

A Study on Synthesis and Characterisation of Al (II) Complex

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Abstract

Aluminium is the third most abundant element in the earth's crust and is much more common. It finds varied industrial applications including food and pharmaceutical industries. It has been used as a protective in treating ulcer, fissures and silicoses. It causes potential toxicity and health hazard when ingested in excess. Aluminium toxicity has been implicated in many dreaded diseases, including Alzheimer's disease. Role of complexation can be envisaged in much of the chemistry & bio-toxicology of aluminium. Complexation of Al^{3+} by the donor compounds in some intermediate stage is likely and might be of single or mixed ligand type. Selectivities or specificities might also play role. Relative stability of these intermediate complexes would be helpful in unrevealing the mechanism of action and related applied chemistry of aluminium.

Keywords: Aluminium, Bio toxicology, element, complex, industries

We are interested in the mixed ligand complexes of Al(III) involving potential chelating ligands with O &/or N donor system of biological importance. We have synthesized and characterized mixed ligand Al(III) complexes of general formula $[AlL_2L']CH_3COO$, where L = deprotonated ONP, DNP, TNP, 1N2N, 8HQ & ONBA; L' = ethylenediamine or propylene-diamine. Melting/decomposition temperatures of the complexes suggest them to be genuine compounds. High values of molar conductivities of these complexes show that they are ionic nature.

Infrared spectral studies of ligands and mixed ligand Al(III) complexes show that ν_{N-H} band at $\sim 3316\text{ cm}^{-1}$, sym δ_{N-H} at 1100 cm^{-1} , antisym δ_{N-H} at 1600 cm^{-1} and rocking NH_2 at 810 cm^{-1} have been shifted, suggestive of coordination of Al metal through nitrogen atom of $-NH_2$ group of ethylenediamine or propylenediamine. The

absorption bands near $1439\text{-}1425\text{ cm}^{-1}$ indicate the presence of CH_3COO^- ion in these complexes. The IR absorption band in the region $521\text{-}455\text{ cm}^{-1}$ & $668\text{-}530\text{ cm}^{-1}$ of all the complexes may be assigned to M-O and M-N band frequencies respectively. The above data confirm the coordination of N &/or O of the organic acid. In electronic absorption spectra, bands in the region $236\text{-}251$ & $326\text{-}390\text{ nm}$ indicate $\pi\text{-}\pi$ transition in aromatic ring and charge transfer respectively.

DISCUSSION

We have synthesized and characterized the mixed ligand Al(III) complexes involving some chelating organic acids, viz., ONP, DNP, TNP, 8HQ, 1N2N,

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OABA, ONBA, SalA or AcSalA and picolinic acid as ligands. The compounds were characterized by elemental analysis and were found to be of general formula, $[AIL_2HL']CH_3COO$ (where L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N, OABA, ONBA, SalA or AcSalA; HL' = picolinic acid).

Higher melting/decomposition temperatures of the complexes than that of the second ligand (picolinic acid), indicate their greater stability. High values of molar conductivities of these complexes show that they are ionic nature.

The IR spectra of all the complexes exhibit new broad & strong bands in the region $3540-3401\text{ cm}^{-1}$ and broad band of a medium intensity in the region $2760-1903\text{ cm}^{-1}$, indicate there is a strong hydrogen bonding which is dominant 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 complexes suggest the coordination of ligand with Al(III) metal through oxygen atom of $-COOH$ (carboxyl) group. The 1580 cm^{-1} band of the ligand is shifted by $10-16\text{ cm}^{-1}$ in the complexes, suggestive of the coordination of ligand with Al(III) metal through nitrogen atom of pyridine ring. The absorption bands near $1466-1453\text{ cm}^{-1}$ indicate the presence of CH_3COO^- ion in these complexes. The band in the region $524-458\text{ cm}^{-1}$ & $665-544\text{ cm}^{-1}$ of all the complexes may be assigned to M-O & M-N band frequencies respectively. These data confirm the coordination of N &/or O of the organic acid, i.e.. first ligand. In electronic absorption spectra, bands in the region $225-283\text{ nm}$ & $326-371\text{ nm}$ indicate $\pi - \pi$ transition in aromatic ring & charge transfer respectively.

We have synthesized & characterized the mixed ligand Al(III) complexes involving some chelating organic acids, viz.. o-nitrophenol(ONP), 2,4-dinitrophenol(DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol(1N2N), o-aminobenzoic acid(OABA), o-nitrobenzoic acid (ONBA), salicylic acid (SalA) or acetylsalicylic acid (AcSalA) and 8-hydroxyquinoline (8HQ) or 5,7-dinitro-8-hydroxyquinoline (DN8HQ) ligands. Analytically, the as compounds were found to be of general formula, $[AILHLICH_3COO]$ (where L deprotonated ONP, DNP, TNP, 1N2N, OABA, ONBA, SalA or AcSalA; HL' = 8-hydroxyquinoline or 5,7-dinitro-8-hydroxyquinoline).

Higher melting/decomposition temperatures of

the complexes as compared to that of the ligands, suggest their greater stability. High values of molar conductivities of the complexes suggest them to be ionic nature. In IR spectra of all the complexes shifting of moderately strong band in the region $\sim 3440\text{ cm}^{-1}$ of the ligands (8HQ & DN8HQ) to $\sim 3420-3368\text{ cm}^{-1}$ and medium band in the region $2760-1850\text{ cm}^{-1}$ in their complexes, suggest that there is a strong hydrogen bonding which is dominant factor in stabilizing these complexes. The absorption bands in the region $1468-1415\text{ cm}^{-1}$ indicate the presence of CH_3COO^- ion in these complexes.

The absorption band at 1120 cm^{-1} (assigned to ν_{C-O}) shifted by $6-10\text{ cm}^{-1}$ indicates coordination of Al(III) metal through hydroxyl oxygen atom. Characteristic absorption bands of $\nu_{C=N}$ at 1580 & 1585 cm^{-1} of ligands either splitted in the region $1600-1603\text{ cm}^{-1}$ or shifted by $5-11\text{ cm}^{-1}$, suggest the coordination of second ligand (8HQ or DN8HQ) with Al(III) metal through nitrogen atom of quinoline ring. The bands in the region $455-510\text{ cm}^{-1}$ & $544-669\text{ cm}^{-1}$ or $540-550\text{ cm}^{-1}$ (in DN8HQ) may be assigned to M-O & M-N band frequencies respectively. These data confirm the coordination of N &/or of the organic acids. In electronic spectra of mixed ligand Al(III) complexes, bands in the region $206-278\text{ nm}$ & $317-390\text{ nm}$ indicate $\pi - \pi$ transition in aromatic ring and charge transfer respectively.

Further, we have used 1-nitroso-2-naphthol as secondary ligand and prepared mixed ligand Al(III) complexes of general formula, $[AIL_2HL']CH_3COO$ (where L= deprotonated ONP, DNP, TNP OABA, ONBA, SalA or AcSalA; HL' = 1-nitroso-2-naphthol (1N2N)). The compounds have been characterized by elemental analysis, molar conductance measurements, infrared and electronic absorption spectral data.

Higher melting/decomposition temperatures of the complexes as compared to that of corresponding ligand suggest their greater stability. High values ($31-45\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of molar conductivities of these complexes show that they are ionic nature. The first recognized mixed ligand complexes of alkali metals of the type $ML.nHL'$ were synthesized by Sidgwick & Brewer in 1925. These were formed by the alkali metal salts of o-nitrophenol and 3 nitro-o-cresol with molecule of salicylaldehyde in non-aqueous solvent. Nyholm *et al.* prepared a number of mixed ligand complexes of alkali metals of the type

ML.nHL' with two different ligands e.g., salicylic acid, o-nitrophenol, isonitrosoacetophenone, 1-nitroso-2 naphthol and 8-hydroxyquinoline.

CONCLUSION

The characteristic bands in the FTIR spectra of 1-nitroso-2 naphthol (1N2N) are 3500-1800, 1640 & 1175 cm^{-1} , due to $\nu_{\text{O-H/O-H.O'}}$, $\nu_{\text{N=O}}$ & $\nu_{\text{C-O}}$ respectively. Mixed ligand Al(III) complexes of it show multiple medium strong absorption band over a wide range 3431-2700 cm^{-1} indicates the presence of strong hydrogen bonding which may be dominant factor for stabilizing these complexes. The absorption bands at 1640 cm^{-1} (assigned to $\nu_{\text{N=O}}$) and 1175 cm^{-1} (assigned to $\nu_{\text{C-O}}$) are shifted down by 32-46 cm^{-1} and 11-17 cm^{-1} respectively in the complexes. Shifting of these bands, suggests coordination of Al(III) metal through nitrogen atom of N=O (nitroso) & oxygen atom of -OH (phenolic) groups of the ligand (1N2N). The absorption bands in the region 1475-1434 cm^{-1} indicate the presence of CH_3COO ion in these complexes. The bands in the region 433-463 & 673-693 of all the complexes may be assigned to M-O & M-N band frequencies respectively. These data confirm the coordination of N &/or O of the organic acid (first ligand). In electronic absorption spectra, bands in the region 231-251 nm and 290-390 nm indicate $\pi - \pi$ transition in aromatic ring and charge transfer respectively.

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