

# Mixed ligand complexes of Aluminium(III) metal chelates of some organic acids with Quinaldinic acid & Quinaldinic Acid-N-oxide.

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## ABSTRACT

Some new mixed ligand complexes of Al(III)metal chelates of different organic acids of general formula  $ML_2L'$  where  $M=Al(III)$ ,  $L$ =deprotonated ONP,DNP,TNP,8HQ and 1N2N; $L'$ =deprotonated quinaldinic acid or quinaldinic acid -N-oxide.The compounds have been synthesized and characterized by elemental analysis,molar conductance measurements, infrared and electronic spectral studies. On the basis of spectral studies ,probable structures of complexes have been proposed.

**KEYWORDS:** Mixed ligand complex, quinaldinic acid ,quinaldinic acid -N-oxide,Al(III) metal chelate, Infrared and UV spectra.

## INTRODUCTION

The preparation and characterisation of mixed ligand complexes of Al(III) metal chelates of some organic acids with quinaldinic acid and quinaldinic acid-N-oxide, higher homologues of picolinic acid and picolinic acid-N-oxide .

Quinaldinic acid and quinaldinic acid-N-oxide have been extensively investigated for their role in analytical determination of metal ions<sup>1-7</sup>. Their complexes with some transition metals, rare earth metals, alkali metals and alkaline earth metals are investigated<sup>8-15</sup>.

In all these complexes, quinaldinic acid-N-oxide acts as a bidentate ligand. Infrared studies indicated the presence of hydrogen bonding in the complexes, which may be one of the factors stabilizing them.

## EXPERIMENTAL:

Analar quality of ONP,DNP,TNP,8HQ,1N2N,quinaldinic acid and quinaldinic acid -N-oxide were used for the prepration of their Al(III)chelates and adducts.

### Preparation of complexes

0.417gm(0.001 mole) aluminium(III) salt of X & 0.173gm(0.001 mole) of quinaldinic acid was taken in 25 ml absolute ethanol in a clean & dry conical flask. The mixture was refluxed on hot plate of magnetic stirrer at 80°C with constant stirring for about one hour. The solution was concentrated, cooled to give yellowish brown colour precipitate. The precipitate was filtered, washed with absolute ethanol and dried in an electric oven at 80°C. Yield : 0.356 gm (75%) .

**Mixed ligand complex of Al(III) salt of X with quinaldinic acid-N-oxide (HQuinO):-**

0.417gm (0.001 mole) aluminium(III) salt of X and 0.189 gm (0.001 mole) of quinaldinic acid-N-oxide was taken in 25 ml absolute ethanol in a clean & dry conical flask. The mixture was refluxed on hot plate of magnetic stirrer at 80°C with constant stirring for about 1-2 hours. The solution was concentrated, cooled to give pale cream colour precipitate. The precipitate was filtered, washed with absolute ethanol and dried in an electric oven at 80°C. Yield : 0.294gm (60%) .

X= ONP,TNP,DNP,8HQ,1N2N.

**RESULTS & DISCUSSION****Physical properties:**

Some physical properties of the ligands(HL') and the new mixed ligand complexes (ML<sub>2</sub>.L') are listed in Table-1. The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, DMSO etc. partly soluble in ethanol and insoluble in non-polar solvents like benzene, acetone, chloroform etc. The complexes are stable under dry conditions.

From Table-1, it is evident that most of complexes undergo a transformation at a higher temperature than the melting point of first ligand (HQuinA or HQuinO), indicating their greater stability. However, some complexes melt or partly melt (transition) at lower temperature.

**Molar conductance:** Molar conductance of all the compounds were measured in methanol solution at 27<sup>0</sup>C at a concentration of 10<sup>-3</sup> M and their values are given in Table-1. The significantly low values (7.5-10.5ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>) of molar conductance of the newly prepared compounds indicate them to be covalent nature TABLE .1

**TABLE 1**

Compound	Colour	M.P./Decomp./Trans. Temp. (°C)	Conductivity *
Quinaldinic acid (HQuinA)	White	156-158m	---
Al(ONP) <sub>2</sub> .QuinA	White	>280	7.5
Al(DNP) <sub>2</sub> .QuinA	White	240m	9.4
Al(TNP) <sub>2</sub> .QuinA	Pale yellow	245md	10.1
Al(8HQ) <sub>2</sub> .QuinA	Light green	>280	9.8
Al(1N2N) <sub>2</sub> .QuinA	Green	>300	9.1
Quinaldinic acid-N-oxide (HQuinO)	Light yellow	168-170m	---
Al(ONP) <sub>2</sub> .QuinO	Pale cream	220d	7.5
Al(DNP) <sub>2</sub> .QuinO	Dirty white	140m	10.8
Al(TNP) <sub>2</sub> .QuinO	Light yellow	260d	10.5
Al(8HQ) <sub>2</sub> .QuinO	Light green	>280	9.8

(\*Molar conductivity ( $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ ) solution in methanol at  $27^\circ\text{C}$  .

### Infrared Spectra:

Infrared spectra of the ligands (quinaldinic acid & quinaldinic acid-N-oxide) and its hitherto unknown complexes were recorded in the region  $4000\text{-}400\text{ cm}^{-1}$  in KBr disc with the help of JASCO-FTIR spectrometer model 5300. The pertinent infrared data are listed in Table-2 & 3

**TABLE-2**

#### Pertinent IR data for ligand (Quinaldinic acid) and its mixed ligand Al(III) complexes

Compound	$\nu\text{O-H}\cdot\text{O}$	$\nu\text{COO-}$	$\nu\text{C=N}$	$\nu\text{M-O/M-N}$
Quinaldinic acid(HQuinA)	2700-1800	1535	1680,1620,1580,1560	.....
Al(ONP)2.QuinA	.....	1518	1666,1600,1570	626,585,522
Al(DNP)2.QuinA	.....	1526	1635,1602,1565	570,490
Al(TNP)2.QuinA	.....	1522	1660,1621	515,490
Al(1N2N)2.QuinA	.....	1523	1653,1605,1570	582,528,493
Al(8HQ)2.QuinA	.....	1500	1675,1605,1580,1535	580,547,490

**TABLE-3**

#### Pertinent IR data for ligand (Quinaldinic acid-N-oxide) and its mixed ligand Al(III) complexes

Compound	$\nu\text{COO-}$	$\nu\text{C=N}$	$\nu\text{N-O}$	$\nu\text{M-O/M-N}$
Quinaldinic acid-N-oxide(HQuinO)	1680br	1610m	1300m,1280m	....
Al(ONP)2.QuinO	1650,1619	.....	1336,1216	575,526,500
Al(DNP)2.QuinO	1650,1625	1603	1338,1267,1216	570,520
Al(1N2N)2.QuinO	1660	1605	1329,1217	518,470
Al(8HQ)2.QuinO	1655	1604	1330,1217	548,490

### Infrared spectra of quinaldinic acid and its complexes :

In the spectrum of the ligand(quinaldinic acid), the pertinent IR bands are  $2700\text{-}1800\nu$ , 1680, 1620, 1580, 1560 &  $1535\text{ cm}^{-1}$ .

The multiple bands in the region  $2700\text{-}1800\text{ cm}^{-1}$  in the spectrum of the ligand point to the presence of strong intramolecular hydrogen bonding involving the carboxyl hydrogen atom and the nitrogen atom of the quinoline ring. In the spectra of the Al(III) complexes, these bands disappear due to replacement of hydrogen of  $-\text{COOH}$  group by the aluminium metal.

Koromantzon et al<sup>23</sup> have reported the antisymmetric stretching frequency of –COOH group in the quinaldonic acid at 1670 cm<sup>-1</sup>. However, we have not found any peak in the spectrum of the ligand at this wave number.

The medium intensity bands at 1680, 1620 and 1535 cm<sup>-1</sup> in the spectrum of the ligand in almost all the complexes, have shifted to lower frequencies by 5-45, 15-20 and 9-35 cm<sup>-1</sup> respectively. These features are suggestive of coordination of the ligand with the aluminium metal through oxygen atom of carboxyl (-COOH) moiety.

In the spectra of almost all the complexes, the 1580 cm<sup>-1</sup> band, assigned to stretching C=N absorption, has shifted to lower frequencies by 10-15 cm<sup>-1</sup> except Al(TNP)<sub>2</sub>.QuinA. These features suggest the coordination of the ligand (HQuinA) with Ag(I) metal through its ring nitrogen atom.

The band in the region 490-547 cm<sup>-1</sup> in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium bands in the region 570-622 cm<sup>-1</sup> assigned to M-N band frequency<sup>24</sup>. These bands are absent in the second ligand (quinaldonic acid). These assignments are based on the assumption<sup>25</sup> that oxygen atom is more electronegative than nitrogen. The M-O vibrations are expected to appear at lower frequencies. The above data confirms the coordination of oxygen atom of O-H (phenolic) group and nitrogen atom of first ligand, i.e., organic acid to the Al(III) metal ion in all the mixed ligand complexes.

#### **Infrared spectra of quinaldonic acid-N-oxide & its complexes :**

The broad band in the region 2800-1900 cm<sup>-1</sup> in the spectrum of ligand (quinaldonic acid-N-oxide) indicates that in the solid state, it contains a strong hydrogen bond possibly of the symmetrical type probably resulting in the dimer<sup>26</sup>.

In the spectra of the mixed ligand complexes of Al(III), this broad band is missing due to replacement of hydrogen of –COOH group by the aluminium metal.

The 1680 cm<sup>-1</sup> broad band, that occurs in the spectrum of the ligand, may, in analogy with the assignments in case of quinaldonic acid-N-oxide<sup>27</sup>, be attributed to asymmetric COO<sup>-</sup> vibrations of the –COOH group. In the complexes, this band gives a negative shift of 20-61 cm<sup>-1</sup>.

The 1610 cm<sup>-1</sup> band of medium intensity present in the ligand may be assigned to  $\nu_{C=C}$  &  $\nu_{C=N}$  absorptions. In complexes, this band show negative shift upto 7 cm<sup>-1</sup>.

Proceeding similarly, the 1280 cm<sup>-1</sup> band in the spectrum of the ligand may be ascribed to symmetrical stretching COO<sup>-</sup> vibrations of the –COOH group. In the spectra of the complexes, this band has shifted to frequencies by 13-64 cm<sup>-1</sup>. These features would seem to suggest the coordination of the ligand(HQuinO) with aluminium metal through hydroxyl oxygen of the –COOH group.

The 1300 cm<sup>-1</sup> band of medium intensity, occurring in the ligand, may be attributed to stretching N-O vibrations and in the spectra of the complexes, this band has shifted to higher frequencies by 29-38 cm<sup>-1</sup>. This is suggestive of coordination of the ligand with aluminium metal through oxygen atom of the N-oxide moiety.



The band in the region  $470\text{-}526\text{ cm}^{-1}$  in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium band in the region  $548\text{-}575\text{ cm}^{-1}$  is assigned to M-N band frequency<sup>24</sup>. These bands are absent in the second ligand (HQuinO). These assignments are based on the assumptions<sup>25</sup> that oxygen atom is more electronegative. The above data confirm the coordination of oxygen atom of phenolate group and nitrogen atom of first ligand, i.e., organic acid to the Al(III) metal ion in all the mixed ligand complexes.

**UV-Vis spectra:** The ultraviolet-visible spectral data were recorded on SHIMADZU UV-Vis 160A spectrophotometer in paraffin solvent. The bands observed in the UV-Vis spectra of the ligands (quinaldonic acid & quinaldonic acid-N-oxide) and the mixed ligand complexes of Al(III) are given in Table-4. Concentrated, cooled to give light grey colour precipitate. The precipitate was filtered, washed with absolute ethanol and dried in an electric oven at  $80^\circ\text{C}$ . Yield – 0.290gm (50%)

**TABLE – 4**

**Major diffuse reflectance bands (in nm) for mixed ligand complexes of Al(III) with quinaldonic acid & quinaldonic acid -N-oxide**

Compound	Diffuse reflectance ( in nm)
Quinaldonic acid (HQuinA)	295, 234
Al(DNP) <sub>2</sub> .QuinA	287, 228
Al(TNP) <sub>2</sub> .QuinA	288, 227
Al(1N2N) <sub>2</sub> .QuinA	287, 210
Quinaldonic acid-N-oxide(HQuinO)	280, 240
Al(ONP) <sub>2</sub> .QuinO	317, 240, 216
Al(TNP) <sub>2</sub> .QuinO	312, 303, 235, 208
Al(8HQ) <sub>2</sub> .QuinO	341, 311, 302, 238

### STRUCTURE & BONDING

Analytical data lead to the general molecular formula  $ML_2.L'$  for these complexes, where M = Al(III), L = deprotonated ONP, DNP, TNP, 1N2N or 8HQ & L' = deprotonated quinaldonic acid(HQuinA) or quinaldonic acid-N-oxide(HQuinO). Their IR spectra suggest that ligand(HQuinA or HQuinO) behaves as a bidentate ligand and that the coordination has taken place through oxygen atom of the  $-\text{COOH}$  group as well as through nitrogen atom of quinoline ring/oxygen atom of N-O moiety. It also suggests the presence of hydrogen bonding in them. These facts suggest the following structure for these complexes (Fig. 23 & 24).

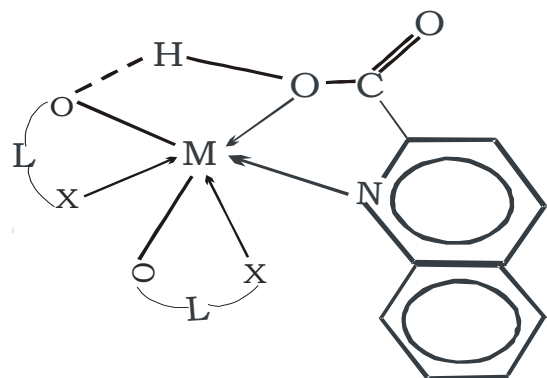


Figure-23

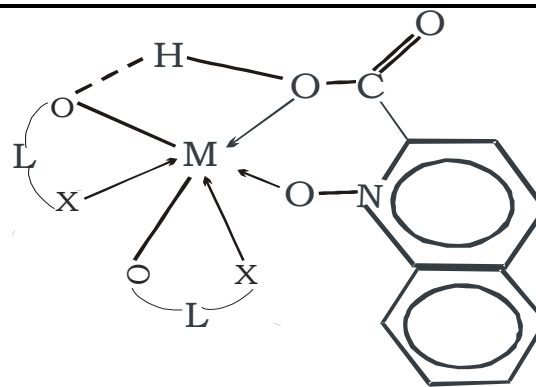


Figure-24

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