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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2020, Vol. 36, No.(6):
Pg. 1225-1228

Brief communication

Mixed Ligand Complexes of Al(III) with Chelating Organic Acids and Ethylenediamine

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http://dx.doi.org/10.13005/ojc/360630

(Received: September 14, 2020; Accepted: November 03, 2020)

ABSTRACT

Mixed ligand complexes of Al(III) with *o*-Nitrophenol, 1-Nitroso-2-naphthol, 2,4-Dinitrophenol, 8-Hydroxyquinoline, 2,4,6-Trinitrophenol or *o*-Nitrobenzoic acid and Ethylenediamine were prepared and studied by elemental analyses, conductometric measurements, FTIR and UV-Vis measurements. These studies indicates the coordination of aluminium metal with *o*-Nitrophenol, 1-Nitroso-2-naphthol, 2,4-Dinitrophenol, 8-Hydroxyquinoline, 2,4,6-Trinitrophenol or *o*-Nitrobenzoic acid through oxygen or/and nitrogen atom and with Ethylenediamine through nitrogen atom.

Keywords: Complexes, Ethylenediamine, UV-Vis, FTIR.

INTRODUCTION

Analyses of complexes with varied ligand are of significance as more than one ligand is associated with the metal ion in the complex[1-3]. The presence of different type of ligand enhances the properties of the complex[4-10]. Ethylenediamine is an important bidentate ligand with two donor atoms which can construct a chelating ring with the metal. Ethylenediamine can form complexes with different metal ions with distinct bonding determined by the reaction conditions and the properties of the metal ion. Kriza *et al* have used azomethines and isopropoxides as ligands for the synthesis of mixed ligand complexes and has proposed monomeric structure for these complexes[11]. The adaptable chelating capacity of Ethylenediamine with several metals is distinctly been established[12,13]. Studies on mixed ligand complexes have been reported by several authors[14-16]. In this paper we describe the preparation and spectral properties of new Al(III) complexes with varied ligand derived from *o*-Nitrophenol, 1-Nitroso-2-naphthol, 2,4-Dinitrophenol, 8-Hydroxyquinoline, 2,4,6-Trinitrophenol or *o*-Nitrobenzoic acid and Ethylenediamine.

MATERIALS AND METHODS

Aluminum basic acetate, *o*-Nitrophenol, 1-Nitroso-2-naphthol, 2,4-Dinitrophenol, 8-Hydroxyquinoline, 2,4,6-Trinitrophenol or *o*-Nitrobenzoic acid and Ethylenediamine which were used are of high purity.

Preparation of Al(III) complexes

0.01 mol of aluminum basic acetate was dissolved in absolute alcohol to form a suspension. 0.02 mol of *o*-Nitrophenol or 1-Nitroso-2-naphthol or 2,4-Dinitrophenol or 8-Hydroxyquinoline or 2,4,6-Trinitrophenol or *o*-Nitrobenzoic acid was then mixed with constant stirring and further 0.01 mol of Ethylenediamine was added. The mixture was refluxed with magnetic stirrer for 1½ h at 80°C. It was then cooled to obtain a characteristic coloured complex. The complex was filtered and the collected precipitate was further washed with absolute alcohol. It was then dried in an electric oven at 100°C. The complex was preserved in desiccator over fused $CaCl_2$.

RESULTS AND DISCUSSION

Mixed ligand complexes of Al(III) in solid state with varied colours were obtained. They are soluble in polar solvents viz. ethanol, DMF, methanol, etc; and insoluble in non-polar solvents viz. toluene, benzene, ether, etc. Higher decomposition temperature of the complexes than the ligand indicates higher stability of the complexes Table 1. The complexes when stored under dry conditions were found to be stable. Elemental analyses for hydrogen, carbon and nitrogen Table 2 were performed on Heraeus B6450 CHN elemental analyzer.

Molar conductance

All the mixed ligand complexes were measured for their molar conductance in DMF at 23°C on Systronics digital direct conductivity meter-306 at a concentration of 10^{-3} M. A value of 32.2-43.5 $ohm^{-1}\ cm^2\ mol^{-1}$ appears characteristic of 1:1 electrolyte and indicates ionic nature of the complexes[17] Table 1.

Table 1: Physical characteristics of Ethylenediamine and the mixed ligand complexes

Complex	Colour	Boiling/Decomposition/transition temp (°C)	Conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$)
$C_2H_8N_2$	Colourless	116.5b	—
$C_{16}H_{19}N_4O_8Al$	Orange yellow	230d	32.2
$C_{16}H_{17}N_6O_{12}Al$	Deep orange	245d	35.5
$C_{16}H_{15}N_8O_{16}Al$	Yellowish brown	260d	42.1
$C_{22}H_{23}N_4O_4Al$	Light green	265d	40.1
$C_{24}H_{23}N_4O_6Al$	Brownish black	260d	43.5
$C_{18}H_{19}N_4O_{10}Al$	Light orange	255d	41.4

Table 2: Elemental analyses of the mixed ligand complexes

Complex	Analysis (%) Found (Calculated)				% Yield
	C	H	N	Al	
$C_{16}H_{19}N_4O_8Al$	45.51	4.38	13.18	6.21	72
	(45.50)	(4.50)	(13.27)	(6.40)	
$C_{16}H_{17}N_6O_{12}Al$	37.39	3.95	16.18	5.11	80
	(37.50)	(4.03)	(16.41)	(5.27)	
$C_{16}H_{15}N_8O_{16}Al$	31.75	2.41	18.48	4.29	72
	(31.89)	(2.49)	(18.60)	(4.48)	
$C_{22}H_{23}N_4O_4Al$	60.75	5.21	12.75	6.01	73
	(60.83)	(5.30)	(12.90)	(6.22)	
$C_{24}H_{23}N_4O_6Al$	58.71	4.61	11.25	5.27	67
	(58.77)	(4.69)	(11.43)	(5.51)	
$C_{18}H_{19}N_4O_{10}Al$	45.12	3.78	11.55	5.38	69
	(45.19)	(3.97)	(11.71)	(5.65)	

Infrared Spectra

Infrared spectrum in the range 4000-400 cm^{-1} in KBr phase was recorded for Ethylenediamine and its various mixed ligand Aluminium(III) complexes. JASCO model-5300 FTIR instrument was employed for recording the Infrared absorption bands. The selected absorption bands are listed in Table 3.

For mixed ligand complexes, the four principle regions of absorption are observed around 3300, 1600, 1100 and 800 cm^{-1} respectively which are ascribed to N-H (str.), N-H (asymm. def.), N-H (symm. def.) and NH_2 (rock.) mode respectively.

For the ligand Ethylenediamine, the peaks at 3377 and 3316 cm^{-1} reflects stretching mode of N-H; N-H (asymm. def.) mode occurs at 1600 cm^{-1}; N-H (symm. def.) mode at 1100 cm^{-1} and peak at 810 cm^{-1} for rocking mode of NH_2 are also observed.

Table 3: Infrared spectrum data for Ethylenediamine and mixed ligand complexes

	Selected infrared absorption spectral bands (in cm^{-1})					
Compound	N-H(str.)	N-H(asymm. def.)	$\upsilon(CH_3COO^-)$	N-H(symm. def.)	NH_2(rock.)	Far IR
$C_2H_8N_2$	3377, 3316	1600	–	1100	810	–
$C_{16}H_{19}N_4O_8Al$	3468	1648, 1610, 1549	1428	1148,1140	848, 814	654, 568, 532, 455
$C_{16}H_{17}N_6O_{12}Al$	3551, 3375	1604, 1566	1430	1135	837	635, 585, 530, 471
$C_{16}H_{15}N_8O_{16}Al$	3425	1625, 1590, 1565	1439	1159	820	668, 546, 521
$C_{22}H_{23}N_4O_4Al$	3423	1601	1435	1170, 1114	826	649, 560, 546, 455

For the mixed ligand complexes, one N-H vibration band appears as broad peak except for $C_{16}H_{17}N_6O_{12}Al$ which has two broad peaks. The 3377 cm^{-1} and 3316 cm^{-1} band for Ethylenediamine are shifted and appears between 3551-3375 cm^{-1} with increased intensity in the mixed ligand complexes. This suggests decrease in the bond order of N-H on complexation. The absorption peaks for CH_3COO^- ion occurs in the region 1439-1428 cm^{-1}.

For the mixed ligand complexes of Al(III), M-O absorption bands lie in the region 521-455 cm^{-1} while medium bands in the region 668-530 cm^{-1} indicates M-N band frequency[18]. These bands are absent in the chelating organic acids and Ethylenediamine. The discussion points that the phenolic –OH group or –COOH (carboxylic) group coordinates to the metal through the oxygen atom; whereas coordination with the metal occurs through nitrogen atom of –NO (in case of 1-Nitroso-2-naphthol) or pyridine ring (in case of 8-Hydroxyquinoline) or oxygen atom of $–NO_2$ (in case of *o*-Nitrophenol, 2,4-Dinitrophenol, 2,4,6-Trinitrophenol and *o*-Nitrobenzoic acid) in the mixed ligand complexes of Al(III).

UV-Visible spectra

UV-Visible spectra were taken using paraffin solvent on Perkin-Elmer-Lambda-15 UV-Vis instrument. Table 4 lists the position of UV-Vis spectral bands for the mixed ligand complexes of Al(III). UV-Visible absorption peaks for the mixed ligand complexes of Al(III) with Ethylenediamine are found at 240 nm and 248 nm which indicate π–π* transitions in these complexes[19] whereas bands in the range 328-390 nm are due to charge transfer spectra Table 4. There is a shift in the spots of π–π* transitions on complexation; the spots of charge transfer transitions also shows a shift. The shifting occurs on account of π-interactions between the ligand and metal orbitals.

Table 4: UV-Visible spectral bands (in nm) for the mixed ligand complexes

Complexes	UV-Vis spectra (in nm)
$C_{16}H_{19}N_4O_8Al$	368, 332, 244
$C_{16}H_{17}N_6O_{12}Al$	353, 250, 236
$C_{16}H_{15}N_8O_{16}Al$	390, 351, 329, 240
$C_{22}H_{23}N_4O_4Al$	371, 328, 248

The elemental analyses, molar conductance measurements, infrared spectrum and UV-Visible spectrum suggest a probable structure for $C_{16}H_{19}N_4O_8Al$ which is shown in Figure 1.

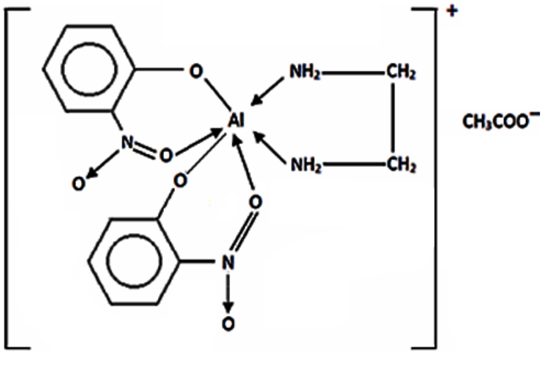

Fig. 1. Structure of the mixed ligand complex, $C_{16}H_{19}N_4O_8Al$

Similarly, the structure for the other prepared mixed ligand complexes of Al(III) may also be suggested.

ACKNOWLEDGEMENT

The authors thankfully acknowledge the

Director, CDRI, Lucknow for providing spectral measurements.

Conflict of interest

The authors declare that there is no conflict of interest.

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