International Journal of Recent Development in Engineering and Technology
Website: www.ijrdet.com (ISSN 2347-6435 (Online) Volume 15, Issue 06, June 2026)

Mixed Ligand Complexes of Transition Metal Chelates of Picolinic Acid, Quinaldinic Acid and 8-Hydroxyquinaline with 1-Nitroso-2-Naphthol

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***Abstract*--Mixed ligand transition metal complexes having general formula $ML_2.HL$, where M = Cu(II) or Pd(II); L = deprotonated picolinic acid, quinaldinic acid, 8-hydroxyquinoline; HL = 1-nitroso-2-naphthol have been synthesized and characterized. The IR spectra of the complexes suggest that the coordination of the ligand with transition metal chelato has taken place through the oxygen atom of COOH/-OH (phenolic) group as well as nitrogen atom of quinoline ring/-NO group. The IR spectra also indicate the presence of hydrogen bonding in them.**

***Keywords*-- Mixed ligand complexes, transition metal, 8-hydroxyquinoline, 1-nitroso-2-naphthol, infrared spectra.**

I. INTRODUCTION

1-Nitroso-2-naphthol has been extensively used in analytical chemistry-al 8-Hydroxyquinoline (oxine) has been primarily used as analytical reagent but in recent years finding new uses in many fields including biology, pathology, pharmacology and bacteriology complexes of 1-nitroso-2-naphthol with alkali metals, alkaline earth metals, some transition metals as well as rare earth metals are well investigated. In continuation, we have synthesized and characterized several mixed ligand Cu(II) & Pd(II) complexes involving the nitrogen and oxygen donor organic acids with 1-nitroso-2-naphthol.

II. EXPERIMENTAL

Picolinic acid (HPicA), quinaldinic acid (HQuinA), I-nitroso-2-naphthol (1N2N) and 8-hydroxyquinolins (SHQ) of Analak grade were used as such.

Preparation of the complexes: To the suspension of 0.01 mole transition metal salt of organic acid (ML) in absolute ethanol, 0.01 mole 1-nitroso-2-naphthol or 8-hydroxyquinoline (HL') 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.

III. RESULTS AND DISCUSSION

Some physical properties and analytical data of the ligands(8HQ & IN2N) and the new mixed ligand complexes obtained are listed in Table - 1.

TABLE-1

Compound	**Colour**	**Melting/ Decomp. Temp.(°C)**	**Molar Conductance**	**Magnetic**	**Analysis % found/(caled.)**			
				moment	**C**	**H**	**N**	**M**
1-Nitroso-2-naphthol (1N2N)	White	157m	….	….	….	…..	….	…..
Cu $(8HQ)_2$ .IN2N	Dark green	246d	4.5	1.76	63.80 (64.12)	3.40 (3.62)	7.80 (8.00)	11.60 (12.00)
Cu $(PicA)_2$ .IN2N	Chocolate	300d	5.2	1.86	54.00 (55.00)	2.96 (3.12)	8.02 (8.45)	12.90 (13.10)
CU $(QuinA)_2$.IN2N	Dark sky	260md	5.2	1.94	61.00 (62.00)	3.10 (3.20)	7.00 (7.20)	10.20 (10.80)
Pd$(QuinA)_2$.IN2N	Brown	240d	9.2	Diamag.	57.20 (57.70)	2.90 (3.00)	6.70 (6.80)	16.50 (17.00)

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 10^{-3}M The values are given in Table-1. Low values of molar conductance (4.5 - 9.2ohm^{-1} cm^{2} mol^{-1}) show that these complexes are non-electrolyte in nature.

Infrared spectra: Infrared spectra of the ligands (picolinic acid & quinaldinic acid) and their mixed ligand Cu(II) or Pd(II) complexes were recorded in KBr phase between 4000-650 cm with the help of JASCO-FTIR spectrophotometer model - 5300. Selected IR absorption bands are shown in Table - 2.

TABLE-2

Compound	Selected IR absorption bands (in cm^{-1})		Absorption band(in nm)
1-Nitroso-2-naphthol (IN2N)	3300br, 3055m	1640s	295, 234
Cu(8HQ)$_2$.1N2N	3400v, 3040m. 2930m	1600s	640.575
Cu(PicA)$_2$.1N2N	3500-3400v, 2910m, 2850m	1650s, 1605s	800, 570
Cu(QuinA)$_2$.IN2N	3450-3250br, 2910m. 2850m	1640s, 1600sh	950,655, 480
Pd(QuinA)$_2$.IN2N	2940mbr	1600sh, 1590m	

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

The broad absorption band observed at 3300 cm^{-1} in 1-nitroso-2-naphthol indicates strong intramolecular hydrogen bonding. None of the mixed-ligand complexes display anomalous or broad bands in the 700–1300 cm^{-1} region; therefore, the formation of an acid-salt structure involving a very short O···H···O bond (approximately 2.4 Å) is highly unlikely.

The infrared spectra of mixed-ligand Cu(II) and Pd(II) complexes containing 1-nitroso-2-naphthol are very similar to those of the corresponding silver complex. This suggests that smaller metal ions may adopt tetrahedral coordination, whereas larger ions are likely to be octahedrally coordinated. Coordination is supported by the presence of an infrared band at 1580 cm^{-1} assigned to the C=N group of the ligand. This band shifts to lower frequencies with increasing atomic weight of the metal and appears at 1570 cm^{-1} for the Pd(II) complex. In Cu(II) complexes, additional bands at 1600 cm^{-1} and 1650 cm^{-1} are observed, which may arise from a third 8-hydroxyquinoline molecule loosely bound to the metal ion.

Among mixed-ligand complexes containing 1-nitroso-2-naphthol, the Pd(II) complex differs from the others by showing a medium broad band at 2940 cm^{-1}. The Cu(II) complexes exhibit variable broad bands centered around 3400 cm^{-1} but show no absorption in the 2200–1800 cm^{-1} region. The N=O stretching band at 1640 cm^{-1} is metal-sensitive and shifts to lower frequencies with increasing metal atomic weight. Additionally, Cu(II) complexes display an extra band at 1650 cm^{-1}.

Electronic absorption spectra of the ligands (1N2N) and their mixed-ligand complexes were recorded in methanol using a Perkin-Elmer Lambda-15 spectrophotometer, and the observed bands are summarized in Table 2. The free ligands exhibit sharp, intense absorption bands in the regions 233–306 nm and 210–362 nm, respectively, corresponding to $\pi \rightarrow \pi^*$ transitions within the aromatic ring system. In the case of 1N2N, a charge-transfer band is also observed at 653 nm.

The mixed-ligand Cu(II) and Pd(II) complexes of 1N2N show electronic absorption bands in the regions 231–251 nm, respectively, indicating the formation of π–π complexes.

The electronic spectra of all mixed-ligand complexes exhibit a charge-transfer band in the wavelength range of 360–410 nm. The observed shift in the π→π* transition band of the ligand, along with the appearance of a charge-transfer band in the complexes, indicates the presence of π-interaction between the metal and ligand orbitals.

The magnetic moments of the mixed-ligand transition metal complexes were determined using a Gouy/Faraday magnetic susceptibility balance at 30 °C, and the obtained values are listed in Table 1. The spin-only magnetic moment for an octahedral Cu(II) complex is 1.73 BM, corresponding to one unpaired electron. The experimentally observed effective magnetic moment (μ_{eff}) values for Cu(II) complexes fall in the range of 1.75–2.00 BM, which supports an octahedral geometry for these complexes. In contrast, the Pd(II) complexes were found to be diamagnetic.

Based on elemental analysis, infrared spectra, electronic spectra, and magnetic measurements, the structure and bonding of the newly synthesized mixed-ligand complexes involving chelating organic acids such as HPicA, HQuinA, 8-hydroxyquinoline, and 1-nitroso-2-naphthol/8-hydroxyquinoline are tentatively proposed as illustrated in Figures 1 and 2.

IV. MICROBIOLOGICAL STUDIES

Minimum inhibitory concentration (MIC) values (□gml^{-1}) of mixed ligand transition metal complexes have been examined by Serial dilute method for activity against some bacteria[11], viz., E. coli. S. aureus and fungi[12] viz. C. albicans. Althought a few of the mixed ligand complexes exhibited significant inhibition whereas other did not show any activity. The results are summarized in Table - 3.

The results of antibacterial and antifungal activity evaluation revealed that four of the mixed ligand complexes, 1-Nitroso-2-naphthol (IN2N), Cu(8HQ)$_2$.1N2N, Cu(PicA)$_2$.1N2N, Cu(QuinA)$_2$.IN2N and Pd(QuinA)$_2$.IN2N were relatively potential inhibitor of the of both the test bacteria and one fungi.

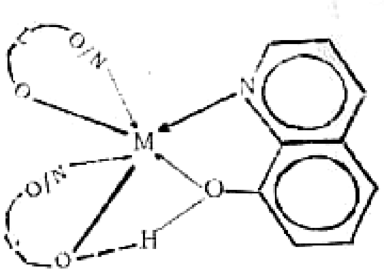
The MIC value of Cu(8HQ)$_2$.1N2N at concentration of 42 µgml^{-1} Cu(QuinA)$_2$.IN2N and Pd(QuinA)$_2$.IN2N and Cu(PicA)$_2$.1N2N at concentration of 21 µgml^{-1} for E. Coli. The MIC values of Cu(8HQ)$_2$.1N2N, and Cu(PicA)$_2$.1N2N at concentration 42 µgml^{-1} and Cu(QuinA)$_2$.IN2N and Pd(QuinA)$_2$.IN2N at concentration 21 µgml^{-1} respectively for fungi C. albicans. The MIC values of all three oxygen bridge transition metal complexes at the same concentration 42 µgml^{-1} for S. aureus.

Table-3

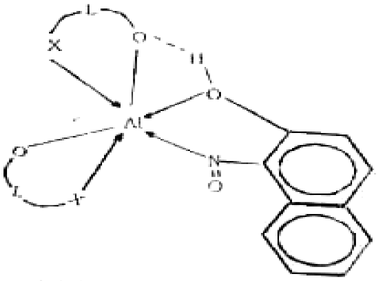
Compound	**Minimum inhibitory concentraction (in µgmol^{1})**		
1-Nitroso-2-naphthol (IN2N)	**E. Coli**	**S. aureus**	**C. albicans**
Cu(8HQ)$_2$.1N2N	42	21	42
Cu(PicA)$_2$.1N2N	21	21	42
Cu(QuinA)$_2$.IN2N	21	21	21
Pd(QuinA)$_2$.IN2N	21	21	21

V. STRUCTURE & BONDING

On the basis of elemental analysis, infrared, electronic spectra and magnetic measurements, the structure and bonding of the newly prepared mixed ligand complexes involving some chelate organic acids, e.g. HPicA, HQuinA, I-hydroxyquinoline/1-nitroso-2-naphthol and 1-nitroso-2-naphthol/8-bydroxyquinoline may tentatively be proposed as shown in Fig 1 & 2.



where L-deprotonated HPicA, HQuinA IN2N; X-O or N (Fig. 1)



where L. deprotonated HPicA, HQuinA or HQ; X-O or N (Fig. 2)

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