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Synthesis and Structural Characterization of Schiff Base Ligand and their Metal Complexes

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ABSTRACT

In the present work, the synthesis and structural characterization of a 2-phenyl- 3(benzamido propyl) quinazoline (3H) -4- one semicarbazone/ thiosemicarbazone hydrochloride and its metal complexes have been reported. All the synthesized compounds were characterized by using various physico-chemical techniques such as Infrared spectra, electronic spectra, molar conductivity and magnetic susceptibility measurements. The ligand and metal ions reacted to form in the 2:1 ratio as found from the elemental analyses and general stiochiometry was determined, $[M(PBPQS)_2X_2]$ and $[M(PBPQT)_2X_2]$; where M = Co(II), Ni(II) and Cu(II); PBPQS = 2-phenyl- 3 (benzamido propyl) quinazoline (3H) -4- one semicarbazone and PBPQT = 2- phenyl- 3 (benzamido propyl) quinazoline (3H) -4- one thiosemicarbazone. On the basis of analytical data, a proposed structure for the Cu(II) complexes are distorted octahedral and those for Co(II) and Ni(II) complexes are octahedral. Ligands PBPQS/ PBPQT have been proposed to act in a bidentate manner co-ordinating to the metal ions though azomethine nitrogen and oxygen/ sulphur atom of either semicarbazone/ thiosemicarbazone moiety. The remaining co-ordination sites are occupied by negative ions such as Cl^-, Br^-, I^- or NO_3^-. The ligands and its metal complexes were tested for their possible antimicrobial potentials.

Keywords: PBPQS/ PBPQT/ Co(II), Ni(II), Cu(II)/ Schiff base/ Antimicrobial studies.

INTRODUCTION

In recent years,[1-10] there has been considerable interest in the chemistry of transition metal of schiff base. This is due to the fact that schiff base transition metal complexes are one of the most adaptable and thoroughly studied systems. The Schiff base complexes have applicable in clinical and analytical fields. They are used as model molecule for biological oxygen carrier systems. Schiff bases metal complexes also exhibit several biocidal potential such as antifungal, anti-cancer, herbicidal and anti-bacterial. Because of their ease in preparation and versatile properties, herein; the syntheses, structural features, spectroscopic characterization of metal complexes of Co(II), Ni(II), Cu(II) with Schiff bases, 2-Phenyl 3(benzamido propyl) quinazoline (3H)-4-one semicarbozone and 2-phenyl-3(benzamido propyl) quinazoline (3H)-4-one thiosemicarbozone are reported.

EXPERIMENTAL

Physical Measurement

All the chemicals and solvents were of reagent grade and were used without further purification.

The ligand and metal complexes were analysed using standard procedure. Analytical data were collected on Perkin-Elmer-2400 CHNO/S elemental analyzer. Infrared spectra were recorded on Parkin-Elmer spectrometer model-577 using KBr disc. Electronic spectra was measured on Cary-2390 spectrophotometer. Molar conductance was using a Systronics conductivity meter model 303 using Ca 10^{-3} M solutions in DMF. Magnetic susceptibility of the samples were made on Guoy balance using mercury tetraisothiocynato cobaltate as a calibrant.

Synthetic Procedure

Preparation of the bidentate Schiff base ligand PBPQS/PBPQT

The compound 2-phenyl-3-(benzamido propyl) quinazolin (3H)-4-one was synthesized by earlier reported method. Ethanolic solution 2-phenyl-3-(benzamido propyl) quinazolin(3H) 4-one was allowed to react with Semicarbazide/ thiosemicarbazide hydrochloride dissolved in 10% ethanolic solution of Sodium acetate. The resulting mixture were heated on water bath for 3-4 hr with frequent stirring. After cooling the precipitate was collected, washed with tetrahydrofuran, treated with dilute sodium carbonate solution and filtered. The solid was washed with water and crystallised twice from ethanol to furnish 2-phenyl-3-benzamido propyl) quinazoline (3H) 4-one semicarbazone/ thiosemicarbazone as colourless compounds m.p. 262 ±1^{O}C for ligand PBPQS and 273 ±1^{0}C for ligand PBPQT yield, 70%.

Preparation of the complexes

The compounds of Co(II), Ni(II) and Cu(II) have been formed by reacting an ethanolic solutions of metal halides/nitrates with ethanolic solutions of the ligand PBPQS/PBPQT in molar ratio 1:2. The resulting reaction mixtures were heated on water bath for 2-3 hours. The solid coloured complexes which separated out on cooling were filtered, washed with ethanol, dried and recrystallised with tetrahydrofuran; yield in all cases 65-70%.

RESULTS AND DISCUSSION

Infrared Spectral Studies

The IR data of the spectra of the ligand PBPQS/PBPQT and its Co(II), Ni(II) and Cu(II) complexes are listed in Table-1. The characteristic IR band for the free ligands, when compared with those of their complexes provide meaningful information regarding the bonding sites of the ligand.

Semicarbazine/ thiosemicarbazone ligands can coordinate as bidentate ligands, in most cases through the azomethine nitrogen and oxygen/sulphur atom of either semicarbazone/ thiosemicarbazone. In the free ligands PBPQS/PBPQT the $\nu_{C=N}$ bands appear in the region of 1645-1635cm^{-1}. In all the complexes, the $\nu_{C=N}$ band is shifted to lower frequency in the range. 1620-1605 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen atom[11]. This is further supported by the appearance of a far IR band in the range 420-390 cm^{-1} in the complexes which may be assigned[12] to ν_{M-N}.

The IR spectrum of the ligand PBPQS exhibit strong and broad band at 1720 cm^{-1} assigned[11] to $\nu_{C=O}$. This band undergoes red shift after complexation proposes co-ordination through carbonyl oxygen atom of semicarbozone moiety. It is further supported by the appearance of a new band in far IR region at 520-505cm^{-1} assigned[12] to ν_{M-O}.

The spectrum of the ligand PBPQT shows a sharp and strong band at 820 cm^{-1} assigned[11] to $\nu_{C=S}$. In the spectra of the complexes this band shows red shift proposes coordination through thione sulphur. This is further supported by the appearance of a far IR band in the region at 480-455 cm^{-1}, assigned[12] to ν_{M-S}.

The co-ordination through halogen atom is confirmed by the appearance of a band in the far IR region at 315-255 cm^{-1} assigned[12] to ν_{M-X} (X= Cl^{-}, Br^{-}, I^{-}). The evidence of metal halogen linkage is further confirmed on the basis of low value of molar conductance measurements of complexes in the range 4.7-11.2 ohm^{-1} cm^{2} mol^{-1} (Table-1). Nitrate

Table 1:Analytical And Physical Data Of The Ligand PBPQS/ PBPQT And Its Metal Complexes

Compounds (Colour)	Molar % Mass	Analysis found (Calculated) M	C	N	H	D.T. °C	μ_{eff} (B.M.)	Ω_m ohm^{-1} cm^2 mol^{-1}	λ_{max} electronic cm^{-1}
PBPQS	472		60.83	17.70	4.97				
Colourless			(61.01)	(17.79)	(5.08)				
PBPQT	488		58.87	17.12	4.86				
(Colourless)			(59.01)	(17.21)	(4.91)				
[Co(PBPQS)$_2$Cl$_2$]	1073.93	5.37	53.41	15.58	4.40	236	5.06	6.7	13640,
Yellowish red		(5.49)	(53.63)	(15.64)	(4.46)				19760
[Co(PBPQT)$_2$Cl$_2$]	1105.93	5.24	51.84	15.08	4.28	242	5.01	6.1	13470,
Yellowish red		(5.32)	(52.08)	(15.19)	(4.34)				19280
[Co(PBPQS)$_2$Br$_2$]	1162.748	4.93	49.38	14.33	4.08	227	4.89	6.9	12810,
Reddish yellow		(5.06)	(49.53)	(14.44)	(4.12)				19640
[Co(PBPQT)$_2$Br$_2$]	1194.748	4.87	48.09	13.97	3.96	238	4.94	6.2	12930,
Reddish yellow		(4.93)	(48.21)	(14.06)	(4.01)				20100
[Co(PBPQS)$_2$I$_2$]	1256.73	4.59	45.70	13.23	3.77	220	4.98	6.4	12960,
Deep yellow		(4.68)	(45.83)	(13.36)	(3.81)				21200
[Co(PBPQT)$_2$I$_2$]	1288.73	4.48	44.53	12.90	3.68	248	4.93	6.3	13010,
Deep yellow		(4.57)	(44.69)	(13.03)	(3.72)				20740
[Co(PBPQS)$_2$(NO$_3$)$_2$]	1126.93	5.14	50.98	144.78	4.20	214	5.12	6.8	13220,
Yellowish red		(5.22)	(51.11)	(14.90)	(4.25)				20960
[Co(PBPQT)$_2$(NO$_3$)$_2$]	1158.93	4.96	49.53	14.36	4.09	209	5.09	6.6	13270,
Yellowish red		(5.08)	(49.70)	(14.49)	(4.14)				19730
[Ni(PBPQS)$_2$Cl$_2$]	1073.71	5.33	53.40	15.56	4.43	253	3.11	4.7	10640,
Brown		(5.46)	(53.64)	(15.64)	(4.47)				15210,
									24390
[Ni(PBPQT)$_2$Cl$_2$]	1105.71	5.22	51.86	15.06	4.29	234	3.09	4.1	10560,
Brown		(5.30)	(52.09)	(15.19)	(4.34)				15340,
									24580
[Ni(PBPQS)$_2$Br$_2$]	1162.52	4.92	49.36	14.32	4.06	213	3.07	4.9	10580,
Brown		(5.05)	(49.54)	(14.45)	(4.12)				15240,
									24600
[Ni(PBPQT)$_2$Br$_2$]	1194.52	4.85	48.06	13.96	3.95	238	3.04	4.89	10320,
Deep red		(4.91)	(48.22)	(14.06)	(4.01)				15710,
									24520
[Ni(PBPQS)$_2$I$_2$]	1256.51	4.60	45.72	13.24	3.78	256	3.06	4.64	10430,
Deep yellow		(4.68)	(45.85)	(13.37)	(3.82)				15460,
									14380
[Ni(PBPQT)$_2$I$_2$]	1288.51	4.49	44.54	12.91	3.67	248	3.12	5.10	10100,
Red		(4.55)	(44.70)	(13.03)	(3.72)				15840,
									24320
[Ni(PBPQS)$_2$(NO$_3$)$_2$]	1126.71	5.14	51.01	14.77	4.02	270	3.17	5.2	10210,
Reddish brown		(5.21)	(51.12)	(14.91)	(4.26)				15740,
									24380
[Ni(PBPQT)$_2$(NO$_3$)$_2$]	1158.71	4.94	49.54	14.37	4.10	261	3.15	5.6	10380,
Reddish brown		(5.06)	(49.71)	(14.449)	(4.14)				15900,
									24240

$[Cu(PBPQS)_2Cl_2]$	1078.54	5.80	53.22	15.49	4.39	280	1.89	11.2	12310,
Blue		(5.89)	(53.40)	(15.57)	(4.45)				17480
$[Cu(PBPQT)_2Cl_2]$	1110.54	5.63	51.72	18.51	4.26	276	1.98	10.8	12240,
Blue		(5.72)	(51.86)	(18.65)	(4.32)				17320
$[Cu(PBPQS)_2Br_2]$	1167.35	5.36	49.22	13.88	4.02	268	1.90	10.2	12140,
Blue		(5.44)	(49.34)	(14.00)	(4.11)				17540
$[Cu(PBPQT)_2Br_2]$	1199.35	5.20	47.83	13.84	6.61	255	1.92	11.3	12540,
Blue		(5.29)	(48.02)	(14.00)	(6.67)				17610
$[Cu(PBPQS)_2(NO_3)_2]$	1131.54	5.52	50.79	14.72	4.19	260	1.94	9.8	12620,
Deep blue		(5.61)	(50.90)	(14.84)	(4.24)				17520
$[Cu(PBPQT)_2(NO_3)_2]$	1163.54	5.37	49.33	14.32	4.07	268	1.93	9.4	12480,
Deep blue		(5.46)	(49.50)	(14.43)	(4.12)				17460

Table 2: Salient Features Of IR Spectral Data For Ligand And Its Metal Complexes

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=S}$	ν_{M-O}	ν_{M-S}	ν_{M-N}	ν_{M-X}
PBPQS	1720 s,b	1635 s,b					
PBPQT		1645 s,b	820 s,b				
$[Co(PBPQS)_2Cl_2]$	1690 m,b	1605 m,b		505 m		405 m	255 m
$[Co(PBPQT)_2Cl_2]$		1610 m,b	795 m,b		460 m	405 m	255 m
$[Co(PBPQS)_2Br_2]$	1695 m,b	1605 m,b		505 m,b		405 m	260 m
$[Co(PBPQT)_2Br_2]$		1610 m,b	790 m,b		455 m	405 m	260 m
$[Co(PBPQS)_2I_2]$	1690 m,b	1600 m,b		500 m,b		405 m	270 m
$[Co(PBPQT)_2I_2]$		1615 m,b	790 m,b		470 m	410 m	270 m
$[Co(PBPQS)_2(NO_3)_2]$	1695 m,b	1600 m,b		515 m		415 m	
$[Co(PBPQT)_2(NO_3)_2]$		1620 m,b	790 m,b		470 m	415 m	
$[Ni(PBPQS)_2Cl_2]$	1690 m,b	1600 m,b		515 m		3415 m	295 m
$[Ni(PBPQT)_2Cl_2]$		1620 m,b	795 m,b		475 m	415 m	295 m
$[Ni(PBPQS)_2Br_2]$	1690 m,b	1600 m,b		510 m		420 m	295 m
$[Ni(PBPQT)_2Br_2]$		1620 m,b	795 m,b		475 m	420 m	295 m
$[Ni(PBPQS)_2I_2]$	1690 m,b	1600 m,b		510 m		420 m	310 m
$[Ni(PBPQT)_2I_2]$		1605 m,b	790 m,b		475 m	420 m	315 m
$[Ni(PBPQS)_2(NO_3)_2]$	1690 m,b	1605 m,b		515 m		410 m	
$[Ni(PBPQT)_2(NO_3)_2]$		1600 m,b	795 m,b		480 m	410 m	
$[Cu(PBPQS)_2Cl_2]$	1690 m,b	1605 m,b		515 m		470 m	285 m
$[Cu(PBPQT)_2Cl_2]$		1600 m,b	795 m,b		480 m	470 m	290 m
$[Cu(PBPQS)_2Br_2]$	1690 m,b	1605 m,b		515 m		410 m	285 m
$[Cu(PBPQT)_2Br_2]$		1600 m,b	795 m,b		480 m	410 m	290 m
$[Cu(PBPQS)_2(NO_3)_2]$	1690 m,b	1690 m,b		515 m		470 m	
$[Cu(PBPQT)_2(NO_3)_2]$		1600 m,b	795 m,b		480 m	410 m	

complexes show characteristic medium intensity bands at 1260 and 1100 cm^{-1} with a separation of 160 cm^{-1} due to monodentate linkage of nitrate group. Combination bands at 1660 and 1640 cm^{-1} with a separation of 20 cm^{-1} confirming the monodentate behavior of the nitrate group.

On the basis of above discussion on IR spectral data it is proposed that the ligand PBPQS/PBPQT acts in a neutral bidentate manner. The remaining coordination positions of metal ions are satisfied by negative ions, such as Cl^-, Br^-, I^- and NO_3^-.

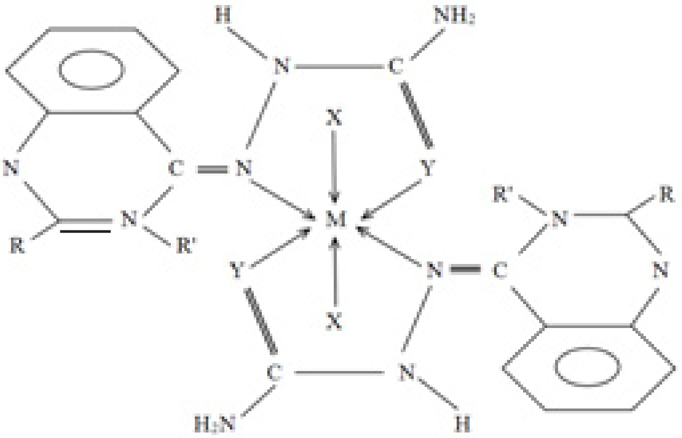

Fig. 1: [M(PBPQS)$_2$]X$_2$ and [M(PBPQT)$_2$]X$_2$ M = Co(II), Ni(II) and Cu(II) ; X = Cl$^-$, Br$^-$, I$^-$ and NO$_3^-$; Y = Oxygen or Sulphur; R = Phenyl; R' = benzamido propyl

Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of all the complexes have been recorded in the region 10000-25000 cm^{-1}. The Co(II) complexes exhibit two bands in the regions at 13470-12870 cm^{-1} and 21200-19280 cm^{-1} assigned to the transitions; $^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$ and $^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$ respectively, proposing octahedral geometry for Co(II) complexes.

The octahedral geometry for Co(II) complexes are further supported by the high magnetic susceptibility in the range 4.89-5.12 BM. The Ni(II) complexes exhibit three spectral bands in the region, 10800-10100 cm^{-1}, 15900-15200 cm^{-1} and 24600-24000 cm^{-1} assigned to the transitions, ; $^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$, $^{4}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$ and $^{4}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$ respectively, proposing octahedral geometry for Ni(II) complexes. The proposed geometry of Ni(II) complexes is further supported by the magnetic susceptibility value in the range 3.04-3.17 BM. The Cu(II) complexes exhibit two spectral bands in the regions, 12600-12100 cm^{-1} and 17900-17300 cm^{-1} assigned to the transitions, $^{2}T_{2g} \leftarrow {}^{2}E_{g}$ and charge transfer band which proposing octahedral geometry for Cu(II) complexes. The magnetic value of Cu(II) complexes lies in the range 1.89-1.98 B.M.

Conductivity Measurement

Molar conductance of the complexes was measured in solvent dimethyl formamide. All the complexes have conductivity value in the range of 4.7-11.2 ohm^{-1}cm^{2}mol^{-1}indicating their non-electrolyte behaviour.

CONCLUSION

Thus on the basis of above physico-chemical studies it is concluded that the ligand PBPQS/PBPQT acts in a neutral bidentate manner and coordination is proposed through azomethine nitrogen and through carbonyl oxygen atom or sulphur atom of semicarbazone/ thiosemicarbazone moiety. The remaining position of metal ion is satisfied by negative ions such as Cl$^-$, Br$^-$, I$^-$ and No$_3^-$. The geometry of the Co(II), Ni(II) and Cu(II) are proposed to be octahedral in nature as shown in Fig.1.

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