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Mixed ligand Al (III) complexes involving some chelating organic acids and picolinic acid

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ABSTRACT

A number of mixed ligand Al (III) complexes involving some chelating organic acids and picolinic acid, having general formula $[ML_2.HL']\ CH_3COO$, where M = Al (III); L=deprotonated ONP, DNP, TNP, 1N2N, 8HQ, DN8HQ, SalA, AcSalA, OABA or ONBA; HL' = picolinic acid. Infrared spectral studies indicate the presence of H-bonding in these complexes, which may be one of the factors stabilizing them.

Key words: Mixed ligand complexes, chelation, picolinic acid.

INTRODUCTION

Picolinic acid has a replaceable hydrogen atom as well as two donor atoms suitably placed to form a five membered chelating ring with metal ion. The versatile chelating ability of picolinic acid with various metals is well established[1]. Structural studies have shown that picolinic acid can form various types of complexes having different types of bonding depending on the nature of the metal ion and reaction conditions[2-5].

EXPERIMENTAL

Aluminium basic acetate, picolinc acid (PicA), o-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-nitrophenol (TNP), 1-nitroso-2-napthol (1N2N), o-aminobenzoic acid (OABA), o-nitrobenzoic acid (ONBA), salicylic acid (SalA), acetylsalicylic acid (AcSalA) of Anala R grage were used as such.

Preparation of the complexes

To a suspension of 1.60g (0.01 mole) aluminium basic acetate in absolute alcohol, 0.02mole of organic acid and 1.23g (0.01mole) picolinic acid (HPicA) were 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 the solvent and dried at 100°C.

RESULTS AND DISCUSSION

Some physical properties and analytical data of the ligand (picolinic acid) and the new mixed ligand complexes obtained are listed in Table 1.

The mixed ligand complexes are generally coloured. They are appreciably soluble in most polar solvents such as methanol, ethanol, 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.

Table 1: Analytical data, m.p.(s), colour etc. of complexes

Compound	Colour	m.p./Decomp/. Trans. Temp. (°C)	Molar. Conductance	Analysis % Found (clacd.)			
				C	H	N	Al
Picolinic acid (HPicA)	White	135m	-	-	-	-	-
$[Al(ONP)_2.HPicA]CH_3COO$	Yellowish cream	220d	35.5	52.28	3.19	9.01	5.75
				(52.51)	(3.28)	(9.19)	(5.90)
$[Al(DNP)_2.HPicA]CH_3COO$	Ligth yellow	196d	36.0	43.75	2.28	17.51	7.76
				(43.87)	(2.37)	(17.19)	(4.93)
$[Al(TNP)_2.HPicA]CH_3COO$	Light yellow	170d	34.4	37.49	1.51	15.21	4.09
				(37.67)	(1.72)	(15.31)	(4.30)
$[Al(8HQ)_2.HPicA]CH_3COO$	Canary yellow	252d	39.3	58.51	3.48	2.47	4.85
				(58.64)	(3.57)	(2.63)	(5.07)
$[Al(1N2N)_2.HPicA]CH_3COO$	Brownish black	180d	36.6	60.65	3.40	4.85	4.75
				(60.86)	(3.44)	(5.07)	(4.89)
$[Al(SalA)_2.HPicA]CH_3COO$	Cream	230d	38.8	54.5	3.41	2.86	5.51
				(54.77)	(3.52)	(2.90)	(5.60)
$[Al(AcSalA)_2.HPicA]CH_3COO$	Cream white	220d	39.5	47.15	3.35	2.15	4.31
				(47.21)	(3.44)	(2.29)	(4.42)
$[Al(OABA)_2.HPicA]CH_3COO$	Light brown	225d	41.1	54.85	3.71	5.75	5.42
				(55.00)	(3.95)	(5.83)	(5.62)
$[Al(ONBA)_2.HPicA]CH_3COO$	Reddish Brown	230d	42.2	41.18	2.30	6.41	4.07
				(41.25)	(2.34)	(6.56)	(4.21)

Molar conductivities

Molar conductivities of all these complexes were measured in DMF at 23°C at a concentration of 10^{-3} M.

A vlaue of Ca. 35-40 $\text{Ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$ is characteristic of a 1:1 electrolyte, whereas ideally molar conductivity of a neutral complex should be zero[7]. High values of molar conductivities show that these complexes ionize in the solvent. The molar conductivity values (34.4-42.2 $\text{Ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) correspond to 1:1 electrolyte which indicate they are ionci nature.

Infrared spectra

Infrared spectra of the ligand (picolinic acid) and its mixed ligand Al (III) complexes were recorded in KBr phase between 4000-400 cm^{-1} with the help of JASCO-FTIR spectrophotometer model-5300. Selected IR absorption bands are shown in Table 2.

The broad band at 3400 cm^{-1} in the spectra of ligand (picolinic acid) indicates strong intramolecular hydrogen bonding in it. The spctra of all the complexes exhibit new broad and strong bands in the region 3540-3401 cm^{-1} of a medium intensity in the region 2760-1903cm^{-1}, which may be assigned to $\nu_{O\text{-}H}$ and $\nu_{O\text{-}H...O/N....H\text{-}O}$ absorptions respectively and it indicates there is a strong hydrogen bonding in them. This suggests hydrogen bonding to be a dominating factor in stabilizing these complexes.

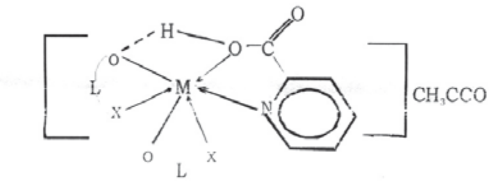
The appreciable shift of 1650, 1600 and 1520 cm^{-1} bands of the ligand (picolinic acid) in the mixed ligand Al (III) complexes suggests the coordination of ligand with Al (III) metal through oxygen atom of carboxylic acid (COO^-) moiety.

The 1580 cm^{-1} band of the ligand (picolinic acid) as shifted by 10-16cm^{-1} in the complexes. These features are quite suggestive of the coordination of ligand with almunium metal through nitrogen atom of pyridine ring. The absorption bands near 1466-1453cm^{-1} occur due to presence of CH_3COO^- ion in these complexes.

The band in the region 524-548 cm^{-1} in the spectra of all mixed ligand Al(III) complexes may be assigned to M-O band frequency while mediumband

Table 2: Pertinent IR data for ligand (Picolinic acid) and its mixed ligand Al (III) complexes

Compound	υO-H	υO-H...O/N..H-O	υCOOO-	υCh_3COO	υC=N	υM-O/M-N
Picolinic acid (HPicA)	3400-	1650, 1600, 1520	-	-	1580	-
$[Al(ONP)_2.HPicA]CH_3COO$	3401	2450	1500	1454	155	648,500,544,458
$[Al(8HQ)_2.HPicA]CH_3COO$	3401	2720	-	1466	1596	649,544,458
$[Al(OABA)_2.HPicA]CH_3COO$	3540,3465	3118,1903	1703,1620,1612	14453	1570	66,524,497,459
$[Al(ONBA)_2.HPicA]CH_3COO$	3538,3464	3117,1950	1685,1636,1611	1454	1565	661,524,496,459
$[Al(SalA)_2.HPicA]CH_3COO$	3464	2760	1686,1606	1454	-	661,570,524,498,460



where M = Al(III); deprotonated ONP, DNP, TNP, 8HQ, 1N2N, OABA, ONBA, SalA or AcSalA ; X = O or N

Fig. 1

Table 3: Major diffuse reflectance bands (in mm) for Picolinic acid and its mixture ligand Al (III) complexes

Compound	Diffuse reflectance (in mm)
Picolinic acid (HPicA)	283
$[Al(8HQ)_2.HPicA]CH_3COO$	371,328,246,232
$[Al(OABA)_2.HPicA]CH_3COO$	326,270
$[Al(ONBA)_2.HPicA]CH_3COO$	261
$[Al(AcSalA)_2.HPicA]CH_3COO$	251,295

in the region 665-544 cm^{-1} is assigned to M-N band frequency[8]. These bands are absent in the second ligand, i.e. picolinic acid. These assignment are based on the assumption[9] that since oxygen is more electronegative than nitrogen; the M-O bond tends to be more ionic than the M-N bond. Consequently M-O vibrations are expected to appear at lower frequencies. The above data conforms the coordination of oxygen atom of O-H (phenolic) group and nitrogen atom of first ligand (organic acid) to the Al (III) metal ion in all the mixed liand complexes.

Electronic spectra

Electronic spectra were recorded on PERKIN ELMER LAMBDA-15 UV-VIS spectrophotometer in paraffin solvent. The band observed in electronic spectra of the ligand (picolinic acid) and its mixed ligand Al (III) complexes are given in Table 3.

Ligand (picolinic acid) exhibits sharp intense badn at 235-283 nm. This band indicates π-π^* transition in the aromatic ring.

Electronic absorption bands of mixed ligand Al(III) complexes with picolinic acid are observed at 225-283nm which indicate π-π^* transition in the complexes.

In electronic spectra of the mixed ligand Al(III) complexes show a charge transfer badns at 326-371 nm.

This shift in position of π-π^* and charge transfer bands of the ligand (picolinic acid) in the complexes show that there is a π-interaction between metal and ligand orbitals.

Structure and bonding

Based on the analytical and spectral (IR & UV-VIS) studies, the structure and bonding of the newly prepared mixed ligand Al (III) complexes involving some chelating organic acids and picolinic acid may tentatively be proposed as shown in Fig. 1.

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