

Structural Aspects of Mixed Ligand Complexes of Ni(II) Metal Chelates of Organic Acids with Propylenediamine

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Abstract: a series of mixed ligand complexes of the general formula ML_2L' have been synthesized and characterized, where $M=Ni$ 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' = propylenediamine. These complexes have been characterized by elemental analysis, molar conductance measurements, magnetic moment measurements, IR and electronic spectra analysis. The IR spectra suggests coordination of transition metal Ni(II) with propylenediamine through the nitrogen atoms and N/O-atoms of the organic acid. The electronic spectra data and magnetic moment value suggests the octahedral geometry of the complexes.

Keywords: Mixed ligand complexes, Propylenediamine, Oxygen and Nitrogen containing organic acids, Metal chelates.

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1. Introduction

A large number of studies on mixed ligand complex formation have been reported. Here we have synthesized mixed ligand complexes of Ni(II) metal chelates of some organic acids with a well known base propylenediamine (Pn) as nitrogen donor bidentate ligand (Fig.1). Complexes of transition and non-transition metals with propylenediamine

(Pn) are well established. A number of mixed ligand complexes of different metals with different organic acids of propylenediamine are reported¹⁻⁴.

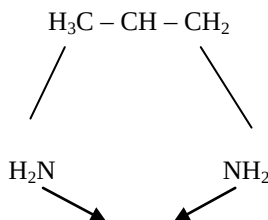


Figure 1.

In spite of these facts, the mixed ligand complexes of propylenediamine with transition metals have been scarcely reported hence we have synthesized and characterized a number of mixed ligand complexes of Ni(II) metal salts of some organic acids such as O-nitrophenol (ONP), 2,4-Dinitrophenol (DNP), 2,4,6-Trinitrophenol (TNP), 8-hydroxyquinoline (8HQ) and O-aminobenzoic acid (OABA) with propylenediamine.

2. Experimental

Propylenediamine (Pn) and organic acids viz. ONP, DNP, TNP etc. are of BDH Anala R quality or E. Merck quality.

3. 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 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) metal chelates got separated. It was filtered, washed with distilled water and dried in an electric oven at 100°C .

4. 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 propylenediamine 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.

5. Detection Method

The elemental analysis was carried out on an elemental analyzers Heracus 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.

6. Results and Discussion

Some physical properties of the second ligand (propylenediamine) and the new mixed ligand Ni(II) complexes obtained are listed in Table-1. Propylenediamine is a colourless liquid which is insoluble in cold water but is soluble in alcohol, benzene, acetone etc. The mixed ligand complexes are generally coloured. They are generally soluble in polar solvents like water, methanol, ethanol, partly soluble in acetone, but sparingly soluble in non-polar solvents, namely chloroform, n-hexane, benzene, dioxane etc.

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), L = deprotonated organic acids such as O-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxy quinoline (8HQ), 1-nitro,so-2-naphthol (1N 2N) and O-aminobenzoic acid, L' = propylenediamine. 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 of molar conductance of the compounds indicate them to be covalent nature. Magnetic measurement of mixed ligand Ni(II) complexes were taken by vibrating sample Magnetometer at 24°C (297 K) and by Faraday method. The values are

given in Table -1. The μ_{eff} values of mixed ligand Ni(II) complexes are lie in the range of 3.01 to 3.45 BM. These μ_{ef} values support the octahedral geometry of the above complexes.

Table 1. Analytical data of the ligand and mixed ligand complexes

Ligand/ Complexes	m.w. foun d	Colour	b.p/m.p/ decomposi tion temp.	Yiel d %	μ_{eff} (B. M)	Mo lar Co nd uc tan ce	Elemental analysis (%) Calculated/(Found)			
							M	C	H	N
Propylene diamine (Pn)		Colour- less	119.56	-	-	-	-	-	-	-
Ni(DNP) ₂ P n	499	Deep Yellow	218 t, 224 d	67	3.11	3.5	11.52	35.85	3.14	16.68
Ni(TNP) ₂ Pn	589	Light Yellow	278 t, 285d	61	3.01	4.1	9.59	30.35	2.21	18.67
Ni(1N2N) ₂ Pn	477	Brown	282 t, 7300 d	86	3.22	3.9	12.12	57.75	4.52	11.58
Ni(8HQ) ₂ P n	421	Greenis h Yellow	187 m.p	92	3.45	3.2	13.82	59.62	5.11	13.15

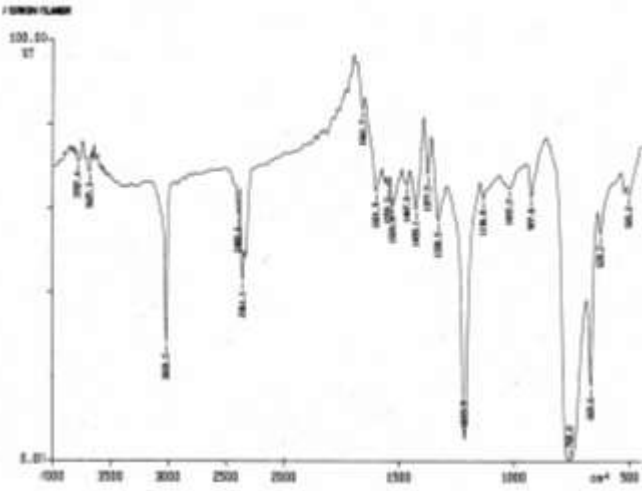
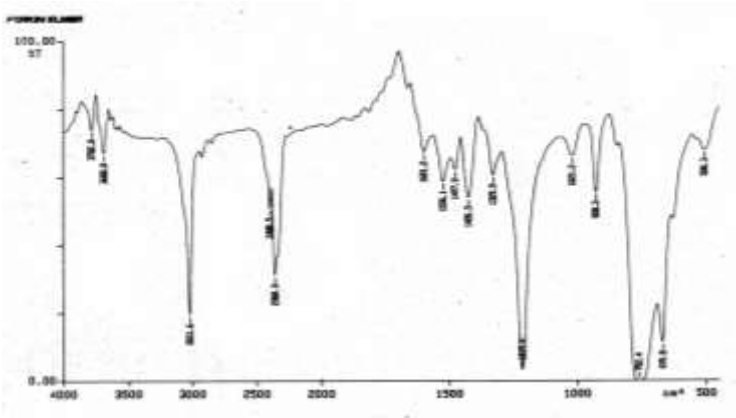
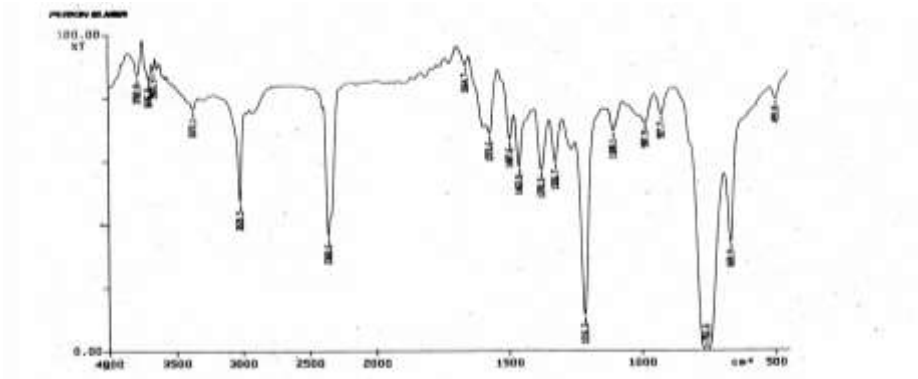
Selected infrared absorption bands are listed in Table-2. An examination of the infrared spectra of complexes of Ni(II) metal salts of some organic acids with propylenediamine show that different NH_2 vibrations are present in the complexes. Though in some cases the vibrations of the organic acid salts of Ni(II) metals overlap the NH_2 vibrations, but in most of the $-\text{NH}_2$ vibrations, can be located. A comparison of the spectra of the acid salt and the complexes formed by propylenediamine, points that there are extra peaks due to the propylenediamine molecule. The two N-H stretching vibration appear as broad or medium peaks between $3400\text{--}3150\text{ cm}^{-1}$. These bands are very much affected in the complexes. This appear between $3400\text{--}3150\text{ cm}^{-1}$ with increased intensity in the complexes, thereby suggesting that the decrease in bond order of N-H on complexation. This shifts in conformity with the coordination through N-H as there has been electron drain from the nitrogen of propylenediamine to the Ni(II). One or two bands have been observed in the region $1603\text{--}1560\text{ cm}^{-1}$ in the complexes of Ni(II) metal salts of some organic acids with propylenediamine. The complexes

also show one or two bands between $1140\text{--}1108\text{ cm}^{-1}$ region. These shifting indicates coordination of Ni(II) metal through N-atom of NH_2 of second ligand (Pn). Further the NH_2 rocking at 815 cm^{-1} shifted to higher frequency region $875\text{--}835\text{ cm}^{-1}$ in all these complexes also suggestive of coordination of Ni(II) metal through nitrogen atom of $-\text{NH}_2$ group of propylenediamine. The band in the region $520\text{--}460\text{ cm}^{-1}$ in the spectra of all mixed ligand Ni(II) complexes may be assigned for M-O band frequency while medium bands in the region $630\text{--}525\text{ cm}^{-1}$ is assigned to M-N band frequency. These bands are not present in the ligand (propylenediamine). 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 of oxygen atom of O-H (phenolic) group and nitrogen atom of N-O (in case of 1N2N) or NO_2 (in case of OND, DNP, TNP) or NH_2 (in case of OABA), group or pyridine ring (in case of 8 HQ) to Ni(II) metal in all the mixed ligand complexes.

Table 2. IR Spectral Data for Ligand and its mixed ligand Ni(II) complexes (cm^{-1})

Compound and Complexes	Selected infrared absorption bands (in cm^{-1})				
	$\nu_{\text{N-H}}$	Asym $\delta_{\text{N-H}}$	Sym $\delta_{\text{N-H}}$	Rocking NH_2	Fair Infrared
Propylenediamine (Pn)	3370, 3300	1610	1095	815	-
Ni(DNP) $_2$ Pn	3400, 3275	1602, 1565	1137	850	628, 563, 525, 505
Ni(TNP) $_2$ Pn	3375, 3255	1604, 1556	1195	835	618, 523, 515, 503

The infrared spectra of some of the compounds are viewed in Figures (I), (II) and (III).



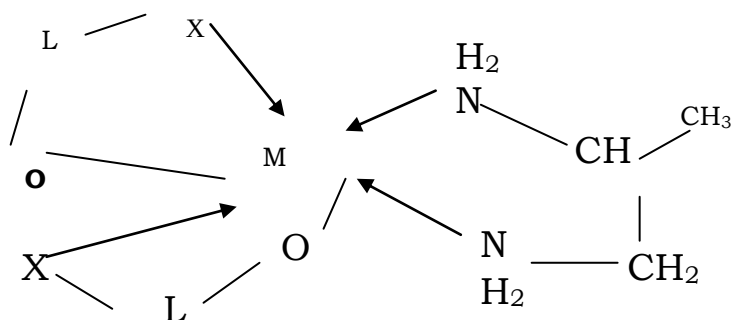
The band observed in electronic spectra of mixed ligand Ni(II) complexes with propylenediamine (Pn) are given in Table-3. Electronic spectral data of mixed ligand Ni(II) complexes show that the $\pi\text{-}\pi^*$ transition and $n\text{-}\pi^*$ transition of the ligand have appreciably shifted. These 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, it is suggested that the complexes have octahedral geometry. Electronic spectra of some of the compounds are shown in Fig. 4.6 to 4.7.

Table 3. Electronic Spectral Data (nm) of the ligand and complexes

Ligand/Complexes	Diffuse reflectance (in nm)
Ni(DNP) ₂ Pn	208, 244, 329, 370
Ni(8HQ) ₂ Pn	242, 350

7. Conclusion

On the basis of analytical data, the general formula of mixed ligand complexes of Ni(II) comes out to be $\text{ML}_2\text{L}'$ where $\text{M} = \text{Ni(II)}$, $\text{L} =$ deprotonated O-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-Nitroso-2-naphthol, $\text{L}' =$ Propylenediamine (Pn). Their infrared, electronic absorption spectra and magnetic moment measurements suggest the coordination of the ligand (Pn) with Ni(II) through the nitrogen atoms of NH_2 groups. This facts lead to the following probable structure for these complexes.



Where $\text{M} = \text{Ni(II)}$, $\text{L} =$ deprotonated ONP, DNP, TNP, 8HQ, $\text{X} = \text{O}$ or N

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