



## COMPLEXES OF MIXED LIGAND Al (III) WITH SOME CHELATING ORGANIC ACIDS & 5, 7 – DINITRO – OXINE

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A series of complexes of the type  $[AlL_2,HL']CH_3COO^-$ , Where L = deprotonated ONP, TNP, 1N2N, OABA & ONBA and HL' = 5,7-dinitro -8-hydroxyquinoline (DN8HQ), Produced synthetically. On the basis of the analysis of elements, ligands and their complexes have been described spectrum research, conductivity measurements, and analysis.

It has been found that the nitrogen atom of the pyridine ring and the oxygen atom of the -OH (phenolic) group coordinate the ligand (DN8HQ).

### INTRODUCTION

The potential application of 8-hydroxyquinoline and its derivatives in the analytical assessment of metal ions has been extensively investigated [1-3]. The 8-hydroxyquinoline and its compound derivatives have been the subject of much research on metal complexes [4–11], but mixed ligand complexes of Al(III) with these ligands have received less attention. As a result, we show a variety of mixed ligand complexes in this work. of Al(III) of the type  $[ML_2,HL']CH_3COO^-$ .

### EXPERIMENTAL

Aluminium basic acetate, 5, 7-dinitro-8-hydroxyquinoline (DN8HQ), o-nitrophenol (ONP), 2,4, 6-trinitrophenol (TNP), 1-nitroso -2-naphthol (1N2N), o-aminobenzoic acid (OABA) of AnalaR grade were used as such.

### PREPARATION OF THE COMPLEXES

In order to prepare the complexes, 0.01 mole of 5, 7-dinitro-8-hydroxyquinoline, 0.02 mole of organic acid (HL), and 1.60 g (0.01 mole) of aluminum basic acetate have been submerged in undiluted alcohol for two hours the entire reaction mixture was refluxed while being constantly stirred over a hot plate of a magnetic stirrer. It was subsequently allowed to cool in order to produce the distinctive coloured solid adduct. The adduct was washed using suitable solvent and then dried at 100<sup>o</sup>c.

### RESULTS & DISCUSSION

Some physical properties and analytical data of the ligands (DN8HQ) and the new mixed ligand Al(III) complexes obtained are listed in Table-1.

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

**Conductivities :** Molar conductivities of all these complexes were measured in methanol at 23<sup>o</sup>C at a concentration of 10<sup>-3</sup> M.



When compared to a neutral complex's ideal molar conductivity of zero, a 1: 1 electrolyte seems to have a Ca value of 35–40  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  [12]. These complexes' having higher molar electrical conductivity (33.1-42.4  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ) are caused by the solvent ionisation of the compounds. The corresponding numbers indicate that they are ionic and approximate to a 1:1 electrolyte.

**Infrared Spectra:** Infrared spectra of the ligand (5, 7-dinitro-8-hydroxyquinoline) and its mixed ligand Al(III) 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.

The ligand (DN8HQ) spectra exhibits a medium broad absorption band with a large range of 3650-3250  $\text{cm}^{-1}$ . The existence of characteristics related to absorption in this area indicates that there's evidence of strong intramolecular hydrogen bonding between the quinoline ring's hydroxyl hydrogen atom and nitrogen atom.

The spectra's of many bands between 2925 and 1875  $\text{cm}^{-1}$  are a result of both C-H stretching vibration and N-H hydrogen bonding. Strong hydrogen bonding causes bands to emerge between 2800 and 1800  $\text{cm}^{-1}$ , whereas poor hydrogen bonding causes bands to occur above 2800  $\text{cm}^{-1}$ .

The bands at 1645, 1585 and 1110  $\text{cm}^{-1}$  are respectively assigned to  $\text{NO}_2$ , C=C/C=N and C-O stretching vibration of the 5, 7 – dinitrooxine ligand.

In all the mixed ligand Al(III) complexes the stretching – OH vibrations bands appeared as a strong broad band in the range of 3420-3437  $\text{cm}^{-1}$  and medium band in the region 2120-2760  $\text{cm}^{-1}$  indicate the presence of strong bonding as well as the complexation of metal through the hydroxyl oxygen atom.

The –  $\text{NO}_2$  group frequency in all the mixed ligand complexes remain almost unchanged.

With the exception of  $\text{Al}(\text{OABA})_2$ , DN8HQ, where it showed as split bands at 1590  $\text{cm}^{-1}$  and 1534  $\text{cm}^{-1}$ . The ligand's 1585  $\text{cm}^{-1}$  band (given to  $\nu\text{C}=\text{N}$ ) has moved to higher frequencies by 10-16  $\text{cm}^{-1}$  in the IR spectra of these complexes. The  $\nu\text{C}=\text{N}$  area appears to be shifting and fragmenting, which suggests that the quinoline ring's nitrogen atom is how the ligand coordinates with Al(III) metal. The absorption bands in the region 1475-1415  $\text{cm}^{-1}$  occur due to the presence of  $\text{CH}_3\text{COO}^-$  ion in these complexes.

All of the mixed ligand complexes such as show a 2-19  $\text{cm}^{-1}$  change in the ligand's C-O stretching frequency, which suggests that the ligand (DN8HQ) coordinates with the Al(III) metal through the hydroxyl oxygen atom.

Table – 1

Compound	Colour	M.P./ Decomp./ Trans. Temp. ( $^{\circ}\text{C}$ )	Molar Cond.	Analysis % found (Calculated)			
				C	H	N	Al
5,7-Dnitro-8-hydroxyquinoline	Yellow	135m	--	--	--	--	--
$[\text{Al}(\text{ONP})_2$ , DN8HQ] $\text{CH}_3\text{COO}$	Pale Yellow	245d	36.5	48.35 (48.50)	2.51 (2.63)	12.12 (12.30)	4.56 (4.74)
$[\text{Al}(\text{TNP})_2$ ,	Yellowish	275d	42.4	35.41	1.38	16.05	3.31

DN8HQ] CH <sub>3</sub> COO	Brown			(35.56)	(1.41)	(16.23)	(3.47)
[Al(1N2N) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	Grey	280d	35.5	60.02 (60.19)	2.94 (3.07)	8.85 (9.06)	4.29 (4.36)
[Al(OABA) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	Yellowish Green	230d	39.9	51.76 (51.90)	3.15 (3.28)	9.47 (9.68)	4.45 (4.67)
[Al(ONBA) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	Yellow	250d	33.3	45.78 (45.94)	2.35 (2.45)	10.65 (10.71)	4.02 (4.13)
[Al(AC SalA) <sub>2</sub> DN8HQ] CH <sub>3</sub> COO	Pale Yellow	235d	33.1	51.85 52.09	3.21 3.37	6.68 6.75	4.17 4.34

**Table – 2**
**Pertinent IR data for ligand (DN8HQ) and their mixed ligand Al(III) complexes**

Compound	$\nu_{O-H}$	$\nu_{O-H \cdots O}$ /N...H-O	$\nu_{C=N}$	$\nu_{CH_3COO^-}$	$\nu_{C=O}$	$\nu_{M-O/M-N}$
5,7-Dnitro-8-hydroxyquinoline	3450	.....	1585	.....	1110	.....
[Al(TNP) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	3430	2760	1596	1475	1127	668,580,540,...
[Al(1N2N) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	3429	2720	1596	1474	1112	670,640,575,540
[Al(OABA) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	3437	2700, 2120	1590, 1534	1415, 1470	1129	667, 581, 540
[Al(AcSalA) <sub>2</sub> , DN8HQ] CH <sub>3</sub> COO	3420	2750	1595	1472	1129	667, 583, 550

All mixed liquid Al(III) complex spectra show a band in the range 540–550 cm<sup>-1</sup> that can be attributed to the M–O band, while the medium-sized band in the range 575–670 cm<sup>-1</sup> is attributed to the M–N band [13]. The related ligand does not have these bands. These assignments are based on the presumption [14] that the M-O bond tends to be more ionic than the M-N bond because oxygen atoms are more electronegative than nitrogen atoms. M-O vibrations are thus anticipated to manifest at lower frequencies. The aforementioned information supports the coordination of the nitrogen atom of the quinoline ring and the oxygen atom of the phenolic group to Al (III) metal in each compound.

**Electronic Spectra:** - On a PERKIN ELMER LAMBDA-15 UV-VIS spectrophotometer, electronic spectra were captured in a paraffin solvent. Table 3 lists the band that was seen in the electronic spectra of the ligand Al(III) complexes. 5, 7-dinitro-8-hydroxyquinoline mixed ligand Al(III) complexes exhibit electronic absorption bands at 233–278 nm, which point to  $\pi-\pi^*$  transition in the complexes. Al(III)

complexes with mixed ligands exhibit charge transfer bands in their electronic spectra between 329 and 390 nm. There is a  $\pi$ - $\pi^*$  interaction between the orbitals of the metal and the ligand, as evidenced by the complexes' shifting of the ligand's  $\pi$ - $\pi^*$  and charge transfer bands.

**Table 3. Major diffuse reflectance bands (in nm) for mixed ligand Al(III) complexes with 5,7-dinitro-8-hydroxyquinoline**

Compound	Diffuse reflectance (in nm)
[Al(TNP) <sub>2</sub> .DN8HQ]CH <sub>3</sub> COO	358, 373, 233
[Al(1N2N) <sub>2</sub> .DN8HQ]CH <sub>3</sub> COO	390, 249
[Al(OABA) <sub>2</sub> .DN8HQ]CH <sub>3</sub> COO	364, 329, 278, 237
[Al(ONBA) <sub>2</sub> .DN8HQ]CH <sub>3</sub> COO	369, 248
[Al(AcSaIA) <sub>2</sub> .DN8HQ]CH <sub>3</sub> COO	369, 251

### STRUCTURE & BONDING

The structure and bonding of the newly synthesised mixed ligand Al(III) complexes including various chelating organic acids and 5, 7-dinitro-8-hydroxyquinoline may be tentatively postulated based on analytical and spectral (IR & UV-VIS) research as shown in Fig. -1

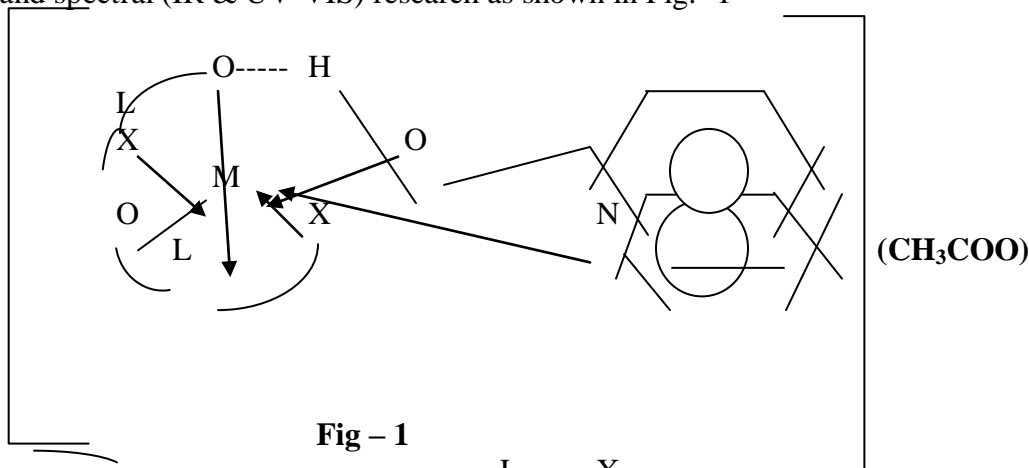
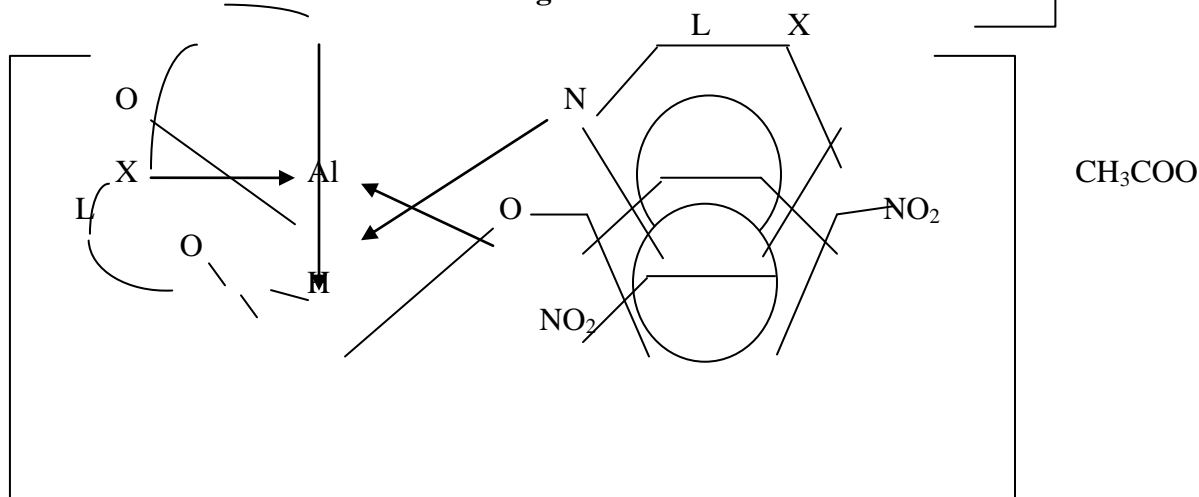


Fig - 1



Where L = Deprotonated ONP, TNP, 1N2N, ONBA or AcSaIA ; X = O or N

Fig. - 2



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