group in coordination. The data indicate that the spectra of the complex indicate lowering of ν(O–H)[16] from 3400 to 3365 cm^{-1}. The linkage through oxygen atom of hydroxyl group is further confirmed by the appearance of a band in far IR region at 540-500 cm^{-1} which may be assigned[17] to ν(M–O). The other infrared band of the ligand shows a sharp and broad band at 1600 cm^{-1} may be assignable[18] to ν(C=N). This band suffers downward shift after complexation proposes linkage of azomethine-N to metal ion. The linkage through N is further confirmed by the appearance of a band[19] at 450-420 cm^{-1} in the complexes may be assignable to ν(M–N). The remaining coordination sites are occupied by N-atoms of NH_3, pyridine, α, β and γ-picolins. The spectra of pyridine as well as picoline adducts shows an additional bands near 650 cm^{-1}, which can be assigned to pyridine and picoline molecule which is well conformity with the literature[20].

TABLE-1
ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA FOR METAL COMPLEXES OF THE TYPE [M(HPQH)$_2$)X$_2$]

Compd./colour	Elemental Analysis: Found (Calcd.) %				Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)	λ_{max} electronic (cm^{-1})	Decom-position temp. (ºC)
	M	C	H	N				
PHQH Colourless		69.47 (69.38)	6.04 (6.12)	19.21 (19.04)				
[Co(PHQH)$_2$(NH$_3$)$_2$] Brown	8.61 (8.67)	60.10 (60.09)	5.95 (5.89)	20.69 (20.62)	16.4	4.99	101000, 16400, 24100	295
[Co(PHQH)$_2$(C$_5$H$_5$N)$_2$] Brown	7.27 (7.33)	65.87 (65.75)	5.52 (5.47)	17.51 (17.43)	15.3	5.00	10200, 16600 23800	290
[Co(PHQH)$_2$(α-pic)$_2$] Reddish brown	7.16 (7.09)	66.57 (66.43)	5.83 (5.77)	16.72 (16.84)	15.8	5.3	9900, 17000 23700	289
[Co(PHQH)$_2$(β-pic)$_2$] Deep brown	7.17 (7.09)	66.60 (66.43)	8.69 (8.61)	16.92 (16.84)	12.6	4.89	10000, 17100, 23900	280
[Co(PHQH)$_2$(γ-pic)$_2$] Chocolate brown	6.94 (7.09)	66.58 (66.43)	5.84 (5.77)	14.76 (16.84)	13.1	4.92	10100, 16800, 24200	283
[Ni(PHQH)(NH$_3$)$_2$] Green	8.73 (8.65)	60.23 (60.11)	5.81 (5.89)	20.53 (20.62)	14.3	3.16	11700, 18400, 23700	325
[Ni(PHQH)$_2$(C$_5$H$_5$N)$_2$] Yellow	7.39 (7.31)	65.88 (65.77)	5.53 (5.48)	7.38 (17.44)	15.7	3.21	12100, 18700, 24000	320
[Ni(PHQH)$_2$(α-pic)$_2$] Deep green	7.13 (7.06)	66.30 (66.44)	5.83 (5.77)	16.94 (16.85)	16.4	3.17	11400, 18400, 23800	330
[Ni(PHQH)$_2$(β-pic)$_2$] Yellowish brown	7.11 (7.06)	66.27 (66.44)	5.69 (5.77)	16.90 (16.85)	12.4	3.20	11600, 18500, 12500	280
[Ni(PHQH)$_2$(γ-pic)$_2$] Greenish yellow	6.96 (7.06)	66.32 (66.44)	5.71 (5.77)	16.79 (16.85)	12.1	3.14	10000, 18300, 23500	288
[Cu(PHQH)$_2$(NH$_3$)$_2$] Greenish blue	9.37 (9.29)	59.77 (59.68)	5.79 (5.85)	20.55 (20.48)	18.3	1.84	13900, 19200	285
[Cu(PHQH)$_2$(C$_5$H$_5$N)$_2$] Light blue	7.78 (7.86)	65.46 (65.38)	5.38 (5.44)	17.42 (17.33)	12.3	1.81	13700, 18900	325
[Cu(PHQH)$_2$(α-pic)$_2$] Green	7.52 (7.60)	66.19 (66.06)	5.70 (5.74)	16.83 (16.75)	12.7	1.87	14000, 19100	335
[Cu(PHQH)$_2$(β-pic)$_2$] Light blue	7.68 (7.60)	66.17 (66.06)	5.79 (5.74)	16.66 (16.75)	18.9	1.84	13800, 19400	300
[Cu(PHQH)$_2$(γ-pic)$_2$] Deep red	7.54 (7.60)	65.93 (66.06)	5.81 (5.72)	16.69 (16.75)	19.3	1.86	13600, 19300	310

Electronic spectra and magnetic susceptibility data: The electronic spectra of Co(II) complexes recorded three band in the regions, 10200-9800, 17200-16800 and 24200-23700 cm^{-1} which proposes octahedral[21] geometry for Co(II) complexes which is further supported[22] by the magnetic susceptibility value in the range 4.89-5.3 BM. Ni(II) complexes

TABLE-2
KEY IR SPECTRAL DATA (cm^{-1}) OF LIGAND PHQH AND
ITS METAL COMPLEXES

Compound	ν(N–H)	ν(O–H)	ν(C=N)	ν(M–O)	ν(M–N)
PHQH	3160 s,b	3400 s,b	1600 s,b		
$[Co(PHQH)_2(NH_3)_2]$	3160 s,b	3370 m,b	1575 m,b	520 m	435 m
$[Co(PHQH)_2(C_5H_5N)_2]$	3160 s,b	3375 m,b	1565 m,b	535 m	435 m
$[Co(PHQH)_2(\alpha\text{-pic})_2]$	3160 s,b	3370 m,b	1570 m,b	520 m	440 m
$[Co(PHQH)_2(\beta\text{-pic})_2]$	3160 s,b	3365 m,b	1570 m,b	515 m	450 m
$[Co(PHQH)_2(\gamma\text{-pic})_2]$	3160 s,b	3370 m,b	1570 m,b	500 m	425 m
$[Ni(PHQH)(NH_3)_2]$	3160 s,b	3365 m,b	1565 m,b	535 m	435 m
$[Ni(PHQH)_2(C_5H_5N)_2]$	3160 s,b	3370 m,b	1565 m,b	540 m	420 m
$[Ni(PHQH)_2(\alpha\text{-pic})_2]$	3160 s,b	3370 m,b	1575 m,b	525 m	435 m
$[Ni(PHQH)_2(\beta\text{-pic})_2]$	3160 s,b	3370 m,b	1570 m,b	530 m	430 m
$[Ni(PHQH)_2(\gamma\text{-pic})_2]$	3160 s,b	3375 m,b	1565 m,b	525 m	440 m
$[Cu(PHQH)_2(NH_3)_2]$	3160 s,b	3375 m,b	1565 m,b	510 m	445 m
$[Cu(PHQH)_2(C_5H_5N)_2]$	3160 s,b	3365 m,b	1570 m,b	515 m	450 m
$[Cu(PHQH)_2(\alpha\text{-pic})_2]$	3160 s,b	3365 m,b	1565 m,b	520 m	435 m
$[Cu(PHQH)_2(\beta\text{-pic})_2]$	3160 s,b	3370 m,b	1575 m,b	535 m	450 m
$[Cu(PHQH)_2(\gamma\text{-pic})_2]$	3160 s,b	3360 m,b	1560 m,b	540 m	445 m

exhibits three bands in the regions, 12200-11300, 18600-18100 and 24000-23300 cm^{-1}, which proposes octahedral geometry[21] for Ni(II) complexes, which is further supported[22] by magnetic susceptibility value in the range, 3.14-3.21 BM. The Cu(II) complexes display two spectral bands in the regions, 14000-13600 and 19400-18900 cm^{-1} which proposes octahedral geometry[21] for Cu(II) complexes. The magnetic susceptibility value for Cu(II) complexes lie in the range 1.81-1.87 BM.

Conductivity measurements: The conductance values of the synthesized complexes have been found to be in the range 12.6-19.3 ohm^{-1} cm^2 mol^{-1}, which proposes to be non-electrolytic[23] in nature.

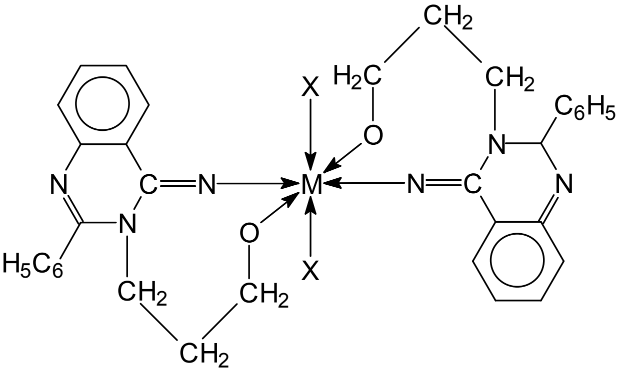
Antifungal study: The ligand PHQH as well as metal complexes were screened for their antifungal activity against *Pencillium expansum* and *Apergillus flavus* as the test fungi by paper-disc plate method[13] at concentration levels of 2.0 and 0.2 % (w/v) medium was used. Filter paper discs of diameter 12 mm were used and the diameters of zones of inhibition formed around each disc after incubating for a period of 72 h at 25-30 ºC were recorded in Table-3. Results were compared with fungicides, Dithane-Z-78. On comparison with reference to fungicide, the complexes were found to more effective than ligand, PHQH.

On the basis of the characterization data, the Schiff base PHQH is coordinated in a bidentate manner through azomethine nitrogen and alcoholic oxygen after deprotonation. The remaining coordinate centers were

TABLE-3
ANTIFUNGAL ACTIVITY OF PHQH AND ITS METAL COMPLEXES

Compounds	*Penicillium expansum*	*Aspergillus flavus*
PHQH	68	53
$[Co(PHQH)_2(NH_3)_2]$	81	59
$[Co(PHQH)_2(C_5H_5N)_2]$	93	58
$[Ni(PHQH)_2(NH_3)_2]$	76	62
$[Ni(PHQH)_2(C_5H_5N)_2]$	91	82
$[Cu(PHQH)_2(NH_3)_2]$	109	74
$[Cu(PHQH)_2(C_5H_5N)_2]$	112	76

occupied by N-atoms of NH_3 pyridine, α, β or γ-picolines. The geometry of the complexes can be proposed to have an octahedral in geometry as shown in Fig. 1.



$[M(PHQH)_2X_2]$
M = Co(II), Ni(II) and Cu(II); X = NH_3, C_5H_5N,
α-picoline, β-picoline and γ-picoline

Fig. 1

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