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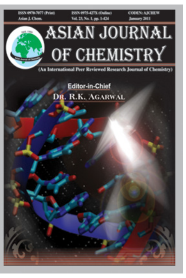

Structural Aspects of Mixed Ligand Complexes of Ni(II) or Cu(II) Metal Chelates of Organic Acids with Ethylenediamine

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A series of mixed ligand complexes of the general formula ML_2L' have been synthesized and characterized, where M = Ni(II) or Cu(II); L = deprotonated organic acids such as *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (IN2N), *o*-aminobenzoic acid (OABA); L' = ethylenediamine. These complexes have been characterized by elemental analysis, molar conductance measurements, magnetic moment measurements, IR, electronic and ^1H NMR spectral analysis. The IR spectra suggest coordination of transition metal Ni(II) or Cu(II) through nitrogen atom of $-NH_2$ group of ethylenediamine and N and/or O of the organic acid. The electronic spectral data and magnetic moment value suggest the octahedral geometry of the complexes.

Key Words: Mixed ligand complex, Ethylenediamine, Oxygen and nitrogen containing organic acids, Metal chelates.

INTRODUCTION

In recent years the formation of complexes containing two different ligands has been special interest to coordination chemists and formation constant of these complexes have been determined[1]. Since all these studies involve transition, rare earth, alkali and alkaline earth metals, it is worthwhile to study the same phenomenon with nickel(II) and copper(II). We are interested in synthesizing the mixed ligand complexes of nickel(II) and copper(II) involving potential chelating ligands with nitrogen donor system, *viz*., ethylenediamine of biological importance. Werner[2] was prepared complexes of ethylenediamine with Co, Ni, Ag, Cu *etc*., by substituting NH_2 of metal amines. A number of Au(III) and Co(III)[3,4] complexes of ethylenediamine have been reported. Complexes of other transition metals with ethylenediamine are also well established[5-9]. Ethylenediamine(en) forms a number of stable adducts with certain alkali metal salt[10]. The crystal structures of two of these compounds, LiCl.2en and LiBr.2en have been reported by Van-Meerssche *et al.*[11] .

The present investigation has been undertaken to examine complexation by Ni(II) and Cu(II) metal chelates of some organic acids, *viz*., *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), *o*-aminobenzoic 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 chelates.

EXPERIMENTAL

Ethylenediamine(en) and organic acids are of BDH AnalaR quality or E. Merck quality.

General procedure

Prepration of metal chelates: An ethanolic solution 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 on magnetic hot plate at 80 ºC *ca.* 2 h with continuous stirring. It was filtered, washed with absolute ethanol and then dried in an electric oven at 80 ºC. Newly prepared sodium salt of organic acid in distilled water in small amount added to aqueous solution of Ni or Cu acetate in 2:1 molar ratio. The resulting mixture was refluxed on magnetic hot plate at 80 ºC for *ca.* 2 h with continuous stirring. The colour of the contents changed and a clear solution was obtained, on cooling Ni(II) or Cu(II) metal chelates got separated. It was filtered, washed with distilled water and dried in an electric oven at 100 ºC.

Preparation of mixed ligand complexes: To the suspension of 0.001 mol of Ni(II) or Cu(II) metal chelates of organic acid in absolute ethanol, 6-8 drops of ethylenediamine was added till the colour changed/precipitate formed. The mixture was refluxed on magnetic hot plate with constant stirring at 80 ºC for 2-3 h. On cooling the solution, orange or yellow precipitate got separated. It was filtered, washed with absolute ethanol and finally dried in an electric oven at 100 ºC.

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 Faraday magnetic susceptibility balance. 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.

RESULTS AND DISCUSSION

Some physical properties of second ligand (ethylenediamine) and the new mixed ligand Ni(II) and Cu(II) complexes obtained are listed in the Table-1. Ethylenediamine is a colourless liquid, insoluble in cold water but soluble in hot water, ethanol and ether. The mixed ligand complexes are generally coloured. They are generally soluble in polar solvents like water, methanol, ethanol, partly soluble in acetone and chloroform, but sparingly soluble in non-polar solvents, namely, *n*-hexane, benzene, dioxane *etc*. The molar conductance[12] of all the compounds were measured in methanol at 27 ºC at a concentration of 10^{-3} M (Table-1). The significantly low values (3.2-5.5 ohm^{-1} cm^2 mol^{-1}) of molar conductance of the compounds indicate them to be covalent nature.

The magnetic measurements (μ_{eff}) were taken by vibrating sample magnetometer at 297 K. The values are given in Table-1. The complex compounds of bivalent Ni(II) d^8-system with coordination number six, the nickel ion is in sp^3d^2 hybridization. The complexes are paramagnetic and have been found to exhibit magnetic moment higher than 'spin only' value expected for two unpaired electrons $\mu_{eff} = \sqrt{2(2 + 2)}$ BM = $\sqrt{8}$ BM = 2.83 BM. In octahedral field, the lowest lying singlet state $^3A_2$ is separated from two triply degenerate $^3T_2$, $^3T^1$, by large energy intervals, this causes the metal ion to behave as if it is in a state for which the orbital contribution is negligible. Experimentally in most of the cases the range for magnetic susceptibility values, 2.83-3.40 BM for octahedral and 3.4-4.2 BM for tetrahedral complexes have been observed[13-15]. In the present case, 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. These values are suggestive of these complexes in octahedral structure. In case of sp^3d^2 hybridization of Cu(II) octahedral complexes, there are one unpaired electron. The spin only value of the magnetic moment of Cu(II) octahedral complexes is given as, $\mu_{eff} = \sqrt{1(1 + 2)}$ = $\sqrt{3}$ BM = 1.73 BM. In present work, the values of μ_{eff} for mixed ligand complexes with copper(II) metal chelates and ethylenediamine are in the range of 1.89-2.25 BM.

Infrared spectra: Infrared spectra of the ligand (ethylenediamine) and its mixed ligand Ni(II) and Cu(II) complexes were recorded in KBr phase between 400-4000 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 mode[16], the asymmetric deformation, the symmetric deformation and the NH_2 rocking mode[17], respectively. In present work, it is found that all the principle regions of absorption 3377 and 3316 cm^{-1} [stretching mode of ν(N-H)], 1600 cm^{-1} [asymmetric deformation, δ(N-H)], *ca.* 1100 cm^{-1} [symmetric deformation, δ(N-H)] and 810 cm^{-1} (rocking NH_2) are present

TABLE-1
ANALYTICAL DATA OF THE LIGAND AND MIXED LIGAND COMPLEXES

Ligand/complexes	m.w. (Found)	Colour	b.p./m.p./decomp. temp. (ºC)	Yield (%)	$\mu_{eff.}$ (BM)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Elemental analysis (%):calcd./(found)			
							M	C	H	N
Ethylenediamine (en)	–	Colourless	116.5 b	–	–	–	–	–	–	–
$Ni(ONP)_2$·en	395	Orange	160 m	60	3.21	3.2	14.87 (14.56)	42.56 (42.35)	4.05 (3.89)	14.19 (14.02)
$Ni(DNP)_2$·en	485	Yellowish brown	225 m	75	3.10	4.1	12.11 (11.95)	34.66 (34.41)	2.89 (2.68)	17.33 (17.12)
$Ni(TNP)_2$·en	575	Deep yellow	186 m	72	2.94	3.8	10.21 (9.95)	29.23 (29.06)	2.08 (1.98)	19.49 (19.25)
$Ni(8HQ)_2$·en	407	Grey brown	>300	68	3.33	4.9	14.43 (14.21)	59.01 (58.85)	4.92 (4.78)	13.77 (13.56)
$Ni(1N2N)_2$·en	463	Deep brown	>300	65	3.01	4.6	12.69 (12.38)	57.10 (56.85)	4.32 (4.18)	12.10 (11.95)
$Cu(ONP)_2$·en	400	Yellow	158 d	61	1.91	4.5	15.90 (15.72)	42.04 (41.82)	4.00 (3.61)	14.02 (13.81)
$Cu(DNP)_2$·en	490	Golden brown	260 d	74	1.89	5.5	12.98 (12.68)	34.32 (34.25)	2.86 (2.71)	17.16 (17.05)
$Cu(TNP)_2$·en	580	Silky brown	132 m	70	1.91	4.5	10.96 (10.59)	28.99 (28.68)	2.07 (1.89)	19.33 (19.12)
$Cu(8HQ)_2$·en	412	Green	260 m	67	2.01	3.9	15.44 (15.19)	58.32 (58.15)	4.86 (4.80)	13.61 (13.36)
$Cu(1N2N)_2$·en	468	Deep brown	128 m	64	1.95	3.5	13.59 (13.38)	56.46 (56.31)	4.28 (4.16)	11.98 (11.72)
$Cu(OABA)_2$·en	396	Grey	278 d	58	2.25	4.8	16.06 (15.86)	48.54 (48.29)	5.06 (4.95)	14.16 (14.03)

TABLE-2
IR SPECTRAL DATA FOR LIGAND AND ITS MIXED LIGAND Ni(II) AND Cu(II) COMPLEXES (cm^{-1})

Ligand/complexes	ν(N-H)	Asym δ(N-H)	Sym δ(N-H)	Rocking NH$_2$	ν(M-N)	ν(M-O)
Ethylenediamine (en)	3275, 3150	1600	1100	810	–	–
Ni(ONP)$_2$·en	3300, 3175	1606	1138	845	569, 525	485
Cu(DNP)$_2$·en	3318, 3268, 3162	1597	1130, 1117	833	630, 550, 528	486
Cu(TNP)$_2$·en	3406, 3325	1608	1111	850	625, 549	500
Cu(8HQ)$_2$·en	3147, 3259	1596	1112	830	629, 565	522, 495

in the ligand(en). The one N-H vibration appears as broad peak between 3406-3147 cm^{-1}. The 3377 and 3316 cm^{-1} bands of ethylenediamine are very much affected in the complexes. These appear between 3406-3147 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 the nitrogen of ethylenediamine to the Ni(II) or Cu(II) metal. Taking into consideration that lower symmetry of *cis* isomer will give rise to multiplicity in the *ca.* 1600 cm^{-1} [asym δ(N-H)] and *ca.* 1100 cm^{-1} [sym δ(N-H)], it is observed that these complexes give relatively simple spectra. Two or three bands have been observed between 1606-1596 cm^{-1}. Extra bands are due to presence of -NO$_2$, -NH$_2$, -NO of first ligand (*i.e.*, organic acids), very much overlap with other ligand vibration. These complexes also show one or two peaks between 1161-1111 cm^{-1}. Further the NH$_2$ rocking at 810 cm^{-1} shifted to higher frequency region 850-833 cm^{-1} in all these complexes also suggestive of coordination of Ni(II) or Cu(II) metal through nitrogen atom of -NH$_2$ group of ethylenediamine. The band in the region 522-485 cm^{-1} in the spectra of all mixed ligand Ni(II) and Cu(II) complexes may be assigned to (M-O) band frequency while medium bands in the region 630-525 cm^{-1} are assigned to (M-N) band frequency[18]. These bands are not present in the ligand (ethylenediamine). The assignments are based on the assumption[19] 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 excepted to appear at lower frequencies. The above data confirm the coordination of oxygen atom of O-H (phenolic) group and nitrogen atom of -NO (in case of 1N2N) or -NO$_2$ (in case of ONP, DNP, TNP) or -NH$_2$ (in case of OABA, en) group or pyridine ring (in case of 8HQ) to Ni(II) or Cu(II) metal in all the mixed ligand complexes.

Electronic spectra: Electronic spectra were recorded on Perkin Elmer Lambda-15 UV-vis spectrophotometer in paraffin solvent. The band observed in electronic spectra of mixed ligand Ni(II) and Cu(II) complexes with ethylenediamine(en) are given in Table-3. A comparative look of the electronic spectral data of ligand and its mixed ligand Ni(II) and Cu(II) complexes show that the π-π* transition(at 235 nm) and n-π* (at 295 nm) 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.

TABLE-3
ELECTRONIC SPECTRAL DATA (nm) OF
THE LIGAND AND COMPLEXES

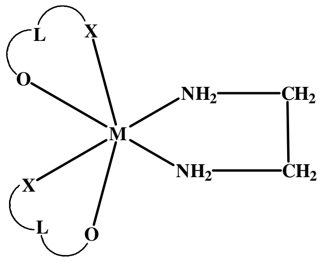
Ligand/complexes	Diffuse reflectance (nm)
Ethylenediamine (en)	235, 295
Ni(DNP)$_2$·en	251, 327, 370
Cu(1N2N)$_2$·en	252, 326, 394
Cu(8HQ)$_2$·en	250, 278

^{1}H NMR spectrum: The ^{1}H NMR spectrum of the second ligand ethylenediamine (en) was recorded in CDCl$_3$ solution. The spectrum exhibits a singlet at δ 2.8 ppm (4H, s, 2CH$_2$) and another singlet at δ 1.18 ppm (4H, s, 2NH$_2$) due to the amine proton.

The NMR spectra of mixed ligand complex Ni(8HQ)$_2$. en, show that there is a singlet peak at δ 2.76 ppm (4H, s, 2CH$_2$) which indicate the peak of 2CH$_2$ group of ethylenediamine and the peak at δ 1.25 ppm (4H, s, 2NH$_2$) indicate the peak of 2NH$_2$ group of ethylenediamine. Among the 12 protons of two 8-hydroxyquinoline ligands 8 protons appear as multiplet at δ 7.2-7.5 ppm and 2 protons appear as doublet at δ 8.15 ppm and the remaining 4 protons appear singlet at δ 8.8 ppm.

Conclusion

On the basis of elemental analysis, the molecular formula of the mixed ligand Ni(II) and Cu(II) complexes with ethylenediamine is found to be ML$_2$.L', where M = Ni(II) and Cu(II), L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N or OABA and L' = ethylenediamine(en). From infrared, electronic absorption spectra, ^{1}H NMR spectral studies and magnetic moment measurements, probable structures for all these complexes have been suggested (Fig. 1).



where M = Ni(II) and Cu(II), L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N or OABA; X = O or N

Fig. 1

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