

Structural Aspects of Mixed Ligand Complexes of Ni(II) and Cu(II) Metal Chelates of Organic Acids with 1,10-Phenanthroline

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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 (1N2N) and *o*-aminobenzoic acid (OABA); $L' = 1,10$ -phenanthroline. These complexes have been characterized by elemental analysis, molar conductance measurements, magnetic moment measurements, IR and electronic spectral analysis. The IR spectra suggest coordination of transition metal Ni(II) or Cu(II) with 1,10-phenanthroline through the nitrogen atoms of its pyridine fragments 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, 1,10-Phenanthroline, Oxygen and nitrogen containing organic acids, Metal chelates.

INTRODUCTION

A large number of studies on mixed ligand complex formation have been reported. Here we have synthesized mixed ligand complexes of nickel(II) and copper(II) metal chelates of some organic acids with a well known polynuclear heterocyclic base 1,10-phenanthroline (phen) as nitrogen donor bidentate ligand. Complexes of transition and non-transition metals with 1,10-phenanthroline are well established. A number of mixed ligand complexes of different metals with different organic acids of 1,10-phenanthroline are reported¹⁻⁴. In spite of these facts, the mixed ligand complexes of 1,10-phenanthroline with transition metals have been scarcely reported hence we have synthesized and characterized a number of mixed ligand complexes of nickel(II) and copper(II) metal salts of some organic acids, such as *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (1N2N) and *o*-aminobenzoic acid (OABA) with 1,10-phenanthroline.

EXPERIMENTAL

1,10-Phenanthroline (phen) and organic acids (*viz.*, ONP, DNP, TNP, *etc.*) are of BDH AnalaR quality or E. Merck quality.

Preparation 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 °C for nearly 2 h 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 to aqueous solution of Ni or Cu acetate in 2:1 molar ratio. The resulting mixture was refluxed on magnetic hot plate at 80 °C for nearly 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 °C.

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, 0.001 mol of 1,10-phenanthroline was added with constant stirring. The mixture was refluxed on magnetic hot plate with constant stirring at 80 °C for 2-3 h. 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.

RESULTS AND DISCUSSION

Some physical properties of the second ligand (1,10-phenanthroline) and the new mixed ligand Ni(II) or Cu(II) complexes obtained are listed in Table-1. 1,10-Phenanthroline is a white powder. It is feebly soluble in water, but soluble in alcohol, benzene, acetone *etc.* The mixed ligand complexes are generally coloured. They are highly soluble in polar solvents like methanol, ethanol *etc.*, partly soluble in acetone, chloroform and insoluble in non-polar solvents like benzene, CCl_4 . The complexes are stable under dry condition, *e.g.*, over anhydrous calcium chloride in a desiccators. From Table-1, it is evident that all these complexes are fairly stable at higher temperature above the melting point of the second ligand, indicating thereby greater stability.

The analytical data of the complexes (Table-1) and IR, UV, ^1H NMR *etc.*, show that all the complexes have the general formula $\text{ML}_2\text{L}'$, 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 (1N2N) and *o*-aminobenzoic acid (OABA); L' = 1,10-phenanthroline.

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 (2.2-6.5 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of molar conductance of the compounds indicate them to be covalent nature. Magnetic measurements of mixed ligand Ni(II) and Cu(II) complexes were taken by vibrating sample magnetometer at 24 °C (297 K). The values are given in Table-1. The μ_{eff} values of mixed ligand Ni(II) complexes are from 2.86-3.24 BM. Experimentally it has been found that μ_{eff} value for octahedral Cu(II) lie in the range of 1.47-5.2

BM. The μ_{eff} values for mixed ligand Cu(II) complexes are from 2.40-2.70 BM. These μ_{eff} values support the octahedral geometry of above complexes^{5,6}.

Selected infrared absorption bands are listed in Table-2. A comprehensive study of the infrared spectra of 1,10-phenanthroline metal complexes in the rock salt region was undertaken by Schilt and Taylor⁷. The pertinent bands in the infrared spectrum of the ligand (1,10-phenanthroline) are 1590, 1505, 1418 and 854 cm^{-1} . The 1590, 1505 and 1418 cm^{-1} bands are the most intense bands in the region 1600-1400 cm^{-1} and is attributed $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ vibrations. The band at 1590 cm^{-1} in the spectrum of the ligand is due to C=N vibration, has shifted to higher frequencies by 10-17 cm^{-1} with additional weak band in the spectra of mixed ligand complexes. The band at 1505 cm^{-1} of the ligand has also showed a negative shift by 23-43 cm^{-1} while band at 1418 cm^{-1} has shifted to higher frequencies by 5-12 cm^{-1} in the spectra of all these complexes, which suggest the coordination of the ligand through nitrogen atom.

Bands in the region 900-700 cm^{-1} are identified with motions of ring hydrogen atom moving in phase out of the plane of the ring. The particular frequency at which absorption occurs will depend upon the number of adjacent hydrogen atoms around the ring. Since 1,10-phenanthroline has three rings, two of which are equivalent with three hydrogen atoms. Only two bands are observed at 738 cm^{-1} (assigned to out-of-plane motions of hydrogen atoms in the heterocyclic rings) and 854 cm^{-1} (hydrogen-atoms on the central ring). On complexation, the multiple splitting of these two bands arise out-of-plane motions other than those in phase and also probably from overtones of low lying fundamentals in resonance. The splitting of these two bands appears to be metal sensitive. These facts suggest the coordination of the nickel(II) or copper(II) metal with 1,10-phenanthroline through the nitrogen atoms of its pyridine fragments.

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

Ligand/complexes	m.w. (found)	Colour	b.p./m.p./ decomp. temp. (°C)	Yield (%)	μ_{eff} (B.M.)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Elemental analysis (%): calcd. (found)			
							M	C	H	N
1,10-Phenanthroline (phen)	—	White	117m	—	—	—	—	—	—	—
Ni(DNP) ₂ .phen	605	Deep yellow	226m	73	2.86	4.0	9.71 (9.55)	47.62 (47.51)	2.32 (2.28)	13.89 (13.65)
Ni(TNP) ₂ .phen	695	Yellow	245d	78	2.96	3.0	8.45 (8.31)	41.46 (41.28)	1.73 (1.65)	16.12 (16.03)
Ni(8HQ) ₂ .phen	527	Yellowish green	>300d	67	2.91	4.5	11.14 (11.02)	68.35 (68.29)	3.80 (3.75)	10.63 (10.51)
Ni(1N2N) ₂ .phen	583	Brown	226d	65	3.24	2.2	10.07 (9.85)	65.90 (65.79)	3.43 (3.38)	9.61 (9.36)
Ni(OABA) ₂ .phen	511	Light brown	235m	56	3.13	4.7	11.49 (11.28)	61.09 (60.91)	3.92 (3.85)	10.97 (10.82)
Cu(DNP) ₂ .phen	610	Pale green	196m	74	2.40	5.2	10.42 (10.62)	47.25 (47.13)	2.30 (2.22)	13.78 (14.17)
Cu(TNP) ₂ .phen	700	Yellow	226m	77	2.70	6.0	9.08 (8.86)	41.17 (41.04)	1.72 (1.62)	16.01 (15.85)
Cu(8HQ) ₂ .phen	532	Green	284m	65	2.62	4.9	11.95 (11.78)	67.73 (67.56)	3.76 (3.65)	10.54 (10.35)
Cu(1N2N) ₂ .phen	588	Deep brown	197m	63	2.54	6.5	10.81 (10.59)	65.36 (65.21)	3.40 (3.35)	9.53 (9.41)
Cu(OABA) ₂ .phen	516	Deep brown	181m	59	2.48	5.3	12.32 (12.20)	60.52 (60.36)	3.88 (3.80)	10.86 (10.79)

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

Compound/complexes	ν(C=C) + ν(C=N)			ν _{ring H-atoms}	ν(M-N)	ν(M-O)
1,10-Phenanthroline(phen)	1590	1505	1418	854	–	–
Ni(TNP) ₂ phen	1605	1475	1426	839	761	630, 532
Ni(1N2N) ₂ phen	1606	1477	1427	843	769	575, 525, 505, 450
Cu(DNP) ₂ phen	1604	1472	1429	841	760	620, 531
Cu(TNP) ₂ phen	1607	1482	1429	838	767	626, 550
Cu(8HQ) ₂ phen	1600	1462	1430	851	756	625, 600

The band in the region 519-450 cm⁻¹ in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium bands in the region 637-525 cm⁻¹ is assigned to M-N band frequency. These bands are not present in the corresponding ligand. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of phenanthroline to metal in all the complexes.

The bands observed in electronic spectra of mixed ligand nickel(II) and copper(II) metal complexes are given in Table-3. Electronic spectral data of mixed ligand Ni(II) and Cu(II) complexes show that the π-π transition and n-π transition of the ligand have appreciably shifted. These shifts 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 is suppose that the complexes are in octahedral geometry.

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

Complexes	Diffuse reflectance (in nm)
Ni(8HQ) ₂ phen	234, 274, 358
Ni(OABA) ₂ phen	238, 278, 330, 365
Cu(1N2N) ₂ phen	238, 330, 347
Cu(OABA) ₂ phen	337, 250, 354

The ¹H NMR spectrum of the second ligand 1,10-phenanthroline (phen) was recorded in CDCl₃ solution. The spectrum exhibit doublet at δ 8.5 ppm (4H), triplet at π 7.5 ppm (2H) and doublet at δ 7.1 ppm (2H).

The NMR spectra of mixed ligand complex Cu(TNP)₂phen, show a singlet peak at δ 9.2 ppm (4H) which indicate the peak of ring hydrogen of 2,4,6-trinitrophenol. Whereas the peak at δ 8.3 ppm (4H) and the peak at δ 7.68 ppm (4H) are the peak of ring hydrogen of 1,10-phenanthroline.

Conclusion

On the basis of analytical data, the general formula of mixed ligand complexes of nickel(II) and copper(II) comes out to be ML₂L', where M = Ni(II) or Cu(II), L = deprotonated *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (1N2N) or *o*-aminobenzoic acid (OABA) and L' = 1,10-phenanthroline (phen). Infrared, electronic absorption spectra and magnetic moment measurements suggested the coordination of the ligand (phen) with Ni(II) or Cu(II) through the nitrogen atoms of its pyridine fragments. This facts lead to the following probable structure for these complexes (Fig. 1).

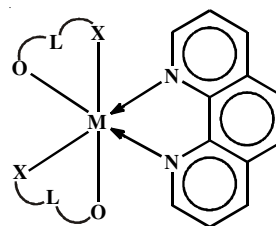


Fig. 1. Where M = Ni(II) or Cu(II) ; X = O or N ; L = deprotonated ONP, DNP, TNP, 1N2N, 8HQ or OABA

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