



MIXED LIGAND COMPLEXES OF TRANSITION METAL CHELATES OF PICOLINIC ACID, QUINALDINIC ACID AND 1- NITROSO-2-NAPHTHOL WITH 8-HYDROXYQUINOLINE

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ABSTRACT

The general formula of mixed ligand transition metal complexes can be represented as $ML_2.HL$ Where $M = Cu(II)$ & $Pd(II)$ $L =$ deprotonated picolinic acid, 1-nitroso-2-naphthol $HL =$ 8-Hydroxyquinoline have been synthesized and characterised.

The IR spectra data indicates that the ligand coordinates to the transition metal chelates through the oxygen atom of the $COOH/$ phenolic $-OH$ group and the nitrogen atom of the quinoline ring/ $-NO$ group. The IR spectra analysis also confirms the existence of hydrogen bonding.

KEY WORDS: Transition metal mixed ligand complexes, 8-hydroxyquinoline, 1-nitroso, 2-naphthol & quinaldinic acid.

INTRODUCTION :

The compound 1-nitroso-2-naphthol has found broad use in field of analytical chemistry^[1-2] 8-Hydroxyquinoline (oxine) has traditionally been used as an analytical reagent however, in been used recent years it has found expanded applications in fields such as biology, pathology pharmacology and bacteriology^[3-5]. A wide range of complexes involving 8-hydroxyquinoline^[6-10] and 1-nitroso-2-naphthol^[11-15]. with alkali, alkaline earth, transition, and rare earth metals have been thoroughly investigated.

In Continuation of this work, several mixed ligand $Cu(II)$ & $Pd(II)$ complexes containing nitrogen-and oxygen-donor organic acids with 8-hydroxyquinoline were synthesized and characterized.

EXPERIMENTAL :

Picolinic acid (HPiCA), 1-nitroso-2-naphthol (1N2N) Quinaldinic (HQuiA) 8-hydroxyquinoline (8HQ) all of AnalaR grade, were directly used in the study.

PREPARATION OF THE COMPLEXES :

A suspension of 0.01 mol of the transition metal salt of the organic acid (ML_2) was prepared in absolute ethanol. To this, 0.01 mol of either 1-nitroso-2-naphthol or 8-hydroxyquinoline (HL') was added. The reaction mixture was refluxed for 1–2 hours with continuous stirring on a magnetic stirrer hot plate. Upon cooling, a characteristic coloured solid adduct was obtained. The resulting product was filtered, washed with absolute ethanol, and dried in an electric oven at $100^\circ C$.

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 moment	Analysis % found/(caled.)			
					C	H	N	M
8-Hydroxy-quinoline (8HQ)	White	135m
Cu(PicA) ₂ .8HQ	Dark green	270t	4.3	1.91	55.40 (55.75)	3.20 (3.31)	8.29 (9.29)	13.20 (13.93)
Cu(IN2N) ₂ .8HQ	Pale green	>300d	3.6	2.10	63.10 (64.00)	3.40 (3.80)	7.60 (7.80)	11.40 (11.60)
Pd(QiunA) ₂ .8HQ	Light orange	250d	7.2	Diamag	58.20 (58.40)	3.00 (3.10)	6.90 (7.00)	17.10 (17.80)
Pd(IN2N) ₂ .8HQ	Brownish green	>300d	6.6	Diamag	57.80 (58.43)	2.90 (3.10)	6.90 (7.30)	16.90 (17.80)

The mixed-ligand complexes are generally coloured and show good solubility in polar solvents such as methanol and DMF, while they remain insoluble in non-polar solvents like benzene, toluene, and ether. These complexes are stable when stored under dry conditions. Their melting or decomposition temperatures are higher than those of the corresponding free ligands, which indicates enhanced stability of the complexes.

Molar conductance: The molar conductance of all the complexes was determined in methanol at 23°C using a concentration of 10⁻³ M. The observed values, listed in Table-1, fall in the range of 3.6–7.2 Ω⁻¹ cm² mol⁻¹. Such low conductance values confirm the non-electrolytic nature of the complexes.

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⁻¹ 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)
8-Hydroxyquinoline (8HQ)	3440br	1580s	283, 235
Cu(PicA) ₂ .8HQ	3460-3400v, 2910m	1650s, 1600m, 1570s	635, 570
Cu(IN2N) ₂ .8HQ	3500-3300v, 2930br	1600m, 1570s	638, 570
Pd(QiunA) ₂ .8HQ	2920m, 2900m, 2880m w	1570m	645, 475
Pd(IN2N) ₂ .8HQ	3460-3300v, 2930m	1570s	1050, 380

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

The broad band at 3440 cm⁻¹ in the spectrum of 8-hydroxyquinoline indicate strong intermolecular hydrogen bonding in them. None of these mixed ligand complexes show anomalous and broad absorption bands between 700-1300 cm as such acid salt structure with very short O...H...O (ca. 2.4Å) is most improvable.

The mixed ligand Cu(II) or Pd(II) complexes with 8-hydroxyquinoline give spectra closely similar to that of silver complex. It is possible that the smaller cations are tetrahedrally coordinated like the silver, while the larger ones are octahedrally coordinated, Coordination, is suggested by the infrared spectral band found at 1580 cm (C=N) in the ligand and at lower frequencies with increase in atomic weight of metal until for Pd it appears at 1570 cm. In Cu(II) complexes, there appears extra bands at 1600 cm⁻¹ and 1650 cm⁻¹ which may be due to third 8-hydroxyquinoline molecule attached loosely.

In mixed ligand complexes with 1-nitroso-2-naphthol, Pd(II) is different from the rest in having a medium broad band at 2940 cm^{-1} . The Cu(II)-complexes show variable and broad bands centred around 3400 cm^{-1} but no band between $2200\text{-}1800\text{ cm}^{-1}$. The N=O band at 1640 again is metal sensitive and shows downward trend with increase in atomic weight. Cu(II)-complexes shows an extra band at 1640 cm and 1650 cm^{-1} .

Electronic absorption spectra: Electronic absorption spectra of the ligands (8HQ & IN2N) and mixed ligand complexes were recorded on PERKIN-ELMER LAMBDA-15 spectrophotometer in methanol and bands observed are given in Table-2.

Ligands (8HQ & IN2N) exhibit sharp intense bands in the region $233\text{-}306\text{ nm}$ and $210\text{-}362\text{ nm}$ respectively. These bands indicate π -transition in aromatic ring. In latter case, charge transfer band at 653 nm also observed.

Electronic absorption bands of the mixed ligand Cu(II) & Pd(II) complexes with 8HQ & 1N2N are observed in the region $240\text{-}320\text{ nm}$ and $231\text{-}251\text{ nm}$ respectively which indicate the formation of π - π^* complexes.

Electronic spectra of all the mixed ligand complexes show a charge transfer band in the region $360\text{-}410\text{ nm}$.

The shift in position of π - π^* transition band of the ligand and appearance of a charge transfer band in the complexes show that there is a π -interaction between metal and ligand orbitals.

Magnetic moment: Magnetic moment of mixed ligand transition metal complexes have been measured by 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 complexes is 1.73 BM . corresponding to one unpaired electron. The magnetic moment (μ_{eff}) values for Cu(II) complexes are in the range of $1.75\text{-}2.00\text{ BM}$. suggest the octahedral geometry of the complexes. The complexes of Pd(II) are diamagnetic.

MICROBIOLOGICAL STUDIES

Minimum inhibitory concentration (MIC) values (μgml^{-1}) of mixed ligand transition metal complexes have been examined by Serial dilute method for activity against some bacteria¹¹, viz., E. coli, S. aureus and fungi¹² viz. C. albicans. Although 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, Cu(PicA)₂.8HQ, Cu(IN2N)₂.8HQ, Pd(QiunA)₂.8HQ and Pd(IN2N)₂.8HQ were relatively potential inhibitor of the of both the test bacteria and one fungi.

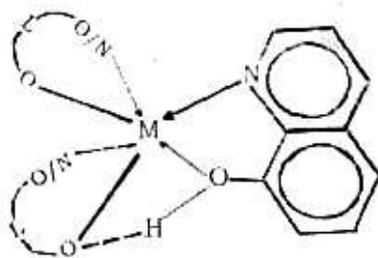
The MIC value of Cu(PicA)₂.8HQ & Cu(IN2N)₂.8HQ at concentration of $42\text{ }\mu\text{gml}^{-1}$ Pd(QiunA)₂.8HQ at concentration of $21\text{ }\mu\text{gml}^{-1}$ for E. Coli. The MIC values of Cu(IN2N)₂.8HQ, Pd(QiunA)₂.8HQ and Pd(IN2N)₂.8HQ at concentration $42\text{ }\mu\text{gml}^{-1}$ and $20\text{ }\mu\text{gml}^{-1}$ respectively for fungi C. albicans. The MIC values of all three oxygen bridge transition metal complexes at the same concentration $42\text{ }\mu\text{gml}^{-1}$ for S. aureus.

Table-3

Compound	Minimum inhibitory concentration (in μgml^{-1})		
	E. Coli	S. aureus	C. albicans
Cu(PicA) ₂ .8HQ	42	21	42
Cu(IN2N) ₂ .8HQ	21	21	42
Pd(QiunA) ₂ .8HQ	21	21	21
Pd(IN2N) ₂ .8HQ	21	21	21

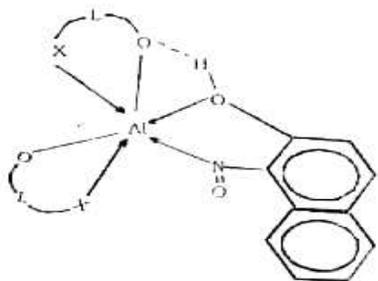
STRUCTURE & BONDING :

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, HQinA, I-hydroxyquinoline/1-nitroso-2-naphthol and 1-nitroso-2-naphthol/8-hydroxyquinoline may tentatively be proposed as shown in Fig 1 & 2.



where L-deprotonated HPicA, HQinA IN2N; X-O or N

(Fig. 1)



where L. deprotonated HPicA, HQinA or HQ; X-O or N

(Fig. 2)

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