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Mixed Ligand Complexes of Transition Metal Chelates of 1-nitroso-2-naphthol and 8-hydroxyquinoline with Picolinic Acid and Quinaldinic acid

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ABSTRACT

Mixed ligand transition metal complexes having general formula $ML_2 \cdot HL'$, where M = Cu(II) or Pd(II); L = deprotonated 1-nitroso-2-naphthol or 8-hydroxyquinoline; HL' = picolinic acid or quinaldinic acid have been synthesised and characterised on the basis of Infrared, electronic absorption spectral data, magnetic and conductance measurements. The above study reveals the octahedral geometry of the complexes.

Key words: Mixed Ligand Complexes, Picolinic acid, Quinaldinic acid.

INTRODUCTION

Picolinic acid and quinaldinic acid have been extensively investigated for their possible roles in analytical determination of metal ions¹⁻⁴. They have replaceable hydrogen atom as well as two donor atoms suitably placed to form a five membered chelating ring with metal ion. The versatile chelating ability of picolinic acid and quinaldinic acid with various metals is well established⁵⁻¹⁰. In the present communication, we report the synthesis and characterization of a number of mixed ligand complexes of Cu(II) or Pd(II) with above mentioned ligands.

EXPERIMENTAL

Picolinic acid (HPicA), quinaldinic acid (HQuinA), 1-nitroso-2-naphthol-(1N2N) and 8-hydroxyquinoline (8HQ) of AnalaR grade were used as such.

Preparation of the complexes

To the suspension of 0.01 mole transition metal salt of organic acid (1N2N or 8HQ) in absolute ethanol, 0.01 mole picolinic acid (HPicA) or quinaldinic acid (HQuinA) was added. The whole reaction mixture was refluxed with constant stirring on a hot plate of magnetic stirrer for 1-2 hours and cooled to give characteristic colour solid adduct. The

adduct was filtered, washed with absolute ethanol and dried in an electric oven at 100°C.

RESULTS AND DISCUSSION

Some physical properties and analytical data of the ligands (HPicA & HQuinA) and the new mixed ligand complexes obtained are listed in Table - 1.

The mixed ligand complexes are generally coloured. They are appreciably soluble in most polar solvents such as methanol, DMF etc but are insoluble in non-polar solvents such as benzene, toluene, ether etc. The complexes are found to be stable when stored under dry conditions. Melting/decomposition temperatures of complexes have been found to be higher than those of the corresponding ligand, indicating thereby their greater stability.

Molar conductance

Molar conductance values of all these complexes were measured in methanol at 23°C at a concentration of 10^{-3} M. The values are given in Table-1. Low values of molar conductance ($2.8-6.2 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) show that these complexes are non-electrolyte in nature.

Infrared spectra

Infrared spectra of the ligands (picolinic acid & quinaldonic acid) and their mixed ligand Cu(II) or Pd(II) complexes were recorded in KBr phase between $4000-400 \text{ cm}^{-1}$ with the help of JASCO-FTIR spectrophotometer model -5300. Selected IR absorption bands are shown in Table - 2.

IR spectra of picolinic acid & its complexes

The broad band at 3400 cm^{-1} in the spectrum of ligand(HPicA) indicates strong intramolecular hydrogen bonding in it. The spectra of all the mixed ligand complexes of picolinic acid with transition metal derivatives of some organic acids(1N2N & 8HQ) show a number of unexpected features. The shift of the -OH band of the second ligand and its reappearance in the region $3075-3060 \text{ cm}^{-1}$ may be assigned to O-H...O/N...H-O absorption and this feature suggests hydrogen bonding to be a dominant factor in stabilizing these complexes.

The appreciable shift of 1650 cm^{-1} , 1600 cm^{-1} and 1520 cm^{-1} bands of the ligand (HPicA) in the mixed ligand complexes suggest the coordination of ligand with Cu(II) or Pd(II) through oxygen atom of carboxylic acid (COO^-) moiety.

The 1580 cm^{-1} band of the ligand (HPicA) as shifted by 5 cm^{-1} in the complexes. These features are quite suggestive of the coordination of ligand with Cu(II) or Pd(II) metal through nitrogen atom of pyridine ring.

IR spectra of quinaldonic acid & its complexes

The broad band at 3400 cm^{-1} and multiple bands in the region $2700-1800 \text{ cm}^{-1}$ in the spectrum of ligand(HQuinA) indicate strong intramolecular hydrogen bonding involving the carboxyl hydrogen atom and nitrogen atom of quinoline ring. In the spectra of mixed ligand complexes, these bands have disappeared. However the spectra of the complexes exhibit new broad bands of weak to medium intensities in the region $3400-3000 \text{ cm}^{-1}$, which may be attributed to O-H...O/N...H-O absorption. This suggests hydrogen bonding to be a dominant factor in stabilizing these complexes.

The medium intensity band at 1680 cm^{-1} in the spectra of ligand, all probability, be assigned to the antisymmetric stretching frequency of the -COOH group, has shifted to lower frequencies by $5-30 \text{ cm}^{-1}$ in almost all the complexes. The 1620 cm^{-1} and 1560 cm^{-1} bands of the ligand too, in almost all the complexes, have shifted to lower frequencies by $10-40 \text{ cm}^{-1}$. The 1535 cm^{-1} , which appear as a medium intensity in the spectrum of the ligand, shows an appreciable shift of about $20-35 \text{ cm}^{-1}$ in the spectra of these complexes. These features are suggestive of coordination of ligand with Cu(II) or Pd(II) through oxygen atom of carboxyl(COO^-) moiety.

The 1580 cm^{-1} (assigned to $\nu_{\text{C=N}}$) band of the ligand has shifted to lower frequencies by $10-15 \text{ cm}^{-1}$ in almost all the complexes. These features suggest the coordination of ligand with Cu(II) or Pd(II) metal through nitrogen atom of quinoline ring.

Electronic absorption spectra

Electronic absorption spectra of the ligands

Table 1:

Compound	Colour	Melting Decomp.	Molar cond.	Magnetic moment	Analysis % found (calcd.)			
					C	H	N	M
Picolinic acid (HPiCA)	White	135	-	-	-	-	-	-
Cu(8HQ) ₂ .HPiCA	Sky blue	280d	2.8	1.75	60.05 (60.15)	3.53 (3.60)	8.86 (8.90)	13.29 (13.36)
Cu(1N2N) ₂ .HPiCA	Light grey	300d	3.1	1.86	58.25 (58.85)	(3.20)	(7.92)	(11.83)
Pd(8HQ) ₂ .HPiCA	Dark yellow	295d	4.5	Diamag.	55.70 (55.80)	3.28 (3.32)	8.12 (8.26)	20.50 (20.72)
Pd(1N2N) ₂ .HPiCA	Greenish black	>300	4.6	Diamag.	54.02 (54.45)	2.54 (2.96)	7.20 (7.32)	18.09 (18.49)
Quinaldinic acid (HQuinA)	White	157m	-	-	-	-	-	-
Cu(8HQ) ₂ .HPiCA	Dark green	275d	5.2	1.96	64.00 (64.10)	3.00 (3.60)	7.90 (8.00)	12.00 (12.90)
Cu(1N2N) ₂ .HPiCA	Greenish grey	260md	5.5	2.00	61.90 (62.06)	3.10 (3.27)	7.24 (7.30)	12.00 (12.18)
Pd(1N2N) ₂ .HPiCA	Greenish brown	280d	6.2	Diamag	55.78 (57.08)	2.90 (3.04)	6.34 (6.74)	16.90 (17.01)

Table 2:

Compound	Selected IR absorption bands (in cm ⁻¹)					Absorption band (in nm)	
Picolinic acid (HPiCA)	3400br	1650s	1600s	1580s	1520s	283, 235	
Cu(8HQ) ₂ .HPiCA	3075w	1640s	1605s	1580w	1500w	600, 570	
Cu(1N2N) ₂ .HPiCA	3075w	1640s	1620s	1580w	1500w	600, 580	
Pd(8HQ) ₂ .HPiCA	3060w	1680m	1600sh	1575s	1500s	645, 475	
Pd(1N2N) ₂ .HPiCA	3075w	1650w	1600sh	1580s	1500s	645, 480	
Quinaldinic acid (HQuinA)	3400br 2700-1800v	1680m	1620s	1580sh	1500s		
Cu(8HQ) ₂ .HQuinA	3500-3200v 2910w	1675sh	1640s	1565m	1535sh	1510s	640, 575
Cu(1N2N) ₂ .HQuinA	3400-3200v 2950m, 2910m	1680sh	1630s	1565m	1540sh	1515w	800, 570
Pd(1N2N) ₂ .HQuinA	3560-3450v	1750sh	1660m	1590sh	1570m	1500s	950, 655, 480

br=broad, m=medium, s=strong, sh=shoulder, v=very strong, w=weak

(picolinic acid & quinaldinic acid) and their mixed ligand Cu(II) or Pd(II) complexes were recorded on PERKIN ELMER LAMBDA-15 UV-VIS spectrophotometer in paraffin solvent. The bands observed are given in Table -2.

A comparative look of electronic absorption spectral data of the ligands and their complexes indicate that n-p and p-p* transition of the ligands have shifted to higher frequencies.

The electronic absorption spectra of mixed ligand Cu(II) complexes show broad band at 600 nm with picolinic acid and in the region 640-800 nm with quinaldinic acid as second ligand.

The strong absorption in the region 570-580 nm in all the complexes attributed to ligand absorption and charge transfer transition, showing coordination of ligand with metal chelates by L-M interaction.. However from the position of spectral bands and their low intensities it is supposed that the complexes are in octahedral geometry.

Magnetic moment

Magnetic moment of mixed ligand transition metal complexes have been measured by Can Faraday magnetic susceptibility balance at 30°C. The magnetic moment values are shown in Table - 1.

The spin only value of magnetic moment of Cu(II) octahedral complex is 1.73 BM corresponding to one unpaired electron. The magnetic moment (μ_{eff}) values for Cu(II) complexes are in the range of 1.75 – 2.00 BM, suggest the octahedral geometry of the complexes. The complexes of Pd(II) are diamagnetic.

Structure & bonding

Based on the analytical and spectral (infrared & electronic absorption) studies, the structure and bonding of the newly prepared mixed ligand Cu(II) or Pd(II) complexes involving some chelating organic acids and picolinic acid or quinaldinic acid may tentatively be proposed as shown in Fig. 1 & 2.

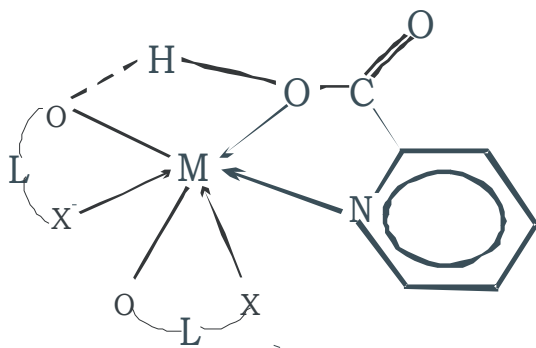


Fig. 1:

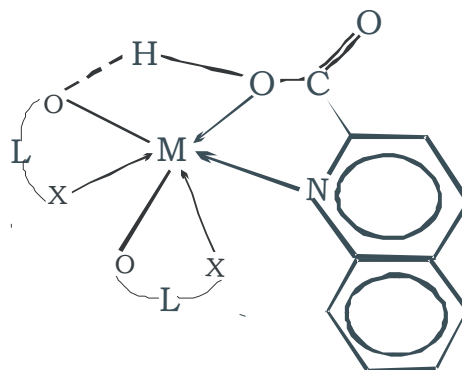


Fig. 2:

where M = Cu(II) or Pd(II); deprotonated 8-hydroxyquinoline or 1-nitroso-2-naphthol; X = O or N

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