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Spectral Studies of Co(II), Ni(II) and Cu(II) Complexes with 3-phenyl-2-thioquinazoline-4-(3H)-one, Semicarbazone and Thiosemicarbazone†

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A series of complexes of the type $M(HL^1)_2$ and $[M(HL^{2-3})_2X_2]$, where M = Co(II), Ni(II) and Cu(II); HL^1 = 3-phenyl-2-thioquinazoline-4-(3H)-one, HL^2 = 3-phenyl-2-thioquinazoline-4-(3H) semicarbazone; HL^3 = 3-phenyl-2-thioquinazoline-4-(3H) thiosemicarbazone; $X = Cl^-$ and Br^-, have been synthesized and characterised by elemental analysis, molar conductivity, infrared spectra, electronic spectra and magnetic moment data. On the basis of experimental data the complexes of the type $M(L^1)_2$ are found to be square-planar whereas complexes of the type $[M(HL^{2-3})_2X_2]$ are found to be octahedral. The complexes are found to be non-electrolytic in nature on the basis of molar conductivity values.

INTRODUCTION

Metal complexes with ligands containing nitrogen and sulphur donor atoms have been found useful as potential drugs[1–5] and fungicidal agents[6,7]. Considering the importance of transition metal complexes containing N and sulphur donor atoms, in the present paper the author reports the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with ligands 3-phenyl-2 thioquinazoline-4-(3H)-one and its semicarbazone and thiosemicarbazone derivatives.

EXPERIMENTAL

Preparation of ligand HL^1

HL^1 was prepared by modifying the literature method[8]. A solution of anthranilic acid (5 g) in hot ethanol (25 mL) was treated with phenyl isothiocynate (5 g, 4.3 mL). The reaction mixture was heated under reflux for 5 min; a crystalline colourless precipitate separated out from the clear solution. It was heated further under reflux for 1 h for complete precipitation. It was then cooled, filtered, washed with cold ethanol and crystallised with ethyl acetate to furnish 3-phenyl-2-

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thioquinazoline-4(3H)-one as colourless needless (7.5 g, yield 80.9%), m.p. 304–305°C.

Preparation of Ligand HL^2

A suspension of 3-phenyl-2-thioquinazoline-4-(3H)-one (2.5 g; 0.01 m) in hot dioxane (20 mL) was heated with semicarbazide hydrochloride (1.2 g) dissolved in 10% alcoholic solution of sodium acetate. The resulting reaction mixture was heated on water bath, when a crystalline colourless solid began to separate after 1 h. It was heated for a further 30 min for complete precipitation. It was then cooled, filtered, washed with aqueous ethanol, dried and crystallised with dimethyl formamide to furnish a crystalline solid, m.p. = 275–276°C, yield 80%.

Preparation of Ligand HL^3: A suspension of 3-phenyl-2-thioquinazoline-4-(3H)-one (2.5 g; 0.01 mL) in hot dioxane (20 mL) was treated with thiosemicarbazide hydrochloride (1.28 g) dissolved in 10% alcoholic solution of sodium acetate. The resulting reaction mixture was heated on a water bath when a crystalline colourless solid began to separate after 1 h. It was heated for a further 30 min for complete precipitation. It was then cooled, filtered, washed with aqueous ethanol, dried and crystallised with dimethyl formamide to furnish a crystalline solid, m.p. 282–283°C, yield 70%.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting an alcoholic solution of metal halides with the ethanolic solutions of the ligand HL^{1-3} in the molar ratio 1 : 2, yield 60–65%.

All the complexes and ligands were found to be insoluble in water and in most of the common organic solvents but soluble in acetone and tetrahydrofuran. The metal contents of all the complexes were analysed using standard procedures[11] and carbon, hydrogen and nitrogen at C.D.R.I., Lucknow. The infrared spectra of the ligands and the complexes were recorded on Perkin-Elmer spectrophotometer. Magnetic susceptibilities were measured by Gouy method using $Hg[Co(CNS)_4]$ as the calibrant. The conductivity measurements were made on Systronics conductometer model 303 using dimethyl sulphoxide as a solvent. Analytical data, colour, magnetic moment, conductivity measurements and electronic spectral data have been given in Table-1.

RESULTS AND DISCUSSION

Infrared spectra

IR spectra of the ligand and metal complexes have been recorded in the range 4000–600 cm^{-1} in KBr pellets. The spectra have been recorded at I.I.T. Kanpur. The bands of structural significance are recorded in Table-2.

TABLE-1
COLOUR, ANALYTICAL DATA, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA FOR METAL COMPELEXES OF THE TYPE $[M(L^1)_2]$ AND $[M(HL^{2-3})_2X_2]$

Compound/ (Colour)	%Analysis found (Calculated)				μ_{eff} (B.M.)	λ_{max} (electronic) (cm^{-1})	Ω_m ($\Omega' cm^2 mol^1$)
	Metal	C	H	N			
HL^1	—	65.89 (66.14)	3.20 (3.90)	10.83 (11.02)	—	—	—
HL^2	—	57.57 (57.87)	4.11 (4.18)	22.36 (22.50)	—	—	—
HL^3	—	54.89 (55.04)	3.87 (3.97)	21.34 (21.40)	—	—	—
$[Co(HL^1)_2]$ (Dark brown)	9.74 (9.86)	56.17 (56.29)	2.89 (3.01)	9.25 (9.38)	2.6	23200	28
$[Ni(HL^1)_2]$ (Yellowish green)	9.71 (9.83)	56.16 (56.30)	2.89 (3.01)	9.25 (9.38)	Diamag.	21000	27
$[Cu(HL^1)_2]$ (Green)	10.42 (10.50)	55.69 (55.85)	2.89 (2.99)	9.21 (9.30)	1.84	15000 19000	25
$[Co(HL^2)_2Cl_2]$ (Yellowish green)	7.72 (7.83)	47.62 (47.88)	3.32 (3.45)	18.53 (18.62)	5.10	21000	20
$[Co(HL^2)_2Br_2]$ (Deep yellow)	6.88 (7.00)	42.69 (42.81)	2.97 (3.09)	16.57 (16.65)	5.20	21400	24
$[Co(HL^3)_2Cl_2]$ (Brown)	7.43 (7.51)	45.76 (45.92)	3.16 (3.31)	17.73 (17.86)	5.30	21600	26
$[Co(HL^3)_2Br_2]$ (Deep brown)	6.54 (6.75)	41.09 (41.24)	2.74 (2.97)	15.89 (16.04)	5.50	21500	29
$[Ni(HL^2)_2Cl_2]$ (Greenish yellow)	7.63 (7.80)	47.68 (47.89)	3.26 (3.45)	18.54 (18.62)	2.80	11400 15300 23500	27
$[Ni(HL^2)_2Br_2]$ (Chocolate)	6.72 (6.98)	42.69 (42.83)	2.93 (3.09)	16.52 (16.65)	2.92	11200 15600 23800	30
$[Ni(HL^3)_2Cl_2]$ (Yellowish green)	7.28 (7.49)	45.86 (45.94)	3.20 (3.31)	17.76 (17.86)	2.99	11000 15800 24000	22
$[Ni(HL^3)_2Br_2]$ (Brown)	6.61 (6.72)	41.12 (41.26)	2.88 (2.97)	15.93 (16.04)	3.10	11300 16000 25200	23
$[Cu(HL^2)_2Cl_2]$ (Deep green)	8.24 (8.39)	47.33 (47.59)	3.29 (3.43)	18.39 (18.50)	2.00	12500 17300	28
$[Cu(HL^2)_2Br_2]$ (Greenish yellow)	7.38 (7.51)	42.36 (42.58)	3.89 (3.07)	16.46 (16.56)	2.15	12800 17000	21
$[Cu(HL^3)_2Cl_2]$ (Yellowish green)	7.93 (8.05)	45.53 (45.65)	3.20 (3.29)	17.62 (17.75)	2.28	12900 17200	20
$[Cu(HL^3)_2Br_2]$ (Greenish red)	7.12 (7.24)	40.91 (41.03)	2.89 (2.96)	17.11 (17.24)	2.30	13000 17400	24

TABLE-2
SALIENT FEATURES OF IR BANDS OF LIGANDS HL^{1-3} AND ITS COMPLEXES (cm^{-1})

Compounds	ν(N—H)	ν(C=O)	ν(C—S)	ν(C=S)	ν(C=N)
HL^1	–	1715 s,m	760 s,b	–	1680 s,b
HL^2	3220 m,b	1660 s,b	–	–	1480 s,m
HL^3	3460 s	–	–	800 s,b	1500 s,b
$Co(HL^1)_2$	–	1720 s,m	780 m,b	–	1660 s,b
$Ni(HL^1)_2$	–	1725 s,m	780 m,b	–	1620 s,b
$Cu(HL^1)_2$	–	1715 s,m	780 m,b	–	1630 s,b
$Co(HL^2)_2Cl_2$	3220 m,b	1670 m,b	–	–	1450 m
$Co(HL^2)_2Br_2$	3220 m,b	1705 m,b	–	–	1460 m
$Ni(HL^2)_2Cl_2$	3220 m,b	1700 m,b	–	–	1455 m,b
$Ni(HL^2)_2Br_2$	3220 m,b	1690 m,b	–	–	1465 m,b
$Cu(HL^2)_2Cl_2$	3220 m,b	1710 m,b	–	–	1450 s,m
$Cu(HL^2)_2Br_2$	3220 m,b	1700 m,b	–	–	1460 s,m
$Co(HL^3)_2Cl_2$	3460 m,b	–	–	760 s,b	1465 m,b
$Co(HL^3)_2Br_2$	3460 m,s	–	–	765 s,b	1470 m,b
$Ni(HL^3)_2Cl_2$	3460 m,b	–	–	755 s,s	1470 m,b
$Ni(HL^3)_2Br_2$	3460 m,b	–	–	760 m,b	1460 m,b
$Cu(HL^3)_2Cl_2$	3460 s	–	–	770 s,s	1460 s,b
$Cu(HL^3)_2Br_2$	3460 s	–	–	775 ss	1470 s,b

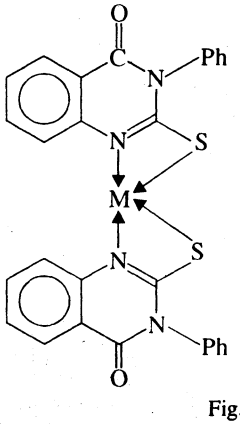
The infrared spectra of the ligand HL^1 exhibit sharp and medium bands at 1720 cm^{-1} which can be assigned to ν(C=O). This remains almost unaffected in the spectra of the complex indicating non-involvement of the carbonyl group in the complex formation. The appearance of two more bands at 760 cm^{-1} and 1680 cm^{-1} can be assigned to ν(C=S) and ν(C=N) respectively. In the spectra of the complexes these bands suffer downward shift indicating coordination takes place through sulphur atom of SH group and N atom of C=N group. This also indicates that the ligand HL^1 has reacted in the mercapto form; the charge of the ligand and metal ions seems to be satisfied by the deprotonation of the S—H group.

The IR spectrum of the ligand HL^2 shows a broad band of medium intensity at 3220 cm^{-1} which can be assigned to ν(N—H) and of the ligand HL^3 shows a band at 3460 cm^{-1} which can also be assigned to ν(N—H) according to literature[12]. The spectra of all the complexes also show this band without any charge, clearly indicating non-involvement of nitrogen atom of amino or imino group in the coordination with metal ion. The spectrum of the ligand HL^2 also shows a sharp and strong band at 1660 cm^{-1} which can be assigned to ν(C=O). In the spectra of the complexes, this band has shifted to a higher frequency region and appears at 1700 cm^{-1} with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of >C=O group of semicarbazone group to the metal ion in an unambiguous manner. The next IR band of structural significance in the spectra of the ligand appears at 1500 cm^{-1}.

This band can be assigned to the ν(C=N) group. This band has also suffered a downward shift 20–30 cm^{-1} and clearly indicates the coordination of the nitrogen to the metal ion.

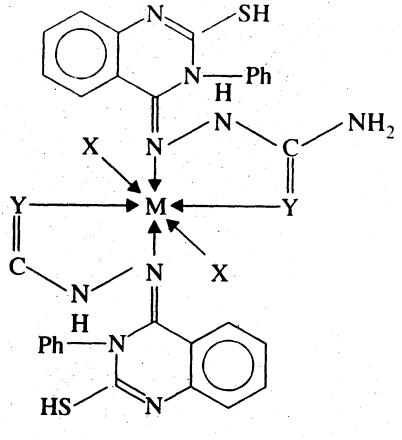
The spectrum of the ligand HL^3 shows strong and broad band at 800 cm^{-1} which can be assigned to ν(C=S). This band suffers a downward shift in the complexes and suggests coordination of the metal ion through sulphur atom of thiosemicarbazone group[13,14]. The next IR band of structural significance in the spectrum of the ligand appears at 1500 cm^{-1}. This band can be ssigned to the ν(C=N) group. This band also suffers a downward shift which clearly indicates the coordination of the nitrogen atom to the metal ion. The remaining bands in the spectrum of the ligands have remain practically unaffected.

The IR spectrum in the far IR region indicates three bands, at 400–300 cm^{-1}, 500–400 cm^{-1} and 600–500 cm^{-1} regions. These bands can be assigned respectively to the ν(M—X) (X = Cl^- or Br^-), ν(M—O) and ν(M—S) stretching frequency. These assignments are supported by Nakamoto[15].



≡$M(L_1)_2$
M = Co(II), Ni(II)
& Cu(I)

Fig. 1



$[M(HL^{2-3})_2X_2]$
M = Co(II), Ni(II) & Cu(II)
X = Cl^- & Br^-
Y = O or S

Fig. 2

The salient features of electronic spectra as well as magnetic moment data are summarised in Table-1. The data indicate complexes of the type $[M(HL^1)_2]$ to be square-planar in geometry whereas those of the type $[M(HL^{2-3})_2X_2]$ are expected to be octahedral. On the basis of above discussion, structure of the complexes of the type $[M(HL^1)_2]$ and $[M(HL^{2-3})_2X_2]$ may be proposed in Figs. 1 and 2.

Conductivities of the complexes were measured in the solvent dimethyl sulphoxide and the complexes of the type $[M(HL^1)_2]$ and $[M(HL^{2-3})_2X_2]$, were found to be non-electrolytic in nature due to low conductivity values in the range 20–30 ohm^{-1} cm^2 mol^{-1}. The conductivity measurements of the above mentioned complexes also support the structural assignment on the basis of IR and electronic spectra and magnetic susceptibility value.

Hence on the basis of infrared spectra, magnetic moment and on the electronic spectra the geometry of Co(II), Ni(II) and Cu(II) complexes of the type $[M(HL^1)_2]$ are square planer in geometry whereas the complexes of the type $[M(HL^{2-3})_2X_2]$ are octahedral in geometry.

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