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Synthesis and Characterization of Some Metal Complexes of Co(II), Ni(II) and Cu(II) with 2-Benzoylhydrazono-4-Thiazolidinone

R.K. PATEL
Department of Chemistry, Regional Engineering College, Rourkela-769 008, India

The metal complexes of the type ML_2X_2 where M = Co(II), Ni(II), Cu(II) X = Cl^-, Br^-, NO_3^- or ClO_4^- and L = 2-benzoyl-hydrazono-4-thiazolidinone are synthesised. The IR spectral data suggest the coordination of ligand through the O and S atom. The UV spectral data and magnetic moment value indicate the octahedral geometry of the complexes.

INTRODUCTION

It is reported that the thiazolidinone compounds show antifungal activity[1]. The complexes of transition metal ions with sulphur and/or oxygen donor ligands show significant antifungal and antimicrobial activities[2, 3]. Keeping all the above in view, the present work has been undertaken.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. Elemental analyses for C, H, N and S were carried out by Ce-440 Elemental Analyser. Metals were estimated by standard methods. Molecular weights were determined by Rast's camphor method. Room temperature magnetic susceptibilities were determined by using Gouy's method. The diamagnetic corrections were made using Pascal's constants. Molar conductance values were determined by CL-301 systronic conductivity bridge. The IR spectra were recorded on a Perkin-Elmer 398 spectrophotometer and electronic spectra (DMF) on a Toshiniwal CL-54 spectrophotometer. The colour, magnetic moment and analytical data of complexes are summarised in Table-1.

Preparation of ligand: The ligand was prepared by taking a mixture of phenylthiosemicarbazide (0.01 mol), α-chloroacetic acid (0.01 mol, 0.94 g) and anhydrous sodium acetate (0.05 g) in ethanolic solution (50 mL) and refluxing on a water bath for 4 h. The resulting solution was concentrated, cooled and poured into ice-cold water. The resulting colourless solid was dried and crystallised from ethanol.

Preparation of metal complexes: The corresponding metal salt MX_2 where M = Co(II), Ni(II) and Cu(II) and X = Cl^-, Br^-, NO_3^- and ClO_4^- and ligand in 1 : 2 molar ratio were refluxed in ethanolic solution for 1/2 h. The resulting coloured

complexes were filtered, washed with ethanol and dried in vacuum over fused calcium chloride.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Complex (Colour)	μ_{eff} (BM)	Analysis %: Found/(Calcd.)					
		M	C	H	N	S	Cl^-/Br^-
BHTZ (Faint yellow)	—	—	51.6 (51.3)	3.6 (3.4)	18.2 (17.9)	13.9 (13.7)	—
$Co(BHTZ)_2Cl_2$ (Bluish white)	4.83	9.4 (9.9)	40.5 (40.1)	3.0 (2.7)	14.3 (14.0)	11.0 (10.7)	12.1 (11.9)
$Co(BHTZ)_2Br_2$ (Faint blue)	4.92	9.0 (8.6)	35.4 (35.0)	2.7 (2.3)	12.5 (12.2)	9.6 (9.3)	23.3 (23.1)
$Co(BHTZ)_2(ClO_4)_2$ (Dark yellow)	4.82	8.4 (8.1)	33.4 (33.1)	2.5 (2.2)	12.0 (11.6)	9.1 (8.8)	10.2 (9.8)
$Co(BHTZ)_2(NO_3)_2$ (Olive green)	4.80	9.4 (9.0)	37.2 (36.9)	2.8 (2.5)	17.5 (17.2)	9.0 (9.8)	—
$Ni(BHTZ)_2Cl_2$ (Canary yellow)	3.18	9.9 (9.8)	40.6 (40.2)	2.9 (2.7)	14.4 (14.1)	11.0 (10.7)	12.2 (11.9)
$Ni(BHTZ)_2Br_2$ (Brown)	3.02	8.9 (8.6)	35.4 (35.0)	2.6 (2.3)	12.5 (12.2)	9.6 (9.3)	23.6 (23.3)
$Ni(BHTZ)_2(ClO_4)_2$ (Violet)	3.16	8.5 (8.1)	33.5 (33.2)	2.4 (2.2)	11.8 (11.5)	9.1 (8.8)	10.1 (9.8)
$Ni(BHTZ)_2(NO_3)_2$ (Brownish yellow)	3.04	9.6 (9.1)	37.3 (36.9)	2.8 (2.4)	17.6 (17.2)	10.1 (9.8)	—
$Cu(BHTZ)_2Cl_2$ (Steel grey)	1.76	10.9 (10.5)	40.1 (39.8)	3.0 (2.6)	14.1 (13.9)	11.0 (10.6)	12.1 (11.8)
$Cu(BHTZ)_2Br_2$ (Grey)	1.74	9.6 (9.2)	35.0 (34.7)	2.7 (2.3)	12.5 (12.2)	9.6 (9.3)	23.4 (23.1)
$Cu(BHTZ)_2(ClO_4)_2$ (Yellow)	1.76	9.1 (8.7)	31.2 (32.9)	2.6 (2.2)	12.0 (11.5)	9.0 (8.8)	10.1 (9.7)
$Cu(BHTZ)_2(NO_3)_2$ (Green)	1.71	10.1 (9.7)	37.0 (36.6)	2.7 (2.4)	17.4 (17.1)	10.1 (9.8)	—

RESULTS AND DISCUSSION

The analytical data (Table-1) suggest that the stoichiometry of the complexes is ML_2X_2 where M = Co(II), Ni(II), Cu(II), L = 2-benzoylhydrazono-4-thiazolidinone, X = Cl^-, Br^-, NO_3^- and ClO_4^-. All the complexes were insoluble in water but soluble in organic solvents like DMF. Molar conductance values (4–60 $\Omega^{-1}cm^2$ $mole^{-1}$) of all the complexes indicate their non-electrolyte nature. The molecular weight measurement by Rast's camphor method indicates the monomeric nature of the complexes.

The infrared spectra of the ligand show a broad band at 3400 cm^{-1} which can be assigned[4] to ν(NH). The medium and sharp bands at 3010–2900 cm^{-1} are assigned to $\nu(CH_2)$ stretching vibration. The next two bands at 1680 and 1650 cm^{-1} are due to free amidic and thiazolidinone carbonyl respectively[5]. There are two twin bands at 1585 and 1560 cm^{-1} which can be assigned to the cyclic ν(C=N) stretching vibration[6] of thiazolidinone ring. The 840 cm^{-1} band was due to ν(C—S) of the thiazolidinone ring[7].

In the spectra of the metal complexes, the band at 1650 cm^{-1} in free ligand is shifted to 1620 cm^{-1} indicating the coordination of free amidic carbonyl oxygen atom. The band at 840 cm^{-1} is shifted to lower frequency by 40–50 cm^{-1} indicate that the sulphur atom of thiazolidinone is involved in the bonding. The other bands of the ligand remain intact or change their position in an irregular way. The new bands at far infrared region appearing at 580–520 cm^{-1} and 370–345 cm^{-1} of the complexes were tentatively assigned to ν(M—O) and ν(M—S) stretches respectively[8, 9]. The nitrato complexes show bands at 1500, 1300, 1330 and 930 cm^{-1}, whereas perchlorato complexes show bands at 1200, 1130 and 1000 cm^{-1} which unanimously suggest the presence of coordinated nitrato[10] and perchlorate group[11]. The above spectral data suggest the coordination of ligand to metal through thiazolidinone sulphur and carbonyl oxygen atom.

Electronic Spectra: The Co(II) complexes exhibit bands at *ca.* 8900, 18000 and 20800 cm^{-1} which can be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\ \nu_1$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\ \nu_2$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\ \nu_3$ respectively in an approximately octahedral field[12]. Another band observed at *ca.* 27000 cm^{-1} may be assigned to charge transfer band. The Racah's parameters are calculated and found to be Dq = 905 cm^{-1}, B = 796 cm^{-1}, β = 0.82, β° = 18, $\nu_2/\nu_1 = 2$. The values further support the octahedral structure of these complexes. The Co(II) complexes possess magnetic moment values of 4.80–4.92 B.M. as expected for octahedral Co(II). The Ni(II) complexes show three well resolved bands observed at *ca.* 9800, 16400 and 25800 cm^{-1} are attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)\ \nu_1$, $^3A_{2g}(F) \rightarrow {}^2T_{1g}(F)\ \nu_2$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)\ \nu_3$ transitions respectively under an octahedral environment around Ni(II)[13]. The complexes of Ni(II) have the magnetic moment values of 3.02–3.18 BM, which are in accordance with the octahedral complexes. As expected the Racah's parameters are found as Dq = 980 cm^{-1}, B = 810.4 cm^{-1}, β = 0.7674, β° = 23.26, $\nu_2/\nu_1 = 1.67$ which support the above structure. The Cu(II) complexes show a broad band at *ca.* 14000 cm^{-1} which can be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$. Another band is observed at *ca.* 26500 cm^{-1} which may be due to charge transfer band. It is reported that the Cu(II) complexes in an octahedral environment show broad band around 12500 cm^{-1}, but it is highly sensitive to John-Teller distortion. The band in the present study indicates that the distortion brought about in the complexes is due to John-Teller effect[13]. The magnetic moment values of Cu(II) complexes possess normal value of 1.71–1.79 BM as expected for octahedral Cu(II).

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