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Synthesis, spectral and antimicrobial screening of Schiff base complexes derived from 2 phenyl- 3 Carboxy methyl quinazoline (3H) 4-one

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ABSTRCAT

Complexes of cobalt(II), nickel(II) and copper(II) with a Schiff base, 2 phenyl- 3 carboxy methyl quinazoline (3H) 4- thiosemicarbazone (PCMQT) have been synthesized. The ligand as well as complexes were characterized by the elemental analyses, molar mass, molar conductance, IR, electronic spectra and magnetic susceptibility measurements.

All the complexes are non electrolytic in nature. From the analytical and spectroscopic investigation the stoichiometry of the complexes has been found to be $[M(PCMQT)_2X_2]$ where M = Co(II), Ni(II) and Cu(II); PCMQT = ligand, X = Cl^-, Br^-, I^- and NO_3^-. On the basis of above observations the geometry of the complexes is proposed to be octahedral in nature. The antimicrobial activities of the ligand and its complexes have been screened against bacteria *E. coli* and fungi *Aspergillus niger*.

Key words: PCMQT/ Schiff base/ Complex/ Antibacterial/ Antifungal.

INTRODUCTION

Transition metal complexes of N and S containing Schiff bases have wide applicability, ranging from synthesis to application in diverse fields. In recent years, there has been a dramatic growth of interest in metal complexes based materials which exhibit unusual properties. Nitrogen and sulphur containing ligand and its complexes have been found to be important precursor for semiconductor materials[1] used as photosensitive for conservation of light energy to electricity[2]. Several Schiff base complexes have been synthesized as models for some of these metalloproteins[3-7]. Transition metal complexes with bi and tridentate chelating ligands bound to the metal ion through oxygen and nitrogen atoms have been extensively investigated with respect to their remarkable efficiency as insulin mimetic complexes[8-10]. These observations and our earlier recent work[11-19] on Schiff base complexes, prompted us to synthesize Co(II), Ni(II) and Cu(II) complexes with a Schif base 2-phenyl-3-carboxy methyl quinazoline (3H) 4-thiosemicarbazone (PCMQT).

EXPERIMENTAL

The chemicals used were of AnalR grade and the reagent were used without further purification.

Preparation of the ligand

The Schiff base were prepared by the condensation reaction of equimolar quantity of 2-phenyl-3-carboxy methyl quinazoline (3H) 4-one (0.01M) dissolved in minimum amount of ethanol and ethanolic solution of thiosemicarbazide hydrochloride (0.01M). The resulting mixture was refluxed on water bath for 3h. Colourless Schiff base was obtained which was washed thoroughly with water and recrystallized with ethanol. m.p. 186±1°C; yield 60%.

General method for the preparation of complexes

The complexes were prepared by reacting respective metal halides of Co(II), Ni(II) and Cu(II) dissolved in minimum volume of ethanol with ethanolic solution of the ligand, 2-phenyl 3-carboxy methyl quinazoline (3H) 4- thiosemicarbazone in molar ratio 1:2. The resulting reaction mixture was refluxed on a water bath for 3-4 h. The procedure carried out in each case was of similar with slight variation of timing of reflux. The precipitated complexes were filtered, washed with aqueous ethanol and dried in oven. Yield 55-60%.

The following general method was adopted for the preparation of nitrate complexes. Ethanolic solution of respective metal nitrate (0.01M) was condensed with ethanolic solution of ligand 2-phenyl 3-carboxy methyl quinazoline (3H) 4- thiosemicarbazone with constant stirring. The resulting solution was heated on water bath for 3-4 h. The coloured complexes were obtained which was filtered, washed several times with ethanol and then dried in air oven. Yield 60-65%.

The complexes were analysed for metal contents by standard procedure[20]. I.R. spectra of the ligand and their complexes were recorded on Perkin Elmer-577 using KBr disc. The electronic spectra were recorded on a Cary 2390 spectrophotometer. Magnetic susceptibility was recorded by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. The molar conductivity was measured by systronics conductivity meter model 303 using DMF as a solvent. Analytical data, colour, electronic spectra, molar conductance measurement, decomposition temperature and molar mass of the ligand and metal complexes are recorded in Table-1 and the important IR bands are recorded in Table-2.

RESULTS AND DISCUSSION

IR spectrum of the ligand PCMQT exhibits a medium and broad band at 3360 cm^{-1} assigned[21,22] to ν_{N-H}. In the spectra of the complex, this band is unaffected which indicate non-participation of amino or imino group in the coordination. IR spectrum of the ligand exhibits a strong and broad band at 1480 cm^{-1} assignable[21,23] to $\nu_{C=N}$. In the spectra of the complexes this band also suffers downward shift that proposes coordination through azomethine N. The next IR spectra of the ligand exhibit strong and broad band at 760 cm^{-1} assignable[21,24] to $\nu_{C=S}$. This band is shifted to higher frequency region with decreased sharpness and intensity in the complexes indicating coordination of metal ion through thione sulphur atom. The coordination through azomethine nitrogen and sulphur atom of thiosemicarbazone moiety are further supported by the appearance of bands in the far IR regions at 480-450 cm^{-1} and 425-395 cm^{-1} assigned[25,26] to ν_{M-N} and ν_{M-S} respectively. The coordination through metal-halogen is confirmed by the appearance of a band in the region 320-265 cm^{-1} assigned[25,26] to ν_{M-X}. (Cl^- , Br^- and I^-). These assignments are supported[27] by the literature. The evidence of metal halogen coordination is further confirmed by the low value of molar conductance in the range 3.2-7.9 ohm^{-1} cm^2 mol^{-1}.

The presence of two IR bands at 1530 and 1410 cm^{-1} with a separation of 120 cm^{-1} suggest mono-coordinated nature of nitrate group[28,29].

Electronic spectra and magnetic susceptibility of the complexes

The Co(II) complexes display three band in the regions 12320-12510 cm^{-1}, 18207-18300 cm^{-1} and 23160-23312 cm^{-1} assigned to the transitions $^4T_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F), $^4A_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F) and $^4T_{1g}$ (P) $\leftarrow$ $^4T_{1g}$ (F) respectively which indicate octahedral[30-31] geometry for Co(II) complex which further supported[32,33] by high μ_{eff} value in the range 4.81-5.14 B.M. The Ni(II) complexes exhibits three bands in the region 10000-10300 cm^{-1}, 13220-14100 cm^{-1} and 24200-24410 cm^{-1} assigned to $^3T_{2g}$ (F) $\leftarrow$ $^3A_{2g}$ (F), $^3T_{1g}$ (F) $\leftarrow$ $^3A_{2g}$ (F) and $^3T_{1g}$ (F) $\leftarrow$ $^3A_{2g}$ (F) respectively, suggesting octahedral[31,34] geometry for Ni(II) complexes. The proposed geometry of Ni(II) complexes is further supported[32,33] by μ_{eff} value of Ni(II) complexes in the range 3.06-3.22 B.M. The Cu(II) complexes exhibit two ligand field bands in the region at 11400-11600 cm^{1} and 25170-25300 cm^{1} assigned to the transitions $^2T_{2g}$ $\leftarrow$ ^2E_g and charge transfer band which suggests octahedral[31,35] geometry for the Cu(II) complexes. The magnetic susceptibility value for Cu(II) complexes lies in the range 1.84-1.94 B.M.[32,33]

Table 1: Analytical, colour, mol. formula, magnetic susceptibility, molar conductance, electronic spectra and decomposition temperature of the ligand PCMQT and its metal complexes

Compounds (Colour)	Mol. formula	Yield %	% Analysis found (calculated) M	C	N	H	μ_{eff} B.M.	Ω_m ohm^{-1} cm^2 mol^{-1}	λ_{max} electronic cm^{-1}	DT° C
PCMQT	358	56		56.79	19.42	5.39				
(Colourless)				56.98)	19.55)	(5.58)				
$[Co(PCMQT)_2Cl_2]$	845.9	58	6.88	48.11	16.33	4.62	4.8	3.2	12320, 18207	204
Red	3		(6.96)	(48.23)	(16.54)	(4.72)	6		, 21212	
$[Co(PCMQT)_2Br_2]$	934.7	58	6.23	43.48	14.88	4.21	4.8	3.9	12370, 18222	209
Red	38		(6.30)	43.64)	14.97)	(4.27)	1		, 23210	
$[Co(PCMQT)_2I_2]$	1028.	61	5.60	39.44	13.47	3.80	4.9	4.1	12400, 18236	213
Red	75		(5.72)	(39.65)	(13.60)	(3.88)	2		, 23280	
$[Co(PCMQT)_2(NO_3)_2]$	898.9	55	6.48	45.22	15.38	4.39	5.0	4.8	12470, 18300	222
Reddish brown	3		(6.55)	45.38)	15.57)	(4.44)	8		, 23160	
$[Ni(PCMQT)_2Cl_2]$	845.7	56	6.88	48.12	16.40	4.66	3.0	4.1	10000, 13300	189
Brown	1		(6.94)	48.24)	(16.55)	(4.72)	6		, 24200	
$[Ni(PCMQT)_2Br_2]$	934.5	55	6.21	43.52	14.88	4.21	3.0	4.2	10200 13270	197
Brown	18		(6.28)	43.65)	14.98)	(4.28)	8		24280	
$[Ni(PCMQT)_2I_2]$	1028.	52	5.62	39.45	13.52	3.83	3.1	4.3	10240 13220	185
Brownish red	53		(5.70)	(39.66)	(13.61)	(3.88)	6		24310	
$[Ni(PCMQT)_2(NO_3)_2]$	898.7	53	6.44	45.11	15.48	4.39	3.2	4.7	10260, 13700	187
Deep red	1		(6.53)	45.39)	15.57)	(4.48)	2		, 24340	
$[Cu(PCMQT)_2Cl_2]$	850.5	50	7.39	47.77	16.32	4.58	1.8	6.3	11400,	226
Blue	4		(7.47)	(47.96)	(16.46)	(4.70)	9		25300	
$[Cu(PCMQT)_2Br_2]$	939.3	51	6.68	43.28	14.77	4.13	1.9	6.9	11510,	228
Blue	48		(6.16)	43.43)	(14.90)	(4.25)	0		25220	
$[Cu(PCMQT)_2(NO_3)_2]$	903.5	52	6.83	45.11	15.32	4.34	1.9	7.9	11600,	201
Blue	1		(7.03)	(45.25)	15.49)	(4.42)	4		25170	

DT = Decomposition Temperature

Table 2: Key ir spectral bands (cm^{-1}) of ligand PPKH and its metal complexes

Compounds	ν_{N-H}	$\nu_{C=N}$	$\nu_{C=S}$	ν_{M-N}	ν_{M-S}	ν_{M-X}
PCMQT	3360 m,b	1480 s,b	760 s,b			
$[Co(PCMQT)_2Cl_2]$	3360 m,b	1455 m,b	740 m,b	470 m	395 m	305 m
$[Co(PCMQT)_2Br_2]$	3360 m,b	1455 m,b	735 m,b	470 m	400 m	280 m
$[Co(PCMQT)_2I_2]$	3360 m,b	1455 m,b	730 m,b	475 m	405 m	275 m
$[Co(PCMQT)_2(NO_3)_2]$	3360 m,b	1450 m,b	730 m,b	470 m	405 m	
$[Ni(PCMQT)_2Cl_2]$	3360 m,b	1460 m,b	740 m,b	480 m	410 m	320 m
$[Ni(PCMQT)_2Br_2]$	3360 m,b	1455 m,b	735 m,b	475 m	410 m	295 m
$[Ni(PCMQT)_2I_2]$	3360 m,b	1455 m,b	735 m,b	480 m	415 m	270 m
$[Ni(PCMQT)_2(NO_3)_2]$	3360 m,b	1455 m,b	735 m,b	475 m	415 m	
$[Cu(PCMQT)_2Cl_2]$	3360 m,b	1450 m,b	735 m,b	460 m	420 m	315 m
$[Cu(PCMQT)_2Br_2]$	3360 m,b	1460 m,b	735 m,b	460 m	425 m	285 m
$[Cu(PCMQT)_2(NO_3)_2]$	3360 m,b	1455 m,b	735 m,b	460 m	425 m	

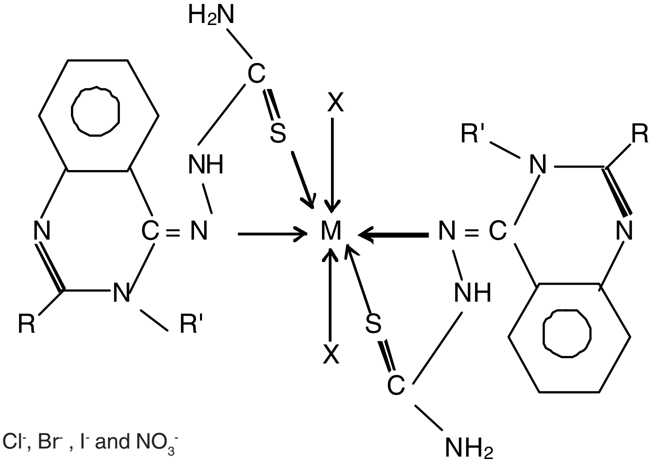
m = medium, s = strong, b = broad

Molar Conductance of the Complexes

Molar conductance value of the complexes were measured in the solvent DMF and the complexes were found to be non electrolytic[36] in nature. The molar conductance value of complexes lies in the range 3.2-7.9 ohm^{-1} cm^2 mol^{-1}.

Antimicrobial activity

The ligand PCMQT and its complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antimicrobial activity against bacteria *Escherichia coli* and antifungal activity against *Aspergillus niger* by disc diffusion method[37] using DMF as solvent at concentration of 50 mg. The biocidal activities was compared with known standard drugs, tetracycline and diethane Z-78, respectively at same concentration[38] 50 m_g. The ligand were found biologically active and their metal complexes were significantly enhanced antibacterial activity and antifungal activity. It is known that chelation tends to make the ligands act as more potent bacterial agents, than the parent ligand. The antimicrobial activity of the compound increases after metal chelation. Chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donar group[39] increasing



M = Co(II) and Ni(II); X = Cl^-, Br^-, I^- and NO_3^-
M = Cu(II); X = Cl^-, Br^-, I^- and NO_3^-

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

lipophilic nature of the central metal ion, which in turn favours its permeation to the lipid layer of the membrane.

CONCLUSION

Thus on the basis of above studies it may be concluded that the complexes possess the octahedral geometry around the central metal ion as shown in Fig.1.

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