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NOTE

Structural Investigations on Co(II), Ni(II) and Cu(II) Biligand Coordination Compounds with 7-Hydroxy-4-Phenyl-6-(α-Naphthyl)-Aminomethyl Coumarin as Primary and 4-Nitroso-1-Hydroxy-2-Naphthoic Acid as Secondary Ligand

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Biligand coordination compounds of Co(II), Ni(II) and Cu(II), with 7-hydroxy-4-phenyl-6-(α-naphthyl)-aminomethyl coumarin (L′ H) as primary and 4-nitroso-1-hydroxy-2-naphthoic acid (L'' H) as secondary ligand have been synthesised. Analytical data suggested 1 : 1 : 1 (M : L′ H : L″ H) stoichiometric composition for the isolated compounds. The conductance data (3.8–4.7 ohm^{-1} cm^2/mol^{-1}) in DMF at the concentration 10^{-3} M indicate non-electrolytic behaviour of the coordination compounds. Magnetic and spectral studies show that the Cu(II) complex is square-planar while Ni(II) and Co(II) complexes are octahedral. TG studies show the presence of two moles of coordinated water in Ni(II) and Co(II) complexes.

Mannich bases prepared from coumarin derivatives by Shah *et al.*[1] have been found to exhibit interesting antibacterial activity. Nitroso-naphthols are widely used as analytical reagents, and they are capable of forming chelates with a number of transition metal ions[2–6]. 1-Hydroxy-2-naphthoic acid was used for the spectrophotometric determination[7] of Fe(III) and U(VI). The present paper deals with the biligand coordination compounds with coumarin Mannich base as primary and nitroso-naphthol derivative as co-ligand.

7-Hydroxy-4-phenyl-6 (α-naphthyl)-amino methyl coumarin was synthesised by refluxing a mixture of 7-hydroxy-4-phenyl coumarin (0.01 mol), α-napthylamine (0.01 mol) and formalin (40% in aqueous ethanol) for 2 h and crystallising the solid product from DMF. Yield 60%, m.p. 198°C. 4-Nitroso-1-hydroxy-2-naphthoic acid was prepared by nitrosation of 1-hydroxy-2-naphthoic acid using the reported procedure.[8] Conductivity measurements were carried out on Toshniwal conductivity bridge. IR spectra were recorded on Perkin-Elmer 621

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spectrophotometer. The magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for diamagnetism[9].

General preparation of the coordination compounds: An aqueous ethanolic (60% v/v) solution of respective metal salt (10 mmol) was refluxed with the methanolic solution of Mannich base (10 mmol) for *ca.* 30–40 min at 80–90°C. The solid products obtained were washed with methanol, dry ether and dried *in vacuo*.

The biligand coordination compounds were prepared by refluxing an aqueous suspension of the complex formed as above with the hot ethanolic solution of 4-nitroso-1-hydroxy-2-naphthoic acid (10 mmol) for *ca.* 2 h over a water bath and cooling to room temperature. The separated chelates were washed, crystallised from absolute ethanol and dried.

Analytical data (Table-1) suggested 1 : 1 : 1 (M-L′-L″) stoichiometric composition for the complexes. The molar conductance data (Table-1) in DMF at the concentration 10^{-3} M revealed their non-electrolytic behaviour. The magnetic moment value of the Cu(II) complex (1.84 B.M.) is consistent with the square-planar geometry, while the magnetic moment values of Ni(II) and Co(II) complexes are 2.92 and 4.58 B.M. which are in better agreement with the octahedral geometry of these complexes.

Thu Cu(II) complex exhibits prominent band at 15,400 cm^{-1}, characteristic of the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ and another band at 18,880 cm^{-1}, which may be assigned to the transition $^2B_{1g} \rightarrow {}^2E_g$. These transitions indicated the presence of square- planar environment around the metal ion[10].

The electronic spectra of Ni(II) complex exhibits three bands at 9,900, 15,000 and 25,200 cm^{-1} assigned to the transitions: $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively. Co(II) complex shows two bands at 8,100 and 19,750 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and $\rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. These bands for Ni(II) and Co(II) complexes correspond to the octahedral arrangement of ligands around the metal ion.

A strong band around 3,500 cm^{-1} occurring in the spectrum of Mannich base as well as in secondary ligand is assigned to ν(OH) (phenolic)[11]. The broadness of this band in the spectra of coordination compounds of Ni(II) and Co(II) may be attributed to the water molecules coordinated to the central metal ions which is confirmed by TGA. The absence of this band in the Cu(II) coordination compound shows the coordination of metal ion through the deprotonated oxygen of the ligands and the absence of water molecules. Further, both the ligands show bands at 1,210–1,200 and 1,130–1,120 cm^{-1} due to the δ(OH) modes. The splitting of the former and the shift of the latter to higher wave number in the spectra of chelates indicate deprotonation of the phenolic OH and participation of the OH in chelation.

In the spectrum of Mannich base, the bands at 3,200 and 3,150 cm^{-1} may be attributed to the symmetric ν(NH) of the imino group. These bands show a negative shift (25–30 cm^{-1}) in the chelates suggesting the involvement of imino nitrogen in coordination.

The nitroso (—N═O) band observed at 1410 cm^{-1} in the spectrum of nitroso ligand remains unaltered in the spectra of complexes showing non-participation in complexation. The bands at 1625 and 1665 cm^{-1} in IR spectrum of nitroso ligand assigned to C═O stretching of the carboxylic group are not located in the spectra of metal complexes indicating the participation of COOH group in chelation with the metal ion. The non-ligand bands appearing at *ca.* 520 and 465–450 cm^{-1} in the spectra of coordination compounds may tentatively be assigned as ν(M—O)/ν(M—N).

Thermogravimetric Analysis: TGA of the chelates was performed for confirming the presence and number of water molecules in them. Ni(II) and Co(II) chelates showed mass loss corresponding to two water molecules within the temperature range 130–180°C, indicating the presence of two water molecules in the coordinated form in them.

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF COORDINATION COMPOUNDS OF Cu(II), Ni(II) AND Co(II) WITH 7-HYDROXY-4-PHENYL-6-(α-NAPHTHYL)-AMINO METHYL COUMARIN AS PRIMARY AND 4-NITROSO-1-HYDROXY-2-NAPHTHOIC ACID AS SECONDARY LIGAND

Compound	C % Calcd. (Found)	H % Calcd. (Found)	N % Calcd. (Found)	Metal % Calcd. (Found)	ΔM (ohm^{-1} cm^2 mol^{-1})
1. (Cu L′L″)	66.11 (65.29)	3.57 (3.54)	4.16 (4.18)	9.46 (9.40)	3.8
2. [NiL′L″$(H_2O)_2$]	63.18 (64.02)	3.98 (3.95)	3.98 (3.96)	8.35 (8.37)	4.7
3. [CoL′L″$(H_2O)_2$]	63.16 (62.45)	3.98 (3.91)	3.98 (3.90)	8.38 (8.32)	4.2

L′ = $C_{26}H_{18}NO_3$ and L″ = $C_{11}H_6NO_4$

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