



NICKEL (II) COMPLEXES OF A FOURTEEN MEMBER HETEROMACROCYCLIC SCHIFF BASE LIGAND DERIVED FROM ACETYLACETONE AND ORTHOPHENYLENEDIAMINE

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ABSTRACT

A series of novel nickel(II) complexes $[\text{Ni}(\text{Abmene})\text{X}_2]$ where $\text{X} = \text{Cl}^-$, NO_3^- , ClO_4^- or CH_3COO^- has been synthesized by the template method and characterized by elemental analysis, molar conductance, magnetic, electronic and infrared spectral measurements. Abmene stands for the ligand 1,5,8,12-tetraaza-6,7:13,14-dibenzo-2,4,9,11-tetramethylcyclotetradeca-1,4,8,11-tetraene which has been derived by Schiff base condensation of acetylacetone and orthophenylenediamine in equimolar proportion in ethanolic medium of high dilution in presence of nickel salts. The low molar conductance values of the complexes indicate their non electrolytic nature. Magnetic and electronic spectral data suggest the complexes to have octahedral stereochemistry. Infrared spectra confirm coordination of the macrocyclic Schiff base ligand through all the azomethinic nitrogens. Anions have been found to behave in an unidentate manner. Macrocyclic effect and electron delocalisation over the entire molecular framework seem to play significant role in providing stability to the complexes.

KEYWORDS:

nickel complexes , Macrocyclic Schiff base ligand , spectral study , acetylaceton orthophenylenediamine

1. INTRODUCTION

By the end of 20th century, acetylaceton established itself as one of the versatile ligand [1] . The present century is dominated by coordination compounds with macrocyclic Schiff base ligands [2] . Acetylaceton with its keto-enol tautomeric forms is a good choice as carbonyl component for Schiff base macrocyclization with aliphatic as well as aromatic vicinal diamines such as orthophenylenediamine [3] . Schiff base condensation gives better yield if performed in presence of metal ions due to its catalytic and organizational roles [4-6]. Consequently , we in the present communication , are reporting on a novel series of nickel(II) complexes with a macrocyclic Schiff base ligand , Abmene , derived from acetylaceton and orthophenylenediamine . In Abmene , A stands for aza , b for benzo , m for methyl and ene for double bonds .

2. EXPERIMENTAL**Materials and methods**

All the reagents such as nickel(II) salts , solvents , acetylaceton, orthophenylenediamine , DMF , DMSO were purchased commercially and used without any further purification . Suppliers were S Merck , CDH and Aldrich .

Preparation of [Ni (Abmene)Cl₂]

Millimolar solutions of nickel chloride hexahydrate, acetylaceton and orthophenylenediamine were prepared in hot ethanol . 20 mL each of acetylaceton and orthophenylenediamine solutions were added to 10 mL of nickel chloride solution with constant stirring with magnetic stirrer and the mixture was refluxed for two hours. It was then allowed to undergo slow evaporation when blue crystals separated out. Crystals were filtered, washed dried and analyzed to give following analytical results:

Found % C 54.97, H 5.16, N 12.14, Cl 15.21,

Ni 12.22 calculated % for [Ni (C₂₂ H₂₄ N₄) Cl₂]

C 55.73, H 5.06, N 11.82, Cl 14.98 Ni 12.39

Preparation of [Ni (Abmene) X₂], X= CH₃ COO⁻, ClO₄⁻ or NO₃⁻

A similar method was followed for the synthesis of complexes by taking corresponding nickel salts in place of nickel chloride. Analytical results were found to be in good agreement with the proposed formulations.

PHYSICAL MEASUREMENTS:

Recrystallised samples were used for obtaining analytical data. Data for C, H and N were obtained from microanalytical laboratory C D R I Lucknow. Nickel was estimated gravimetrically as bis(dimethylglyoximate) nickel (II). Shimadzu 160A spectrometer was used for recording electronic spectra. Infrared spectra in KBr discs were recorded on a Beckman 20 spectrophotometer. Conductivity measurements were made on a Systronics conductivity meter model 303 using DMS as a solvent. Magnetic susceptibility were measured on a Guoy balance using Hg [Co(SCN)₄] as the calibrant.

3. RESULTS AND DISCUSSION

On the basis of elemental analysis, molecular formula of the complexes have been found to be of the type [Ni (C₂₂ H₂₄ N₄) X₂] where X stands for the anions chloride, acetate, nitrate or perchlorate. Synthetic reactions taking place may be represented as shown below:



MOLAR CONDUCTIVITY

Molar conductivity has been found to lie in the range 5-10 Siemens cm² mol⁻¹. This indicates complexes to be non electrolytic in nature supporting anions to behave in an unidentate coordination mode.

MAGNETIC MOMENT AND ELECTRONIC SPECTRA

Magnetic moment of the complexes has been found in the range of 3.18-3.26 B. M. A pair of electronic spectral bands have been observed in the range 11, 300 - 11, 700 and 17, 400 - 17, 600 cm⁻¹. The bands may be associated with the transitions ³A₂ g (F) - ³T₁ g (P) and ³A₂ g (F) - ³T₁ g (P) respectively. Magnetic moment and electronic spectra suggest octahedral geometry for the complexes.

INFRARED SPECTRA

Infrared bands of structural significance are recorded in table - 1.

Table - 1

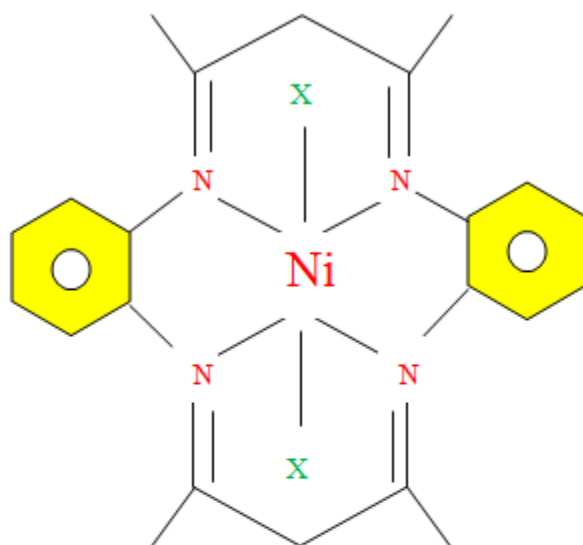
Selected I. r. spectral bands (cm-1).

COMPLEXES	$\nu_{C=N}$	ν_{Ni-N}	$\nu_{Ni-O/Cl}$
[Ni(Abmene)Cl ₂]	1610, 1583	626	424
[Ni(Abmene)(NO ₃) ₂]	1605,1590	634	520
[Ni(Abmene)(ClO ₄) ₂]	1607,1578	652	560
[Ni(Abmene)(CH ₃ COO) ₂]	1610,1575	650	554

The absence of bands corresponding to N-H stretching frequency of free amino groups (orthophenylenediamine) as well as carbonyl stretching frequency of acetylacetonate on one hand and appearance of new bands characteristic of Ni-N, Ni-Cl, Ni-O and C=N stretch on the other indicate the formation of macrocyclic cavity in which nickel ion is embedded. Infrared spectra also corroborate the behaviour of anions to act in an unidentate coordination mode [7-9].

4. CONCLUSION

On the basis of magnetic moment, electronic spectra, molar conductivity and infrared spectral data, an octahedral geometry has been proposed for the complexes with certain amount of tetragonal distortion as shown in Fig. 1.



[2+2]MACROCYCLIZATION

Fig -1

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