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Studies on Some Complexes of Cobalt(II) and Nickel(II) with bis-(2-Hydroxyimino-1-Phenyl Propylidene)-1,4-Diamino Benzene

K. SAHU*, URMILA KUMARI and SHIV CHANDRA YADAV
Postgraduate Department of Chemistry, B.R.B. College, Samastipur, India

A series of metal complexes of bis-(2-hydroxyimino-1-phenyl propylidene)-1,4-diamino benzene types $M_2L_2{\cdot}4H_2O$ and $M_2(LH_2)_2x_4$ where M = Co(II), Ni(II), $X = Cl^-, Br^- I^-$ have been synthesised and characterised on the basis of elemental analyses, magnetic moment, infrared and electronic spectral data.

Key Words: Co(II), Ni(II), Complexes, Bis-(2-Hydroxyimino-1-Phenyl Propylidene)-1,4-Diamino benzene

INTRODUCTION

In recent years a series of variously constituted polydentate ligands which can coordinate to two or more metal ions have been reported[1–5]. The present paper deals with the isolation and structural elucidation of a series of Ni(II) and Co(II) complexes with the ligand obtained by the condensation of 2-hydroxyimino-1-phenyl propylidene and 1,4-diamino benzene.

EXPERIMENTL

Preparation of bis-(2-hydroxyimino-1-phenyl propylidene)-1,4-diamino benzene

1-Phenyl-1,2-propanolione-2-oxime (0.1 mol) and 1,4-diamino benzene (0.05 mol) were mixed with the help of agate and mortar. They went into an intimate mixture which subsequently turned into a homogeneous liquid after being triturated together for about 1 h. The product was kept *in vacuo* for four or five days when it turned into solid mass. The compound having light yellow colour was powdered, recrystallised from ethyl alcohol and analysed (m.p. 168 ± 1°C).

Preparation of (tetrahydrate), di-[bis-(2-hydroxyimino-1-phenyl propylidene)-1,4-diamino benzene] dinickel(II). $Ni_2L_2{\cdot}4H_2O$

The ligand (0.01 mol) was dissolved in about 25 mL hot absolute alcohol. An ethanolic solution of nickel(II) acetate tetrahydrate (0.01 mol) was added to the above solution. The whole mixture was refluxed for 1/2 h. The mixture was cooled and concentrated at room temperature until reddish brown crystals were separated. They were filtered and dried *in vacuo.* After drying, the compound was analysed for its constituents.

Similar procedures were adopted also for the preparation of other neutral complexes.

Preparation of (tetrachloro) di-[bis-(2-hydroxyimino-1-phenyl propylidene)-1,4-diamino benzene] dinickel(II), $Ni_2(H_2L)_2Cl_4$

Nickel(II) chloride hexahydrate (0.01 mol) was dissolved in 15 mL of rectified spirit with one or two drops of 6 N HCl. It was added to an acetone solution of the ligand (0.01 mol) with constant shaking. A light yellow compound appeared. It was allowed to stand for 1/2 h and filtered. The compound was washed with acetone and dried *in vacuo.* The dried product was analysed. Other halo complexes of Ni(II) and Co(II) were prepared by adopting similar procedures.

RESULTS AND DISCUSSIONS

The analytical data of the complexes are reported in Table-1.

TABLE-1
ANALYTICAL DATA OF THE BINUCLEAR COMPLEXES OF Ni(III) AND Co(III) DERIVED FROM IMINE-OXIME LIGAND

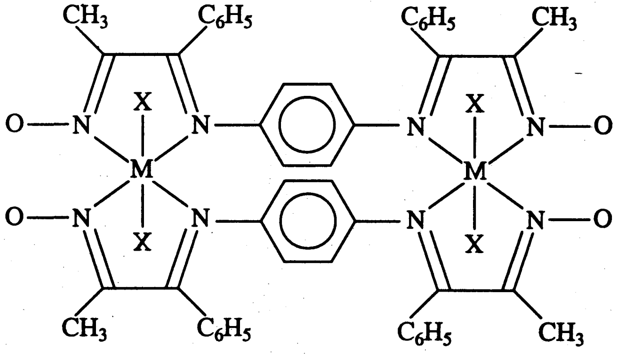
Complexes (Colour)	% Analysis; Found (Calcd)				$\mu_{eff.}$ (B.M.)
	M	N	C	Halogen	
$Ni_2L_2 \cdot 4H_2O$	11.05	11.12	58.02	—	2.92
(Reddish brown)	(11.91)	(11.36)	(58.45)		
$Ni_2(LH_2)_2Cl_4$	10.85	10.20	53.85	12.96	2.83
(Light yellow)	(11.13)	(10.56)	(54.33)	(13.39)	
$Ni_2(LH_2)_2Br_4$	9.02	8.85	46.25	12.03	2.97
(Light brown)	(9.48)	(9.04)	(46.52)	(12.90)	
$Ni_2(LH_2)_2I_4$	7.08	7.25	39.95	34.93	3.15
(Yellowish brown)	(8.03)	(7.81)	(40.4)	(35.65)	
$Co_2L_2 \cdot 4H_2O$	11.45	10.95	58.07	—	2.92
(Chocolate brown)	(11.96)	(11.35)	(58.41)		
$Co_2(LH_2)_2Cl_4$	10.83	10.02	54.07	13.13	1.85
(Yellowish green)	(11.13)	(10.56)	(54.33)	(13.38)	
$Co_2(LH_2)_2Br_4$	8.78	8.96	46.12	23.23	2.10
(Light brown)	(9.50)	(9.09)	(46.75)	(23.97)	
$Co_2(LH_2)_2I_4$	7.96	7.32	39.47	84.06	1.90
(Reddish brown)	(8.27)	(7.85)	(40.39)	(85.62)	

The infrared spectrum of the ligand shows a broad band centred at 3200 cm^{-1} which may be ascribed to ν(O—H) mode of the N—O—H group involved in intra or intermolecular hydrogen bonding. Neutral complexes of Ni(II) and Co(II) of the type $M_2L_2 \cdot 4H_2O$ show strong and broad bands near 3310 cm^{-1} which have significantly different characteristics from the hydrogen bonded N—OH vibrations. These bands are due to the asymmetric and symmetric modes of water and their centres of peak near 3310 cm^{-1} imply coordination of water molecules to the metal ions. Halo complexes of Co(II) and Ni(II) contain coordinated halides and show the O—H bands having the characteristic features of the N—O—H band. The centres of the bands lie around 3220 cm^{-1} and manifest continued existence of hydrogen bonded structure of N—O—H groups of the neutral ligand.

The ligand shows a strong band at 1605 cm^{-1} followed by a comparatively low intensity band at 1590 cm^{-1}. The higher frequency band is more perturbed on complexation and is ascribed to ν(C=N) vibrations and the second band, which has a characteristic shoulder on its low frequency side is assigned to ring breathing vibrations of the phenyl ring. In the presence of two different ν(C=N) groups in the ligand, there appears no other band with intensity comparable to that at 1605 cm^{-1}. This suggests that all the (C=N) groups possess similar vibrational energies, probably due to high degree of conjugation present in the ligand. In the metal complexes, the ν(C=N) band of the ligand shifts to a lower frequency region and appears at 1585 cm^{-1} overlapping with the phenyl ring vibrations. This suggests coordination of the nitrogen atoms with the metal ions. Apart from the above mentioned bands, two or three bands are located in the region 1510–1460 cm^{-1} whose positions are much less influenced on complexation and hence these are assigned to phenyl ring vibrations. A band around 1360 cm^{-1} in the ligand remains unperturbed on complexation. It has been assigned to the deformation modes of C—H of the methyl groups.

The ligand shows a sharp band of medium intensity at 1250 cm^{-1} which shifts towards lower frequency side and appears near 1235 cm^{-1} with a reduced intensity in the metal complexes. This band is attributed to ν(C=N) mode. Two more structurally significant bands are observed at 1015 and 970 cm^{-1} in the free ligand. Both of these are assigned to N—O stretching vibrations of the oxime groups as their positions are affected on coordination. In the metal complexes the bands appear as strong and sharp absorptions in 1110–1010 cm^{-1} region. On complexation, the N—O bonds of the free oxime are considerably shortened in the metal chelates while the (C=N) band distances are much less affected[6,7].

The spectral data indicate symmetric bi-bidentate bonding of the ligand with the metal ions in the complexes with the stoichiometry $M_2L_2 \cdot nH_2O$ (Fig. 1). The halo complexes of Co(II) and Ni(II) possess structure where two ligand molecules form a hydrogen bonded macrocycle with halide ions occupying axial positions.



M = Co(II), Ni(II), X = H_2O

Fig. 1

In the present study, nickel(II) complexes show magnetic moment 2.83 to 3.15 B.M. at ordinary temperature implying octahedral arrangement of the ligand atoms around the central nickel(II) ion with small amount of tetragonal distortion[8]. The electronic spectra of these complexes consist of four bands. The band near 11,200 cm^{-1} is ascribed to the $^3B_{1g} \rightarrow {}^3T_{2g}$ transition. The next two high energy bands which appear at 16,100 and 19,300 cm^{-1} are attributed to the $^3B_{1g} \rightarrow {}^3A_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ transitions respectively. The fourth band which is observed at 26,500 cm^{-1} is assigned to $^3B_{1g} \rightarrow {}^3T_{1g}(P)$ transition.

The magnetic moments of halo complexes of Co(II) have been found in the region 1.85 to 2.10 B.M. while the neutral complex shows a magnetic moment of 2.9 B.M.

Magnetic moment values suggest that the cobalt(II) complexes are of low spin type with one unpaired electron[9]. A slightly high value may be due to spin orbit interaction of $^2A_{1h}$ state and mixing takes place with $^2A_{2g}$ and other higher levels.

The electronic spectra of Co(II) complexes show ligand field transition for chloro and bromo complexes near 16,000 and 20,000 cm^{-1}. The spectral results show that the Co(II) ion in the present series of complexes is under tetragonal ligand field having D_{4h} symmetry.

The low frequency band at 16,200 cm^{-1} is assigned to $^2A_{2g} \rightarrow {}^2A_{2g}$ transition. The second band of greater intensity at 20,100 cm^{-1} is attributed to $^2A_{1g} \rightarrow {}^2E_g$ transition. A high energy band near 27,000 cm^{-1} of high intensity may be due to charge transfer transition. The ligand possesses πu(filled) and πg(vacant) orbitals and there is a possibility of flow of a d-electron of Co(II) towards vacant πg orbitals of ligand resulting in a [M → L(πg)] charge transfer transition.

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