

CHEMISTRY OF MIXED LIGAND COMPLEXES OF NI (II) METAL CHELATES OF ORGANIC ACIDS WITH ETHYLENE DIAMINE

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Ethylene diamine is a important bidentate legand. It forms more stable five membered ring with Nickel (II) metal ion.

Nickel compounds were used as medicine in ancient times. Nickel bromide has been used as an antiseptic drug and a nickel sulphate in severe diarrhoea. Research were carried out on the toxicity of nickel and it was found to be a very toxic element. The use of NI salts as drugs were therefore abandoned. Our body contains many trace elements such as nickel, zinc, arsenic, manganese, chromium etc. Nickel is present in blood, human hair and nails. NI has been measured quantitavely in liver, blood, hair, wings and heart. Nickel carbonyl is most poisonous because inside the body it disintegrates into NI and CO.

We have synthesised and characterised several mixed ligand complexes of NI (II) metal chelates of some organic acids with ethylenediamine having the general formula ML_2L^1 . Where M = NI (II), L=deprotonated ortho-nitrophenol, 2, 4 - Dinitrophenol, 2, 4, 6 - Trinitrophenol, 1 - Nitroso -2- Naphthol, 8-hydroxyquinoline, orthoaminobenzoic acid, L^1 = ethylenediamine. The structure of these complexes have been confirmed by analytical data, molar conductivities, infrared and UV-visible spectral data. Significantaly low values of molar conductivities of the mixed ligand complexes indicate they have covalent nature. The IR data also suggest that the coordination of NI(II) metal through the Nitrogen atom of -NH₂ group of ethylenediamine.

Keywords : Mixed legand complex, Ethylenediamine, oxygen and Nitrogen containing organic acids, Metal chelates.

INTRODUCTION

A large number of studies on mixed ligand complex formation have been reported. The present investigation has been undertaken to examine complexation by Ni(II) metal chelates of some organic acids, viz, o-nitrophenol (ONP), 2,4-Dinitrophenol (DNP), 2, 4, 6 - trinitrophenol (TNP), 1-nitroso-2-naphthol (INZN), 8-hydroxyquinoline (8HQ), O- amino acid (OABA) with ethylenediamine. Coordination site in all, the second ligand is only nitrogen atoms and it acts as bidentate ligand and expected to form five or six membered salts.

EXPERIMENTAL

Nickel (II) acetate and organic acids (viz, ONP, DNP, TNP etc.) are of BDH Analar quality or E Merck quality.

Preparation of metal chelates :

An ethanolic solutions of 0.1 mol. of NaOH was slowly added to 0.1 mol of organic acid solution in 25 ml. of absolute ethanol. The mixture was refluxed as magnetic hot plate as 80°C about 2 hr. with continuous stirring. The coloured product was obtained. It was filtered, washed with absolute ethanol and then dried in an electric oven at 80°C. Newly prepared sodium salt of organic acid in distilled water in small amount added of aqueous solution of Ni acetate in 2:1 molar ratio. The resulting mixture was refluxed on magnetic hot plate at 80°C for nearly 2 hr. with continuous stirring. The colour of the contents changed and a clear solution was obtained, on cooling Ni (II) metal chelates got separated. It was filtered, washed with distilled water and dried in an electric oven at 100°C.

Preparation of mixed ligand complexes :

To the suspension of 0.001 mol of Ni(II) metal chelates of organic acid in absolute ethanol, 0.001 mol. Of 1,10 ethylenediamine was added with constant stirring. The mixture was refluxed on magnetic hot plate with constant stirring at 80°C for 2-3 hr. on cooling the solution, coloured precipitate got separated. It was filtered, washed with absolute ethanol and finally dried in an electric oven at 100°C.

Detection Method :

The elemental analysis was carried out on an elemental analyzers Heraeus Vario EL III Carlo Erba 1108. The molar conductivity was measured on Systronics Digital Direct Reading Conductivity Meter-304. Magnetic measurements of the compounds were taken by vibrating sample magnetometer. Infrared spectra were recorded in KBr phase between 4000-400 cm^{-1} with the help of JASCO-FTIR Spectrometer model-5300. Electronic spectra were recorded on Perkin Elmer Lambda-15 UV-VIS spectrophotometer in paraffin solvent. ^1H NMR spectrum of compound was recorded at room temperature on a model Bruker Advance DRX-300 spectrometer operating at 300 MHz.

RESULT & DISCUSSION :

Some physical properties of second ligand (ethylenediamine) and the new mixed ligand Ni (II) complexes obtained are listed in the table - 1.

Table – 1

Ligand Compound	M.W. Found	Colour	MP/BP Delom position point (0°C)	Yield %	Helt (B.M.)	Molar Conduct	Elemental Analysis			
							M	C	H	N
Ethylenediamine (en)		Colourless	116.5b			--				
Ni (DNP) ₂ en.	484.7	Yellowish brown	225m	66%	3.89	4.1	11.95 (F) 12.11 (C)	34.41 (F) 34.66 (E)	2.68 (F) 2.89 (e)	17.12 (F) 17.33 (C)
Ni (ONP) ₂ en	394.7	Orange	160m	75%	1.91	3.2	14.56 (F) 14.87 (c)	42.35 (F) 42.56 (c)	3.89 (F) 4.05 (c)	14.02 (F) 14.19 (c)
Ni (TNP) ₂ en	574.7	Deep Yellow	186m	61%	2.94	3.8	9.95 (F) 10.21 (c)	29.06 (F) 29.23 (c)	1.98 (F) 2.08 (c)	19.25 (F) 19.49 (c)
Ni (8HQ) ₂ en	406.7	Gray Brown	7300m	91%	3.33	4.9	14.21 (F) 14.43 (c)	58.85 (F) 59.01 (c)	4.78 (F) 4.92 (c)	13.56 (F) 13.77 (c)
Ni (IN2N)	462.7	Deep Brown	7300m	85%	3.01	4.6	12.38 (F) 12.69 (C)	56.85 (F) 57.10 (C)	4.18 (F) 4.32 (C)	11.98 (F) 12.10 (C)

* Molar conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) solution in MeOH at 27°C;

where *b* = boiling point, *m* = melting point & *d* = decomposition temperature.

Ethylenediamine is a colourless liquid, insoluble in cold water but soluble in hot water, ethanol and ether. It sublimes below its melting point and it is steam volatile.

The mixed ligand complexes are generally coloured. They are generally soluble in polar solvents like water, methanol, ethanol, partly soluble in acetone & chloroform, but sparingly soluble in non-polar solvents, namely, n-hexane, benzene, dioxane etc.

Molar conductance : Molar conductance of all the compounds were measured in methanol at 27°C at a concentration of 10^{-3} M. The values are given in Table-1. The

significantly low values (3.2-4.6) $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) of molar conductance of the compounds indicate them to be covalent nature.

Infrared spectra : Infrared spectra of the ligand (ethylenediamine) and its mixed ligand Ni (II) complex recorded in KBr phase between $4000\text{-}400 \text{ cm}^{-1}$ with the help of JASCO-FTIR spectrophotometer model 5300. Selected absorption bands are listed in Table -2.

In metal amine complexes, the four principle regions of absorptions are -3300 , -1600 , -1100 and -810 cm^{-1} . These have been assigned to the N-H stretching modes, the asymmetric deformation, the symmetric deformation and NH_2 rocking mode respectively.

Table - 2

Pertinent IR data for ligand (ethylenediamine) & its mixed ligand Ni (II) complexes

Compound	Selected infrared absorption bands (in cm^{-1})				
	UN-H	Asym δ N-H	Sym δ N-H	Rocking NH_2	Far Infrared
Ethylenediamine (en)	3275, 3150	1600	1100	810	-
Ni (ONP) ₂ en	3300, 3175	1606	1138	845	596, 525, 485

In view of the increasing importance of far infrared techniques, Hughes & Mc Whinnie thought it worth while to extend these studies to the region, in which metal-ligand vibrations are observed. In present work, we have found that all the principle regions of absorption 3377 and 3316 cm^{-1} (stretching mode of $\nu\text{N-H}$), 1600 cm^{-1} (asymmetric deformation, δ N-H) - 1100 cm^{-1} (symmetric deformation, δ N-H) and 810 cm^{-1} (rocking NH_2) are present in the ligand (en).

The one N-H vibration occurs as broad peak between $3406\text{-}3147 \text{ cm}^{-1}$. The 3377 & 3316 cm^{-1} bands of ethylenediamine are very much affected in the complexes. These appear between $3406\text{-}3147 \text{ cm}^{-1}$ with increased intensity in the complexes, thereby suggesting that there has been decrease in the bond order of N-H on complexation. The higher shifting of bands are in conformity with the coordination through the N-H as there has been electron drain from nitrogen of ethylenediamine to the Ni (II) metal.

Taking into consideration symmetry, if isomer give rise to multiplicity in the -1600 cm^{-1} (asym δ N-H) and -1100 cm^{-1} (sym δ N-H), it is observed that these complexes give relatively simply spectra. Two or three bands have been observed between $1606\text{-}1596 \text{ cm}^{-1}$ Extra bands are due to presence of NO_2 , - $\text{NH}_2\text{-NO}$ of first ligand (*i.e.*, organic acids). These complexes also show one or two peaks between $1161\text{-}1111 \text{ cm}^{-1}$.

Further the NH_2 rocking at 810 cm^{-1} which shifted to higher frequency region $850\text{-}833 \text{ cm}^{-1}$ in all these complexes may be assigned to M-O band frequency while medium bands in the region $525\text{-}630 \text{ cm}^{-1}$ are assigned to M-N band frequency. These bands are not present in the ligand (ethylenediamine). The assignments are based on the assumption that since oxygen atom is more electronegative than nitrogen, the M-O bond tends to be more ionic than the M-N bond. Consequently M-O vibrations are expected to appear at lower frequencies. The above data confirm the coordination atom of O-H (phenolic) group and nitrogen atom of Ni (in case

of 1N2N) or $-\text{NO}_2$ (in case of ONP, DNP, TNP) or $-\text{NH}_2$ (in case of OABA, en) group or pyridine ring (in case of 8 HQ) to Ni (II) metal in all the mixed ligand complexes.

The IR spectra of source of the compounds are viewed in Fig.1.

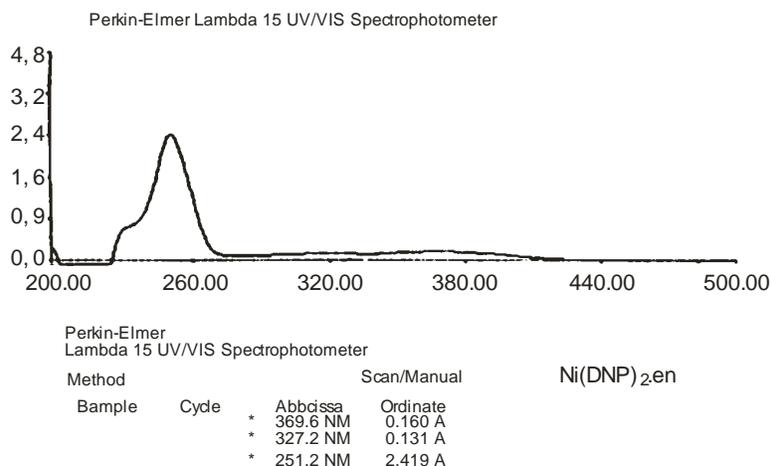


Fig. 1.

Electronic Spectra :

Electronic Spectra were recorded in perkin Elmer Lambda-15 UV-VIS spectrophotometer in paraffin solvent. The band observed in electronic spectra of mixed ligand NI (II) complexes with ethylenimine (en) are given in Table - 3.

A comparative look of the electronic spectral data of ligand and mixed ligand Ni (II) complexes show that the $\pi - \pi^*$ transition and $n - \pi^*$ transition of the ligand have appreciably shifted. These shift indicate the coordination of the ligand with the metal chelates. There are some more bands which may be assigned to $d-d$ transition. However, from the position of the spectral bands and their low intensities it suggests that the complexes are in octahedral geometry. Electronic absorption spectra of some compounds are shown in Fig. 2.

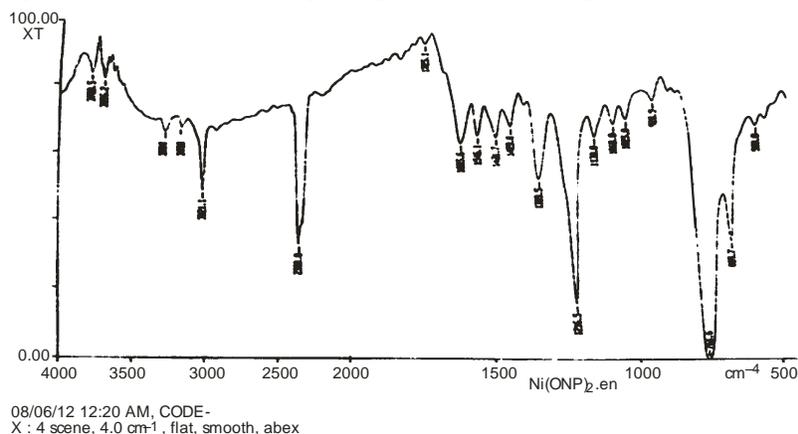


Fig. 2.

Table 3

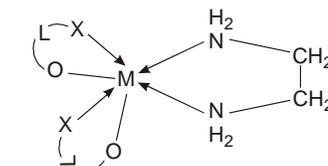
Major diffuse reflectance bands (in nm) for mixed ligand complexes of Ni(II) metal with ethylenediamine (en)

Compound	Diffuse reflectance (in nm)
Ethylenediamine (en)	235, 295
Ni (DNP) ₂ en	251, 327, 370

The magnetic moment values for the mixed ligand complexes with Ni (II) metal chelates with ethylenediamine are in the range 2.94-3.33 BM are suggested are given in Table -1. These values are suggestive of these complexes in octahedral structure. IR, UV-visible Spectra also support this fact.

CONCLUSIONS

On the basis of analytical data, the general formula of mixed ligand complexes of Ni (II) comes out to be ML_2L^1 where $M=Ni$ (II), L =deprotonated, O =Nitrophenol (ONP), 2, 4 - dinitrophenol (DNP), 2, 4, 6 - Trinitrophenol (TNP), 8-Hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (IN2N) or o -aninobenzoic acid (OABA) and L^1 = ethylenediamine. Infrared, electronic absorption spectra and magnetic moment measurements suggested the coordination of the ligand (en) with Ni (II) through the nitrogen atoms of its pyridine fragments. This facts lead to the following probable structure for these complexes (Fig 1)



Where $M = Ni$ (II) and Cu (II), L = deprotonated ONP, DNP, TNP, 8HQ, IN2P, $X = O$ or N

Fig. 3

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