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Coordination Compounds of Co(II), Ni(II) and Cu(II) with Thiosemicarbazone of a Series of Quinazolone Derivatives: Their Preparation, Characterization and Structural Investigation

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Complexes of Co(II), Ni(II) and Cu(II) with 2-phenyl-[-3-(hydroxyethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PHEQTSC), 2-phenyl-6,8-dibromo-[3-(hydroxy-ethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PDBHEQTSC) and 2-phenyl-6-bromo-[3-(hydroxyethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PBHEQTSC) have been synthesized and characterised on the basis of elemental analysis, IR, electronic spectra, conductivity and magnetic moment data. The ligand can function as a binegative tridentate chelating agent coordinating through nitrogen, oxygen and sulphur atoms with the metal ions forming complexes in molar ratio 2 : 1 having the empirical formula $[M\{L^{1-3}\}_2]$ and can be presumed to have octahedral geometry.

INTRODUCTION

Quinazolone derivatives show a wide variety of physiological and pharmacological properties such as antitubercular, antibacterial[1, 2] and for the production of some commercial dyes and pigments are used both on natural and man-made fibres[3, 4]. The biological activity of a ligand is altered manyfold on coordinating with a suitable metal ion[5].

In view of these observations and in continuation of earlier research work on transition metal complexes with quinazolone derivatives[6], in the present paper the synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with ligands 2-phenyl-[-3-(hydroxyethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PHEQTSC), 2-phenyl-6,8-dibromo-[3-(hydroxy-ethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PDBHEQTSC) and 2-phenyl-6-bromo-[3-(hydroxyethyl)]-3,1-(4H)-quinazoline-4-thiosemicarbazone (PBHEQTSC) are reported.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade and the solvents were used without further purification. The ligand PHEQTSC, PDBHQTSC and PBHEQTSC was prepared by earlier reported method[7, 8].

Preparation of the complexes

The respective ligand was dissolved in tetrahydrofuran and the appropriate

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metal salts were dissolved in ethanol and mixed in a conical flask. The mixture were refluxed on a water bath for 3 to 4 h, till the solids were separated out after which the contents were kept on a water bath for 30 min. It was then cooled, filtered, washed with ethanol followed by ether. The solids were dried and then analysed.

The complexes were analysed using standard procedures[9] and carbon, hydrogen and nitrogen by semi-micro-combustion methods. Analytical data, colour, conductivity value, electronic spectral data and magnetic moments are recorded in Table-1.

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

Compound/Colour	% Analysis, Found (Calculated)				λ_{max} electronic (cm^{-1})	μ_{eff} (B.M.)	Ω_{max} ($ohm^{-1}\ cm^{-1}\ mol^{-1}$)
	M	C	N	H			
PHEQTSC(L^1) Yellow	—	63.06 (63.35)	21.69 (21.73)	4.83 (4.96)	—	—	—
PDBHEQTSC(L^2) Yellow	—	50.86 (51.01)	17.34 (17.50)	3.39 (3.50)	—	—	—
PBHEQTSC(L^3) Yellow	—	56.37 (56.51)	19.24 (19.39)	4.02 (4.15)	—	—	—
$[Co(PHEQTSC)_2]$ Yellowish red	8.26 (8.37)	57.24 (57.47)	19.79 (19.91)	4.42 (4.55)	9310 15430	4.82	12.6
$[Co(PDBHEQTSC)_2]$ Brown	6.67 (6.85)	47.39 (47.50)	16.11 (16.30)	3.13 (3.26)	9330 13400	4.71	13.9
$[Co(PBHEQTSC)_2]$ Dark brown	7.47 (7.54)	52.09 (52.25)	17.82 (17.93)	3.71 (3.84)	9350 15420	4.79	11.2
$[Ni(PHEQTSC)_2]$ Violet	8.23 (8.35)	57.89 (58.06)	19.84 (19.92)	3.99 (4.09)	10310 16700 23600	2.83	14.7
$[Ni(PDBHEQTSC)_2]$ Reddish brown	6.74 (6.83)	47.34 (47.52)	16.21 (16.30)	3.11 (3.26)	10330 16900 23620	3.10	13.6
$[Ni(PBHEQTSC)_2]$ Dark green	7.43 (7.51)	52.01 (52.26)	17.82 (17.93)	3.79 (3.84)	10320 16800 23610	2.86	11.7
$[Cu(PHEQTSC)_2]$ Light green	8.89 (8.98)	57.43 (57.66)	19.63 (19.78)	4.44 (4.52)	14510	1.92	10.7
$[Cu(PDBHEQTSC)_2]$ Green	7.24 (7.35)	47.18 (47.25)	16.13 (16.21)	3.15 (3.24)	14500	1.81	14.1
$[Cu(PBHEQTSC)_2]$ Deep green	8.01 (8.08)	51.76 (51.94)	17.68 (17.82)	3.69 (3.81)	14520	1.99	10.9

The IR spectra of the ligands as well as metal complexes were recorded on Beckman IR-20 spectrophotometer and data have been given in Table-2. The conductivity measurement made on a Systronics conductometer model 303 using

dimethyl sulphoxide as a solvent. Magnetic moments were measured by Gouy method using mercury tetraisothiocyanato cobaltate as the calibrant.

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

Compounds	ν(O—H)	ν(N—H)	ν(C=N)	ν(C=S)	ν(M—N)	ν(M—O)	ν(M—S)
PHEQTSC (L^1)	3400 s	3200 s	1640 s	760 s			
PDBHEQTSC (L^2)	3420 s	3205 s	1645 s	769 s			
PBHEQTSC (L^3)	3410 s	3210 s	1640 s	750 s			
[Co(PHEQTSC)$_2$]		3215 s	1620 s	720 s	522 m,b	410 m,b	370 m,b
[Co(PDBHEQTSC)$_2$]		3220 s	1615 s	715 s	516 m,b	470 m,b	360 m,b
[Co(PBHEQTSC)$_2$]		3210 s	1605 s	720 s	520 m,b	435 m,b	355 m,b
[Ni(PHEQTSC)$_2$]		3220 s	1610 s	705 s,b	532 m,b	425 m,b	380 m,b
[Ni(PDBHEQTSC)$_2$]		3205 s	1600 s,b	700 s	540 m,b	420 m,b	390 m,b
[Ni(PBHEQTSC)$_2$]		3200 s	1630 s	710 s	526 m,b	415 m,b	370 m,b
[Cu(PHEQTSC)$_2$]		3210 s	1630 s	725 s	527 m,b	420 m,b	360 m,s
[Cu(PDBHEQTSC)$_2$]		3205 s	1600 s	705 s	536 m,b	410 m,s	350 m,s
[Cu(PBHEQTSC)$_2$]		3200 s	1620 s	710 s	540 m,b	425 m,b	340 m,b

RESULTS AND DISCUSSION

In view of the previous assignments[10] the thiosemicarbazone cordinate through S and N^1 (>C=N^1—N^2H—(C=X)—N^3<). The IR spectra of all the three ligands exhibit sharp and strong peaks at 3400 cm^{-1}, 3200 cm^{-1}, 1640 cm^{-1}, 760 cm^{-1} which can be assigned to ν(O—H), ν(N—H), ν(C=N) and ν(C=S) respectively. The absence of absorption bands in region greater than 3400 cm^{-1} of IR spectra of complexes suggests that oxygen atom of hydroxyl group (hydroxyl ethyl moiety of quinazolone side chain) is involved in coordination with metal ion after deprotonation. In the spectra of the complexes ν(C=N) and ν(C=S) peaks indicate a significant red shift whereas ν(N—H) remains almost unaffected. The above observations clearly indicate that the ligands PHEQTSC, PDBHEQTSC and PBHEQTSC can coordinate through N-atom of the azomethine group, sulphur atom of thiosemicarbazone moiety as well as oxygen atom of hydroxyl group. Additional peaks due to ν(M—N),[11] ν(M—O)[12] and ν(M—S)[13] appear in the spectra of the complexes in the far IR region.

Electronic spectra and magnetic moment

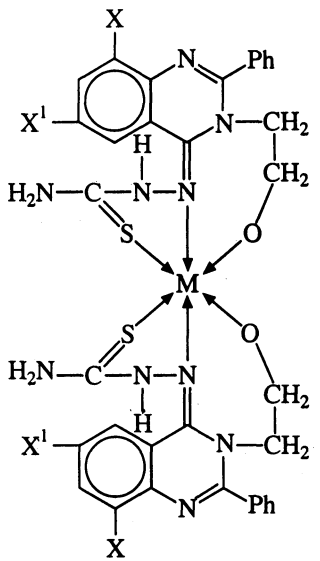
The room temperature magnetic moment data of Co(II), Ni(II) and Cu(II) complexes are found to be 4.71–4.83, 2.86–3.10 and 1.81–1.99 respectively[14]. The Co(II) complexes exhibit bands at 9300 and 15400 cm^{-1} corresponding to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ respectively[15]. The Ni(II) complexes exhibit simple spectra consisting of three transitions from

$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels. These are reported to occur in the following regions: 10300, 16900 and 23600 cm^{-1} corresponding to that of octahedral complexes[15]. The Cu(II) complexes show a broad band around 15400 cm^{-1} which may be assigned[15] to the transition $^2E_g \rightarrow {}^2T_{1g}$. The electronic spectra as well as magnetic moment data suggest octahedral geometry for all the complexes.

Conductivity measurement

Conductivity of the complexes is measured in the solvent DMSO and the complexes were found to be non-electrolytic in nature due to low conductivity values in the range 10–15 ohm^{-1} cm^2 mol^{-1}.

Hence on the basis of IR spectra, electronic spectra, magnetic moment data and conductivity measurements the geometry of the Co(II), Ni(II) and Cu(II) complexes of all the three ligands is proposed to be octahedral and shown in Fig. 1.



$[M(L^{1-3})_2]$

$(M = Co^{2+}, Ni^{2+} \text{ or } Cu^{2+})$

Fig. 1

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