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Synthesis and Characterisation of Co(II) Complexes with Some New Quinazolone Oximes

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A series of complexes having the formula $Co(HL)_2$, $Co(HL)_2X_2$ and $Co(HL)_2Y_2$, where HL = 3-phenyl-quinazolone-4(3H) one-2-carboxaldehydoxime, $X = Cl^-$, Br^-, I^-, NO_3^- and ClO_4^- and $Y = NH_3$ or pyridine have been synthesized by allowing ethanolic solutions of cobalt(II) salts to react with solution of the ligand in tetrahydrofuran in the molar ratio 1 : 2 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 $[Co(HL)_2]$ are found to be square planar whereas complexes of the type $[Co(HL)_2X_2]$ and $[Co(HL)_2Y_2]$ are found to be octahedral. The complexes are found to be non-electrolytic in nature on the basis of low value of molar conductivities.

INTRODUCTION

Quinazolone derivatives show a wide variety of physiological and pharmacological properties such as central nervous system depressant[1–3], anticonvulsant[4–5], anticarcinogenic[6], muscle relaxant[6, 7] and antiparkinsonian[8, 9] activities. In view of these observations and in continuation of our earlier research work on transition metal complexes with oximes[10–13], it was thought worthwhile to synthesize some new quinazolone derivative and used as chelating ligands to form coordination compound with cobalt(II).

EXPERIMENTAL

All the chemicals and solvents used for synthesis were LR grade except 3-phenyl quinazolone-4(3H), a carboxaldehyde, which was prepared by reported method[14].

Preparation of Ligand HL

3-Phenyl quinazolone-4(3H)-one 2-carboxaldehyde (1 g) dissolved in freshly distilled pyridine (10 mL) was treated with hydroxylamine hydrochloride (0.32 g) and the reaction mixture was kept over night. It was poured into crushed ice, a white solid was obtained which was filtered, wasned with water and crystallised from ethyl acetate to afford 3-phenyl quinazolone-4-(3H)one-2-carboxaldehydoxime as colourless needles (0.8 g; 75.4%), m.p. 205–206°C. The compound was soluble in aqueous alkali and reprecipitated on acidification having no change in melting point.

Preparation of the complexes

The first series of complexes have been formed by reacting an ethanolic solution of cobalt acetate with the ligand dissolved in the tetrahydrofuran in the

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molar ratio 1 : 2 and the second series of the complexes have been formed by treating an ethanolic solution of the corresponding cobalt salt with ligand dissolved in tetrahydrofuran in the molar ratio 1 : 2. The third series of the complexes have been formed when metal complexes of the first series were refluxed with ammonia or pyridine in the molar ratio 1 : 2.

Elemental analysis and metal contents of the complexes have been determined by standard methods[15]. The infrared spectra of ligands and the complexes were recorded on a Perkin-Elmer spectrophotometer. Electronic spectra are recorded on a Cary-2390 spectrophotometer. Magnetic susceptibilities are measured by Gouy method using mercury tetra isothiocyanato cobaltate(II) as the calibrant. The conductivity measurements are made on a systronic conductometer model 303 using DMSO as a solvent. Analytical data, colour, electronic spectral data, conductivity measurements and magnetic moments are recorded in Table-1.

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA OF COBALT(II) COMPLEXES WITH OXIME (HL)

Compound (Colour)	% Analysis, found (calculated)				λ_{max} electronic cm^{-1}	Λ_m ohm^{-1} cm^{-1} mol^{-1}	μ_{eff} (B.M.)
	Co	N	C	H			
HL	—	15.71 (15.84)	67.83 (67.92)	4.02 (4.15)	—	—	—
$Co(HL)_2$ (Green)	—9,83 (10.00)	14.08 (14.26)	60.89 (61.12)	3.61 (3.73)	20500	21	2.20
$Co(HL)_2Cl_2$ (Green)	8.84 (8.93)	12.61 (12.72)	54.42 (54.55)	3.21 (3.33)	18500	30	4.82
$Co(HL)_2Br_2$ (Yellowish green)	7.74 (7.87)	11.06 (11.21)	47.89 (48.08)	2.84 (2.93)	19200	29	4.92
$Co(HL)_2I_2$ (Dark brown)	6.83 (6.99)	9.79 (9.96)	42.56 (42.71)	2.53 (2.61)	19400	27	4.85
$Co(HL)_2(NO_3)_2$ (Greenish brown)	8.21 (8.35)	15.68 (15.87)	50.86 (51.03)	2.98 (3.11)	19600	25	5.00
$Co(HL)_2(ClO_4)_2$ (Yellowish red)	7.36 (7.47)	10.49 (10.66)	45.47 (45.68)	2.68 (2.79)	19100	23	4.95
$Co(HL)_2(NH_3)_2$ (Red)	9.31 (9.46)	17.76 (17.97)	57.53 (57.79)	4.31 (4.40)	18600	20	4.87
$Co(HL)_2(Py)_2$ (Green)	7.69 (7.88)	14.67 (14.99)	64.03 (64.26)	4.12 (4.28)	18700	24	4.93

RESULTS AND DISCUSSION

The infrared spectra of the ligand exhibit sharp and strong peaks at 3200 cm^{-1}, 1700 cm^{-1}, 1600 cm^{-1}, 1500 cm^{-1} and 1100 cm^{-1} which can be assigned to ν(O—H), ν(C=O), ν(C=N) (azomethine), ν(C=N) (oxime) and ν(N—O) respectively which is in agreement with early reports[16].

In the spectra of the complexes ν(C=N) band indicates a significant red shift whereas ν(N—O), ν(C=O) and ν(O—H) remain almost unperturbed indicating co-ordination to take place through N-atom of azomethine as well as N-atom of oxime. Additional peak due to ν(M—N) and ν(M—X) appears in the spectra of the complexes in the far infrared region[17, 18]. The complexes of the type $[Co(HL)_2Y_2]$ show additional band at 1680 cm^{-1} and 1580 cm^{-1} suggesting co-ordination of ligands pyridine and ammonia through N-atom[19]. The infrared spectral data are recorded in Table-2.

TABLE-2
INFRARED SPECTRAL DATA OF LIGAND (HL) AND Co(II) COMPLEXES

Compounds	ν(O—H)	ν(C=N) (azomethine)	ν(C=N) (oxime)	ν(C=O)	ν(N—O)	ν(M—N)
HL	3200b	1600s	1500s	1700s	1100m	–
$[Co(HL)_2]$	3205b	1630s	1480m	1700s	1105m	610s
$[Co(HL)_2Cl_2]$	3200b	1660s	1475m	1700s	1105m	610s
$[Co(HL)_2Br_2]$	3200b	1625s	1470m	1700s	1105m	600s
$[Co(HL)_2I_2]$	3205b	1645s	1475m	1705s	1005m	610s
$[Co(HL)_2(NO_3)_2]$	3200b	1620s	1480m	1710s	1100m	610s
$[Co(HL)_2(ClO_4)_2]$	3205b	1635s	1480m	1710s	1100m	615s
$[Co(HL)_2(NH_3)_2]$	3205b	1640s	1470m	1715s	1105m	620s
$[Co(HL)_2(Py_2)_2]$	3200b	1640s	1480m	1705s	1105m	600s

Electronic spectra and magnetic moment of the complexes

The electronic spectra of the complexes of the type $[Co(HL)_2]$ show a broad band in the region 20,000 cm^{-1} which suggests Co(II) ion to be in a square planar environment and the band presumably arises due to the transition $^2A_{1g} \rightarrow {}^1b_{1g}$ $d_{(x^2-y^2)}$ where $^2A_{1g}$ is probably the ground state for low spin cobalt(II) ion in a square planar environment and b_{1g} is the empty antibonding orbital. The electronic spectra of the complexes of the type $[Co(HL)_2X_2]$ and $[Co(HL)_2Y_2]$ exhibits a multiplet band in the region 20,000–18,500 cm^{-1}, the band width spreading over 2000 cm^{-1} which corresponds to an octahedral geometry. This band can be assigned to the transition $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$. The magnetic moment data of the complexes of the type $[Co(HL)_2]$ is 2.2 B.M. and suggest square planar geometry. The magnetic moment data of the complexes of the type $[Co(HL)_2X_2]$ and $[Co(HL)_2Y_2]$ lie in the range of 4.82 to 5.00 B.M. which indicate the octahedral structure of these complexes.

Conductivity of the complexes was measured in the solvent dimethyl sulphoxide and the complexes of the type $[Co(HL)_2]$, $[Co(HL)_2X_2]$ and $[Co(HL)_2Y_2]$ have conductivity value in the range of 20–30 ohm^{-1} cm^2 mol^{-1} and indicate them to be non-electrolytic in nature due to low value of conductivity.

On the basis of elemental analysis data, infrared spectral data, electronic spectra and magnetic moment data indicate that the complexes of type [Co(HL)$_2$] are square planar in geometry whereas the complexes of the type [Co(HL)$_2$X$_2$] and [Co(HL)$_2$Y$_2$] are octahedral in geometry. Representative structures of both types has been shown in Figs. 1 to 4.

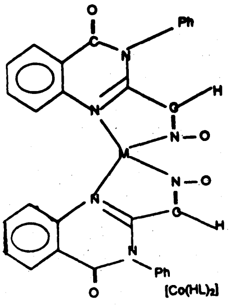

Fig. 1

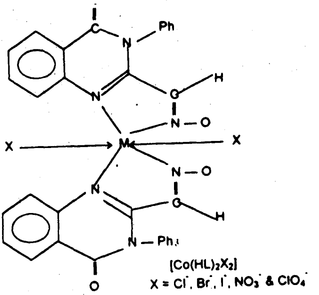

Fig. 2

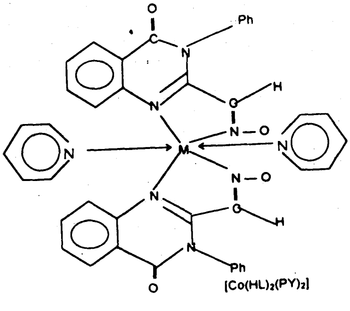

Fig. 3

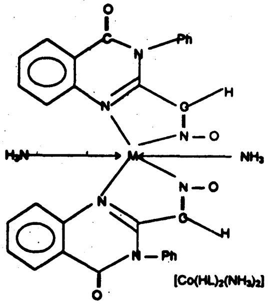

Fig. 4

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