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Synthesis and Studies of Co(II), Ni(II) and Cu(II) Complexes with Some Tridentate Schiff Bases

B.K. RAI*, KAUSHLENDRA SHARMA† and A.K. SINGH‡
Department of Chemistry, L.N.T. College
Muzaffarpur-842 001, India

Complexes of Co(II), Ni(II) and Cu(II) with 3-phenyl-3-(*p*-aminophenyl)-4-quinazolone semicarbazone (PAPQSC) and 3-phenyl-3-(*p*-aminophenyl)-4-quinazolone thiosemicarbazone (PAPQTSC) have been synthesized and characterized on the basis of elemental analysis, IR spectra, electronic spectra, magnetic moment data and conductivity measurements. The analytical data of the complexes indicate 1 : 2 metal-ligand stoichiometry of the type $[M(HL^{1-2})_2]$ where M = Co(II), Ni(II) and Cu(II). The ligands behaved as binegative tridentate chelating agents and bonded to the metal ion through amine and imine nitrogen and oxygen/sulphur atoms of either semicarbazone or thiosemicarbazone moiety.

Key Words: Cobalt, Nickel, Copper, 3-Phenyl-3-(*p*-aminophenyl)-4-quinazolone, Semicarbazone, Thiosemicarbazone.

INTRODUCTION

In recent years the coordination behaviour of organometallic compounds with several oxygen, sulphur and nitrogen containing ligands has been studied extensively. As a consequeence of their biological potency these complexes have received great attention[1,2]. It is well established that the biological activity of an active ligand is altered quantitatively on coordinating with suitable metal ions[3,4]. A number of Schiff base ligands have been reported for their bactericidal[5], fungicidal[6], antipyretic[7], antitumour[8], antitubercular[9], anticancer[10] and sterease inhibiting[11] activities. Some of Schiff bases were used as chelating agents[12], analytical reagents[13] for transition metal analysis and as catalysts for epoxidation of olefins[14]. Keeping the above facts in mind and in continuation of our earlier research work[15–17] on transition metal complexes with Schiff bases, the present paper describes the synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with the ligands 3-phenyl-3-(*p*-aminophenyl)-4-quinazolone semicarbazone (PAPQSC) and 3-phenyl-3-(*p*-aminophenyl)-4-quinazolone thiosemicarbazone (PAPQTSC).

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†Research Scholar, B.R.A. Bihar University, Muzaffarpur, India.

‡Deptt. of Chemistry, D.B.R.K. Government Inter College, Patna City, India.

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EXPERIMENTAL

All the reagents used were of B.D.H. grade.

Preparation of the ligand PAPQSC and PAPQTSC

Ethanolic solution of 2-phenyl-3-(*p*-aminophenyl)-4-quinazolone was treated with semicarbazide hydrochloride or thiosemicarbazide hydrochloride dissolved in 10% ethanolic solution of sodium acetate. The resulting reaction mixtures were heated on a water bath for 3–4 h; then a crystalline colourless solid began to separate after allowing the solution to stand for some time. The solids were cooled, filtered, washed with aqueous ethanol, dried and crystallised with tetrahydrofuran to furnish colourless crystalline solids. (Yield 65–70%, m.p. PAPQSC = 280°C; PAPQTSC = 305°C).

Preparation of the Complexes

The complexes of Co(II), Ni(II) and Cu(II) were formed by reacting an ethanolic solution of metal acetate with the ethanolic solutions of the ligands PAPQSC or PAPQTSC, in the molar ratio 1 : 2. The solid coloured complexes which separated on cooling were filtered, washed with ethanol, dried and recrystallised with tetrahydrofuran. Yield 70–75%.

TABLE-1

COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH LIGANDS PAPQSC AND PAPQTSC

Compound/ Colour	%Analysis found (Calculated)				Ω_{max} ohm^{-1} cm^2 mol^{-1}	μ_{eff} (B.M.)	λ_{max} electronic (cm^{-1})
	Metal	C	H	N			
PAPQSC	–	68.24	4.72	22.96	–	–	–
		(68.10)	(4.86)	(22.70)			
PAPQTSC	–	65.10	4.79	21.65	–	–	–
		(65.28)	(4.66)	(21.76)			
$[Co(PAPQSC)_2]$	7.51	63.31	4.42	20.93	12.9	4.71	9100, 13300
(Dark brown)	(7.38)	(63.16)	(4.51)	(21.05)			19800, 26200
$[Co(PAPQTSC)_2]$	7.22	60.61	4.44	20.11	12.7	5.06	9200, 13200
(Reddish Brown)	(7.10)	(60.72)	(4.33)	(20.24)			19700, 26100
$[Ni(PAPQSC)_2]$	7.19	63.32	4.43	20.90	14.7	3.39	10100, 15900
(Brown)	(7.35)	(63.18)	(4.51)	(21.06)			23200
$[Ni(PAPQTSC)_2]$	7.13	60.59	4.51	20.06	14.2	3.26	10200, 15800
(Violet)	(7.07)	(60.74)	(4.33)	(20.24)			23210
$[Cu(PAPQSC)_2]$	7.80	62.93	4.61	22.81	9.8	1.81	17600
(Yellowish green)	(7.91)	(62.80)	(4.48)	(20.93)			28100
$[Cu(PAPQTSC)_2]$	7.53	60.56	4.39	20.33	9.9	1.94	17300
(Dark green)	(7.61)	(60.39)	(4.31)	(20.13)			27600

The metal contents of the complexes were analysed using standard procedures[18]. Carbon, hydrogen, nitrogen and sulphur were determined at C.D.R.I., Lucknow. The IR spectra of the ligands as well as metal complexes were recorded on Perkin-Elmer spectrophotometer model 398 in the range 4000–200 cm^{-1} employing KBr pellets. The electronic spectra were recorded on a Cary-2390 spectrometer in DMF. Magnetic moments were measured by Gouy method using mercury tetraisothiocyanato cobaltate as the calibrant. The conductivity measurements were made on Systronics conductometer model 303 using acetonitrile as a solvent. Analytical data, colour, magnetic moment, conductivity measurements and electronic spectra are recorded in Table-1 and salient features of IR spectral data are recorded in Table-2.

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF LIGANDS PAPQSC, PAPQTSC AND THEIR METAL COMPLEXES

Compounds	ν(N—H)	ν(C=N)	ν(C=O)	ν(C=S)	ν(M—O)	ν(M—S)	ν(M—N)
PAPQSC	3200 s,b	1660 s,b	1760 s,b	–	–	–	–
PAPQTSC	3140 s,b	1640 s,b	–	820 s,b	–	–	–
[Co(PAPQSC)$_2$]	3170 s,b	1630 s,b	1730 s,b	–	520 m	–	375 m
[Co(PAPQTSC)$_2$]	3110 s,b	1610 s,b	–	790 s,b	–	440 m	390 m
[Ni(PAPQSC)$_2$]	3175 s,b	1635 s,b	1725 s,b	–	570 m	–	380 m
[Ni(PAPQTSC)$_2$]	3115 s,b	1615 s,b	–	795 s,b	–	460 m	385 m
[Cu(PAPQSC)$_2$]	3180 s,b	1625 s,b	1735 s,b	–	550 m	–	380 m
[Cu(PAPQTSC)$_2$]	3105 s,b	1610 s,b	–	800 s,b	–	430 m	370 m

s = strong, b = broad, m = medium

RESULTS AND DISCUSSION

It is well documented[19] that the semicarbazone and thiosemicarbazone derivatives can coordinate to the central metal ion through oxygen or sulphur and N^1(>C=N^1—N^{2}H—(C=X)—N^3<) of either semicarbazone or thiosemicarbazone moiety (X = O or S). The infrared spectra of both the ligands PAPQSC and PAPQTSC observed strong and broad bands in 3200–3140 cm^{-1} region which can be assigned[20] to ν(N—H) of amino group of the side chain of quinazolone ring. In the spectra of the complexes this band shows red shift indicating that coordination takes place through N atom of secondary amino group. The IR spectrum of the ligand PAPQSC exhibits two more bands at 1760 cm^{-1} and 1660 cm^{-1} which can be assigned to ν(C=O)[21] and ν(C=N)[22] respectively. In the spectra of the complexes these bands show red shift indicating coordination takes place through carbonyl oxygen as well as imine nitrogen of semicarbazone moiety.

The IR spectrum of the ligand PAPQTSC shows a strong and broad band at 1640 cm^{-1} and another at 820 cm^{-1} which can be assigned to ν(C=N) and ν(C=S) respectively.[23] In the spectra of the complexes these bands show red shift, clearly indicating coordination takes place through imine nitrogen and thione S of thiosemicarbazone moiety. The coordination through O, N and S donor atoms is further confirmed by the occurrence of three bands in the far IR regions of 570–520 cm^{-1}, 460–430 cm^{-1} and 390–370 cm^{-1} may be assigned to the ν(M—O)[23], ν(M—S)[24] and ν(M—N)[25] bonds respectively.

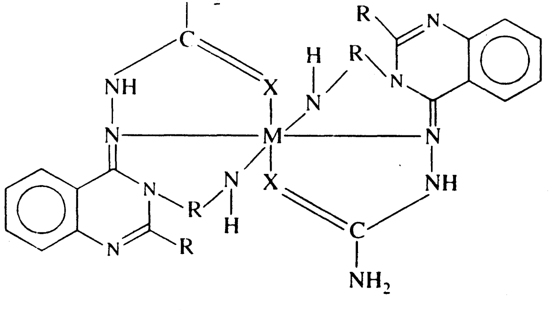
Electronic spectra and magnetic moment of the complexes

The Co(II) complexes exhibit bands at 9200, 13200 and 19700 cm^{-1} which may be assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(P)$ which indicate an octahedral[26] arrangement around Co(II) metal ion. The high frequency band observed at 26100 cm^{-1} may be due to charge transfer. The proposed geometry is further confirmed[27] by high μ_{eff} value in the range 4.71–5.06 B.M. for all the Co(II) complexes. The Ni(II) complexes exhibit bands at 10000 cm^{-1}, 15900 cm^{-1} and 23200 cm^{-1} which may be assigned to the transitions from ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3T_{1g}(F)$, ${}^3T_{1g}(P)$ levels respectively which corresponds to that of octahedral[28] complexes. The proposed geometries of Ni(II) complexes are further confirmed[27] by the μ_{eff} value in the range 3.26–3.38 B.M. for all the Ni(II) complexes. The Cu(II) complexes exhibit bands at 17600–17300 cm^{-1} and 28100–27600 cm^{-1} which may be assigned to the transition ${}^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band. The electronic spectra of all the Cu(II) complex suggest an octahedral geometry for all the Cu(II) complexes[29]. The proposed geometries of all the Cu(II) complexes are further confirmed[27] by the μ_{eff} values in the range of 1.81–1.94 B.M. respectively.

Conductivity Measurements

Conductivity of the complexes were measured in the solvent acetonitrile at the concentration 10^{-3} M and all the complexes were found to be non-electrolytic[30] in nature due to low conductivity values in the range 9.8–14.7 ohm^{-1} cm^2 mol^{-1}.

Hence on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic moment data and conductivity measurement the geometry of the complexes of Co(II), Ni(II) and Cu(II) of the type $[M(PAPQSC)_2]$ and $[M(PAPQTSC)_2]$ can be presumed to have octahedral geometry as shown in Fig. 1.



$[M(HL^{1-2})_2]$

M = Co(II), Ni(II) and Cu(II); R = Phenyl, X = O or S

Fig. 1

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