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Synthesis and characterization of 16-membered octaaza macrocyclic Ni (II) complexes

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ABSTRACT

A series of Ni (II) complexes with a tetradentate nitrogen donor octaazamacrocyclic ligand was synthesized. On the basis of elemental analysis , the formula of the complex was derived and found to be of the type [Ni(L)]X 2 (Where L=1, 4, 5, 8, 9, 12, 13, 16 – octaaza - 2,3,6,7,10,11,14,15, - octamethyl - cyclohexadeca-1,3,5,7,9,11,13,15 - octaene, X= Cl - , Ac - which was obtained by the metal ion catalyzed template Schiff base condensation of diacetyl with hydrazine) The molar conductance value of the Ni (II) complex in acetonitrile was 202 S cm 2 mol -1 , indicating a 1:2 electrolytic nature. The complex was found to be diamagnetic. Based on spectral studies, square planar geometry was proposed. Infrared spectra suggest co-ordination to take place with four of the eight azomethinic nitrogen donor atoms. Nitrogen atoms giving rise to 5:7:5:7 system of chelate ring.

Keywords: Octaazamacrocyclic ligand, Ni (II) complex, characterization.

1.0 INTRODUCTION

Transition metal polyaaza macrocyclic complexes have received much attention as an active part of metalloenzymes due to their resemblance with natural counter parts 1-18 . Building up polyaaza macrocyclic systems on the appropriate matrices is carried out by the interaction of compounds containing amine or imine groups with aldehydes, ketones, organic halogen derivatives and components containing unsaturated C-C bonds.

In this paper, the synthesis and spectroscopic characterization of Ni (II) complexes with 16-membered macrocyclic Schiff base ligand is reported.

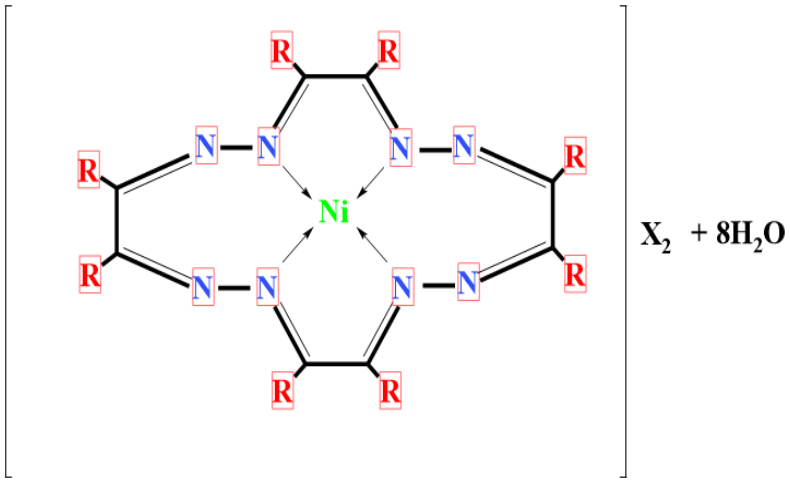
2.0 EXPERIMENTAL

All the chemicals used were of analytical grade and procured from Sigma — Aldrich (USA) and Fluka (USA). The metal salts were purchased from E. Merck (Germany) and were used as received.

2.1 SYNTHESIS OF COMPLEX

The hot ethanolic solution (20 ml) of hydrazine hydrate(0.02 mol.), ethanolic solution of diacetyl (0.02 mol.) and ethanolic solution of nickel (II) salts (0.005 mol.) were mixed together under constant s tirring in the presence of a few drops of conc. HCl. The reaction mixture was refluxed at 80-85° C for 4 hours. On cooling the solution, shiny red coloured crystal s separated out. It was filtered, washed, recrystallized from 50% ethanol and dried under vacuum over P4O 10 . The synthetic reactions taking place may be presented as shown below.

$NiX_2.\ 6H_2O$ + 4 dicarbonlys + 4 hydrazine hydrate $\xrightarrow[\text{pH, 3-4}]{\text{Reflux, 4Hrs}}$



R =CH_3

L = $C_{16}H_{24}N_8$

Analytical results along with color, yield, molar conductivity were presented in Table – I

TABLE – I

Complexes	Mol. Cond.	Color	Yield %	Found (Cal %)			
				Ni	C	H	N
$[Ni(L)]Cl_2$	202	Shiny Pink	66	12.72 (12.88)	41.62 (41.92)	5.22 (5.24)	22.18 (22.31)
$[Ni(L)]Ac_2$	212	Red	75	11.38 (11.68)	47.08 (47.52)	5.56 (5.94)	11.80 (11.84)

2.2 PHYSICAL MEASURMENTS

The C and H contents of the complexes were determined on a carlo-Erba 1106 elemental analyzer (C.D.R.I. Lucknow India) whereas the N content was determined using the Kjeldhal method l 2 . By volumetric analysis, metal content was determined. The molar conductance value was measured on Systronics conductometer model — 303 at 298 K in acetonitrile. The magnetic susceptibility values were measured at room temperature on a Guoy balance using CuSO4, 5H2O as the calibrant. Correction for diamagnetism were realized used Pascal constant. The IR spectra were recorded as KBr pellets on a Beckman-20 spectrophotometer.

3.0 RESULTS AND DISCUSSION

The complexes were assigned the composition [Ni(L)] X2 on the basis of elemental analysis. The molar conductance value indicating a 1:2 electrolytic nature. Thus, the complex may be formulated as [Ni(L)] X 2 , where L=16, membered octaazamacrocyclic ligand , X = Cl, Ac. The complexes were diamagnetic as expected for a square planar d 8 system. The electronic spectra of the Ni (II) complex exhibits transitions near 735, 478 and 402 nm. These bands may be assigned to the transitions between 1 A 1g and 1 A 2g , 1 A 1g and 1 B 2g and 1 A 1g and 1 E g respectively.

4.0 CONCLUSIONS

The present study revealed square planar geometry for Ni (II) complexes. The macrocyclic ligand acts in a tetradentate manner coordinating through four of its azomethine nitrogen, the remaining four azomethine nitrogen being unutilized. Macrocyclic effect and conjugated π electrons impart stability to the complex.

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