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SYNTHESIS AND SPECTRAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES: ALUMINIUM(III) CHELATES OF ORGANIC ACIDS WITH 1-NITROSO-2-NAPHTHOL

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ABSTRACT

Seven novel mixed ligand Aluminium(III) complexes with 1-Nitroso-2-naphthol have been synthesized and their characterization was carried out by conductivity measurements, infrared spectrum, electronic spectrum and elemental determination. The complexes are ionic and are of high stability. Relevant conclusions concerning the ligating behavior of the ligand 1-Nitroso-2-naphthol and the structure of mixed ligand Aluminium(III) complexes together with the nature of metal-ligand bonding indicate coordination of Aluminium metal through nitrogen or oxygen atom of the ligand.

Keywords: Aluminium(III), Electronic Spectra, 1-Nitroso-2-naphthol, Infrared Spectra, Mixed Ligand Complexes
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INTRODUCTION

1-Nitroso-2-naphthol is a crystalline solid (m.p. 104-108 °C) which is readily soluble in a common organic solvent such as alcohol, ether but sparingly soluble in water. 1-Nitroso-2-naphthol has been extensively used in analytical chemistry.[1-4] It forms complexes with transition metals, rare earth metals, alkaline earth metals as well as alkali metals.[5-13] Shchavlel *et al* studied the interactions of intermolecular hydrogen bonding in the ligand 1-Nitroso-2-naphthol and its monoxime tautomers.[14] Studies on mixed ligand complexes of divalent and trivalent transition metal ions with 2-Aminobenzoic acid and (E)-2-(4-(dimethylamino) benzylidene)amino phenol have been reported.[15] Prakash *et al* had synthesized several mixed ligand complexes by using ligand 2-Nitroso-1-naphthol and *α*-Benzoin-monoxime with alkali metal salts of organic acids in non-aqueous solvents such as absolute ethanol and benzene.[16] This inspired us to study the complexing behavior of a p-block element, Aluminium with 1-Nitroso-2-naphthol. In this research communication, we describe the synthesis and characterization of seven novel mixed ligand Aluminium(III) complexes with 1-Nitroso-2-naphthol and some organic acids.

EXPERIMENTAL

Material and Methods

A.R. grade quality of Aluminium basic acetate, 1-Nitroso-2-naphthol, *o*-Aminobenzoic acid, *o*-Nitrophenol, *o*-Nitrobenzoic acid, Salicylic acid, 2,4-Dinitrophenol, Acetylsalicylic acid and2,4,6-Trinitrophenol were used for the experiment. Conductance measurements of the prepared complexes were performed in methanol solutions of 10^{-3} M at 23 °C using Systronics(model-306) digital conductivity meter. For elemental analysis, Heraeus B6450 CHN elemental analyzer was used. The IR spectra were observed between 4000-400 cm^{-1} on JASCO-FTIR spectrophotometer-5300. Electronic spectra were assessed on a Perkin-Elmer-Lambda-15 spectrophotometer in paraffin solvent.

Preparation of Mixed Ligand Complexes

A suspension of 0.01 mol of aluminium basic acetate in absolute alcohol was taken and 0.02 mol of *o*-Aminobenzoic acid or *o*-Nitrophenol or *o*-Nitrobenzoic acid or Salicylic acid or 2,4-Dinitrophenol or

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Acetylsalicylic acid or 2,4,6-Trinitrophenol was added with continuous stirring. Further 0.01 mol of 1-Nitroso-2-naphthol was added and the resulting mixture was thoroughly refluxed for two hours over a hot plate with a magnetic stirrer. On cooling, a colored precipitate of the solid complex was obtained. The complex was separated by filtration. It was washed with absolute alcohol and dried at 80 °C.

RESULTS AND DISCUSSION

The physical attributes of the ligand 1-Nitroso-2-naphthol and the new mixed ligand Aluminium(III) complexes are tabulated in Table-1. The complexes obtained are colored and solid in the state. The complexes are appreciably soluble in most polar solvents like DMF, methanol, etc. but insoluble in non-polar solvents like toluene, ether, benzene, etc. The complexes are stable in the air. Decomposition or melting temperature of the mixed ligand Aluminium(III) complexes are higher than 1-Nitroso-2-naphthol. This indicates greater stability of the complexes. The elemental determination of the mixed ligand Aluminium(III) complexes are described in Table-2.

Molar Conductivities

Molar conductivities of all prepared Aluminium(III) mixed ligand complexes were observed in methyl alcohol (10^{-3} M) at 25 °C. High values of molar conductivity (31.1-44.5 $ohm^{-1}cm^2mol^{-1}$) for the complexes are observed [Table-1]. Molar conductance values in this range indicate the ionic nature of complexes. These values appear characteristic of a 1:1 electrolyte.[17]

Table-1: Physical Properties of 1-Nitroso-2-naphthol and mixed ligand Aluminium(III) Complexes

Complex	Color	Decomposition temp. (°C)	Conductivity($ohm^{-1}\,cm^2\,mol^{-1}$)
$C_{10}H_7O_2N$	Brown	108d	—
$C_{24}H_{18}N_3O_{10}Al$	Dark brown	235d	31.1
$C_{24}H_{16}N_5O_{14}Al$	Brownish green	200d	41.5
$C_{24}H_{14}N_7O_{18}Al$	Dark brown	190d	43.2
$C_{26}H_{22}N_3O_8Al$	Dark brown	250d	33.3
$C_{26}H_{18}N_3O_{12}Al$	Brownish green	260d	38.2
$C_{26}H_{20}NO_{10}Al$	Dark brown	245d	44.5
$C_{30}H_{24}NO_{12}Al$	Dark brown	235d	35.9

Table-2: Elemental Analyses Data of the mixed ligand Aluminium(III) Complexes

Complex	Analysis (%) Found(Calculated)				% Yield
	C	H	N	Al	
$C_{24}H_{18}N_3O_{10}Al$	53.85 (53.93)	3.08 (3.16)	7.65 (7.86)	4.95 (5.05)	80
$C_{24}H_{16}N_5O_{14}Al$	46.01 (46.15)	2.31 (2.40)	11.05 (11.21)	4.15 (4.32)	75
$C_{24}H_{14}N_7O_{18}Al$	40.21 (40.33)	1.65 (1.82)	13.52 (13.72)	3.61 (3.78)	85
$C_{26}H_{22}N_3O_8Al$	58.51 (58.64)	3.48 (3.57)	2.47 (2.63)	4.85 (5.07)	69
$C_{26}H_{18}N_3O_{12}Al$	52.85 (53.06)	2.31 (2.55)	7.01 (7.14)	4.32 (4.59)	78
$C_{26}H_{20}NO_{10}Al$	59.45 (59.57)	4.61 (4.78)	2.25 (2.48)	4.61 (4.78)	79
$C_{30}H_{24}NO_{12}Al$	62.15 (62.27)	3.21 (3.33)	2.73 (2.79)	5.51 (5.38)	73

Infrared Spectra

Infrared spectra of the ligand 1-Nitroso-2-naphthol and its mixed ligand Aluminium(III) complexes are displayed in Table-3. The characteristic bands in the FTIR spectra of 1-Nitroso-2-naphthol are observed at 1175, 1640 and 3500-1800 cm^{-1} which are due to υ(C–O)str., υ(N=O)str. and υ(O–H)str. modes respectively. The mixed ligand Aluminium(III) complexes show multiple absorption bands of medium and strong intensity in the region 3431-2700 cm^{-1}. The observed absorption details in this region indicate strong hydrogen bonding in the mixed ligandAluminium(III) complexes. A sharp band in the infrared

spectra of 1-Nitroso-2-naphthol due to (N=O)str. shifts to lower frequency by 32-46 cm^{-1} in the mixed ligand complexes. This suggests the involvement of Aluminium(III) metal ion through nitrogen atom of nitroso (N=O) group. The absorption bands in the region 1474-1436 cm^{-1} occur due to the presence of CH_3COO^- ion in these complexes. The absorption band at 1175 cm^{-1} in 1-Nitroso-2-naphthol is due to C–O stretching vibration. In the mixed ligand complexes, this band gets displaced towards the lower frequency side by 66-72 cm^{-1}. This suggests the coordination of Aluminium(III) metal ion through the oxygen atom of the O–H (phenolic) group.

The spectral bands in the mixed ligand Aluminium(III) complexes in the region 533-463 $cm^{-1}$are assigned to M–O str.; the medium intensity spectral bands in the region 673-522 cm^{-1} is due to M–N str.[18] Assignment of higher frequencies for M–O str. is due to the higher ionic character of M–O band.[19] These data confirm the coordination of phenolic group or carboxylic group or nitro group to Aluminium(III) metal ion through oxygen atom; amino group or nitroso group or quinoline ring to Aluminium(III) metal ion through a nitrogen atom in the mixed ligand complexes.

Table-3: Infrared Spectrum Data for 1-Nitroso-2-naphthol and mixed ligand Aluminium(III) Complexes

Complex	Selected Infrared Absorption Spectral Bands (in cm^{-1})				
	υ(O-H) str.	υ(N=O) str.	υ(CH_3COO^-)	υ(C-O) str.	υ(M-O/M-N)
$C_{10}H_7O_2N$	3500-1800	1640	–	1175	–
$C_{24}H_{18}N_3O_{10}Al$	3431, 2720	1598	1436, 1472	1109	618
$C_{26}H_{20}NO_{10}Al$	3405, 2700	1594	1437, 1474	1103	670, 617, 522, 468
$C_{30}H_{24}NO_{12}Al$	3400	1608	1474	1105	673, 593, 533, 463

Electronic Spectra

The electronic spectra of the ligand 1-Nitroso-2-naphthol and the prepared mixed ligand Aluminium(III) complexes were recorded in the range 200-800 nm at room temperature. The observed bands are listed in Table-4. The ligand 1-Nitroso-2-naphthol exhibits sharp and intense bands at 210, 256, 362 and 653 nm. These bands indicate $\pi-\pi^*$ transition as well as charge transfer in the aromatic ring.[20]

For the mixed ligand Aluminium(III) complexes, the electronic absorption wavelengths are observed in the range 231-290 nm which indicates$\pi-\pi^*$a transition in the complexes. A band at 390 nm indicates charge transfer spectra. There are π-interactions between the metal and ligand orbitals due to which the position of $\pi-\pi^*$ transitions, as well as the position of charge transfer bands of the ligand 1-Nitroso-2-naphthol, gets shifted after the formation of Aluminium(III) mixed ligand complexes.

Based on the above discussion and with the aid of analytical data, infrared and electronic spectral studies, the probable structure for the mixed ligand Aluminium(III) complexes may be suggested. The probable structure for the complex $C_{24}H_{18}N_3O_{10}Al$ has been proposed in Fig.-1.

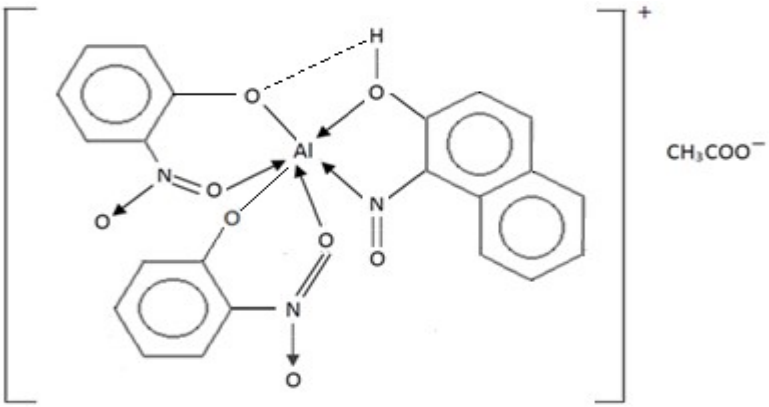

Fig.-1: Structure of the Mixed Ligand Complex, $C_{24}H_{18}N_3O_{10}Al$

Table-4: Electronic Spectral Bands (in nm) for 1-Nitroso-2-naphthol and mixed ligand Aluminium(III) Complexes

Complexes	Electronic spectra (in nm)
$C_{10}H_7O_2N$	210, 256, 362, 653

$C_{24}H_{18}N_3O_{10}Al$	390, 251
$C_{26}H_{20}NO_{10}Al$	390, 231
$C_{30}H_{24}NO_{12}Al$	290, 235

CONCLUSION

Seven novel mixed ligand Aluminium(III) complexes with 1-Nitroso-2-naphthol were successfully synthesized and characterized. Molar conductance studies revealed the ionic nature of these complexes. The complexes obtained are of high stability. The infrared spectra suggest the coordination of Aluminium(III) metal ions through nitrogen or oxygen atom of the ligand. A strong hydrogen bonding is present in all the prepared mixed ligand Aluminium(III) complexes. The electronic spectrum of the mixed ligand Aluminium(III) complexes reflects $\pi-\pi^*$ transition as well as charge transfer in the prepared complexes.

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