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Synthesis and Characterization of Complexes of Cobalt(II), Nickel(II) and Copper(II) with Substituted Pyrazoline

N.S. CHATTREE and T.C. SHARMA*
School of Studies in Chemistry
Vikram University, Ujjain-456 010, India

Crystalline complexes of Co(II), Ni(II) and Cu(II) with ligand 3-phenyl 5-(2-hydroxyphenyl) pyrazoline have been synthesised by extraction method in a M : L ratio of 1 : 2. Finally extracted complexes are refluxed in benzene. The cobalt and copper complexes are paramagnetic whereas nickel is dimagnetic. The complexes of Co(II), Ni(II) and Cu(II) has been assigned as ML_2 type showing Cu(II) of square-planer species and Co(II) and Ni(II) of six coordinated octahedral geometry.

INTRODUCTION

Certain pyrazolines have been used as non-toxic local anaesthetics[1], some have been reported for their toxicity[2], whereas some of them are also used as antioxidants[3], lubricating oil, dyes, catalysts of decarboxylation, inhibitors in plant growth, etc. Shah *et al.*[4–6] have studied transition metal complexes with substituted pyrazolines. The present paper deals with the preparation and characterization of complexes of Co(II), Ni(II) and Cu(II) with 3-phenyl 5-(2-hydroxyphenyl) pyrozoline.

EXPERIMENTAL

All the chemicals used were of reagent grade quality. The ligand 3-phenyl 5-(2-hydroxyphenyl) pyrazoline is synthesised by refluxing 2-hydroxy chalcone and hydrazine hydrate (100%) in presence of ethanol as a solvent and characterised on the basis of spectral data (IR and ^1H NMR) and elemental analysis.

The following general procedure is adopted for the preparation of all the complexes. 0.01 M (10 ml) metal salt solution is added dropwise to a 0.01 M (20 ml) solution of ligand in benzene with constant stirring. On standing, the benzene layer is separated by separating funnel. This reaction mixture was refluxed on a water bath for 5–6 h., cooled, then evaporated on an evaporating disc up to dryness. The solid obtained was washed several times with hot water and benzene until the washings were free from the excess ligand. These complexes were finally dried *in vacuo* over fused calcium chloride.

RESULTS AND DISCUSSIONS

All the complexes are crystalline, stable at room temperature, non-hygroscopic, thermally stable to varying degrees, insoluble in water and soluble in most of the organic solvents. The elemental analysis (Table 1) suggests 1 : 2 (metal : ligand) stoichiometry for all the complexes. The molecular conductances of 0.001 M solutions of the complexes in DMF are in the range of 7–22 ohm^{-1} cm^2 mol^{-1} indicating their non-ionic nature[7].

IR spectrum of lignad (Table 2) shows a medium and broad band around 3080 cm^{-1} which is assigned as intramolecular hydrogen bonded –OH. The bands at 1595 cm^{-1} and 3320 cm^{-1} can be attributed to (>C=N) and (>NH) vibrations. The aromatic phenolic group is observed at 1400 cm^{-1}.[8] The complexes show additional peaks at 470 cm^{-1}, which may be due to M–N stretching and 690 cm^{-1} correspond to M–O stretching[9–11].

TABLE 1

ANALYTICAL DATA OF THE COMPOUND

Compound	Found (Calc) %			
	Metal	C	H	N
$Co(Py)_2$	11.50 (11.77)	67.17 (66.72)	5.72 (5.18)	11.05 (10.37)
$Ni(Py)_2$	10.65 (10.67)	70.22 (67.32)	6.13 (5.23)	11.25 (10.47)
$Cu(Py)_2$	10.97 (11.01)	67.73 (67.29)	5.76 (5.22)	11.63 (10.46)

TABLE 2

PERTINENT IR DATA (cm^{-1}) OF THE COMPOUNDS

Assignment	Ligand	$Co(Py)_2$	$Ni(Py)_2$	$Cu(Py)_2$
–OH*	3080	—	—	—
(>NH)	3320	—	—	—
(M–O)	—	690	685	685
(M–N)	—	470	470	470
(>C=N)	1595	1600	1600	1600

*Intramolecular hydrogen bonding.

The disappearance of –OH band in the metal complexes indicates complexes formation by deprotonation of –OH[12]. The > NH band in the metal complexes also disappears suggest the removal of proton from the > NH group.

The Co(II) and Cu(II) complexes possess magnetic moments corresponding to one unpaired electron while Ni(II) is diamagnetic.

Electronic spectral data of Co(II) consist of three bands around 8000, 15000–16000 and 19700 cm^{-1} which may be assigned to the spin allowed transitions $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$; $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_2)$; and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ respectively, characteristic of octahedral geometry around Co(II)[13].

Electronic spectra of Ni(II) complexes exhibit three bands around 9544, 15200 and 23200 cm^{-1} which may be assigned to the transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)(\nu_1)$ $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)(\nu_2)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)(\nu_3)$ respectively, characteristic of octahedral geometry around Ni(II).[14]

The electronic spectra of Cu(II) complex exhibit strong bands around 14500 and 2800 cm^{-1} which may be assigned to $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ transitions, respectively, characteristic of square-planer geometry[15].

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