

Mixed ligand complexes of Aluminium (III) metal chelates of some organic acids with β -Alanine

MEHADI IMAM¹, RAJNISH KUMAR¹, MANOJ KUMAR SINGH²,

1. Deptt. Of Chemistry, Patna University, Patna-800005

2. Assistant professor, Deptt. Of Chemistry, R.R.S.D.C.E. BEGUSARAI

ABSTRACT:

An increasing number of studies on mixed ligand complex formation has become an usual feature in coordination chemistry in recent years. We have synthesized and characterized a number of mixed ligand complexes of aluminium(III) salts of some organic acids with β -alanine. They have the general formula, ML_2L' , where $M=Al(III)$, L =deprotonated o-nitrophenol(ONP), 2,4-dinitrophenol(DNP), 2,4,6-trinitrophenol(TNP), 8-hydroxy quinoline(8HQ) and 1-nitroso-2-naphthol(1N2N), L' =deprotonated β -alanine.

KEYWORDS: Mixed ligand complex, Aluminium(III) metal chelates, β -Alanine, Infrared spectra

INTRODUCTION

β -alanine (3-amino-propanoic acid) is the only naturally occurring beta amino acid. It is not used in the biosynthesis of any major proteins or enzymes. It is a component of the naturally occurring peptides carnosine and anserine and also of pantothenic acid (vitamin B₅) which itself is a component of coenzyme -A. Under normal conditions, It is metabolized into acetic acid.

Even though much weaker than glycine (and thus with a debated role as a physiological transmitter), β -alanine is an agonist next in activity to the cognate ligand glycine itself, for strychnine-sensitive inhibitory glycine receptors (GlyRs) (the agonist order: glycine >> β -alanine > taurine >> alanine, L-serine > proline)¹.

We have taken β -alanine as ligand to investigate its adduct formation ability towards the alkaline earth metal chelates in a view that the presence of methylene ($-CH_2-$) group may produce a steric effect on formation of mixed ligand complexes.

β -alanine(A) forms addition compounds with lithium and sodium halides. The product obtained is of the type, $ALiX \cdot \frac{1}{2}H_2O$ (where $X = Cl, Br \& I$), $ANaI$ and $A_2LiI \cdot \frac{3}{2}H_2O$. King & Rutherford² suggest that these compounds should be considered as alkali metal complexes, although no unequivocal structure is apparent.

EXPERIMENTAL:

Analar quality of ONP, DNP, TNP, 1N2N, 8HQ and β -alanine were used for the preparation of Aluminium(III) metal chelates.

PREPARATION OF MIXED LIGAND COMPLEXES:

The suspension of 0.541gm (0.001mole) of $Al(ONP)_3$, $Al(TNP)_3$, $Al(DNP)_3$, $Al(1N2N)_3$, $Al(8HQ)_3$ in absolute ethanol was mixed with 0.089g (0.001mole) of β -alanine. The mixture was refluxed on magnetic hot plate with constant stirring at 60-70°C for 60 minutes. In the process of refluxing, the whole mass went into the solution. On cooling, white precipitate was obtained. It was filtered, washed with the solvent and finally dried in an electric oven at 80°C. TABLE 1.

| Compound | Colour | M.Pt./Decomp./ Trans. temp.(^o C) | Molar conductance* |
|---------------------------------------|-----------------|---|-----------------------|
| β - Alanine | White | 204-206d | – |
| Al(ONP) ₂ . β - ALA | White | > 280 | 7.5 |
| Al(DNP) ₂ . β - ALA | Light yellow | 230d | 9.0 |
| Al(TNP) ₂ . β - ALA | Yellow | 260md | 8.5 |
| Al(8HQ) ₂ . β - ALA | Light green | >280 | 6.5 |
| Al(1N2N) ₂ . β - ALA | Yellowish brown | >280 | 9.5 |

RESULTS & DISCUSSION

Physical properties: Some physical properties of the second ligand(β -alanine) and the mixed ligand complexes($ML_2.L'$) obtained are listed in Table- 1.

β -alanine is a white crystalline solid, highly soluble in water but sparingly soluble in ethanol, chloroform and benzene but insoluble in ether, acetone, carbon disulphide and petroleum ether. The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like water, methanol, ethanol, DMF; partly soluble in pyridine, acetone etc; but they are sparingly soluble in non-polar solvents namely chloroform, n-hexane, benzene and dioxane. Almost all the complexes have considerably higher melting/transition/decomposition temperatures than the melting point of the ligand used, indicating their greater stability.

Molar conductances: Molar conductances of all the compounds were measured in ethanol at 27°C at a concentration of 10^{-3} M with the help of Systronics conductivity meter- 306. The values are given in Table - 1. The significantly low values of the molar conductance ($6.5\text{--}9.5 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) of the mixed ligand complexes, indicates them to be covalent in nature.

Infrared spectra

Infrared spectra of the ligand(β -alanine) and its hitherto unknown complexes were recorded in the region $4000\text{--}400 \text{ cm}^{-1}$ in KBr disc with the help of JASCO-FTIR spectrometer model -5300. The pertinent infrared data are listed in Table-2.

The spectrum of the amino acid, β -alanine shows a very broad poorly resolved ($-\text{NH}_3^+$) N-H stretching band at 3409 cm^{-1} , typical of strongly hydrogen bonded $-\text{NH}_2$ group, extended by combination band at 2361 cm^{-1} . This observation is due to the existence of free β -alanine in zwitterion ($^+\text{NH}_3\text{CH}_2\text{CH}_2\text{COO}^-$) form.

Primary amines display two weak absorption bands, one near 3500 cm^{-1} and the other near 3400 cm^{-1} . These bands represent respectively the free asymmetrical and symmetrical N-H stretching modes⁹. In the mixed ligand complexes, medium or weak absorption band in the region $3386\text{--}3452 \text{ cm}^{-1}$.

The strong band at 1594 cm^{-1} in the spectra of ligand (β -alanine) is in all probably due to the asymmetric $-\text{COO}^-$ stretching vibration. In the mixed ligand complexes, the bands appear in the region $1500\text{--}1579\text{ cm}^{-1}$. The general shifting of the band to lower frequency by upto 94 cm^{-1} , suggest the interaction of oxygen atom of $-\text{COOH}$ group with the metal atoms. Since the $-\text{COOH}$ group becomes more asymmetrical as the metal-oxygen interaction become stronger. The other bands below 1596 may be appeared due to the presence of the functional groups of the first ligands.

The weak band at 1427 cm^{-1} , in the spectra of the ligand (β -alanine) represents symmetric $-\text{COO}^-$ stretching vibration.

TABLE-2

Pertinent IR data for ligand (β -alanine) and its mixed ligand

Al(III) complexes

| Compound | $\nu\text{N-H}$ | $\delta_{\text{as}}(\text{NH}_3^+)$ | $\nu_{\text{as}}(\text{COO}^-)$ | $\nu_{\text{s}}(\text{COO}^-)$ | $\delta(\text{COO}^-)$ | $\nu\text{M-O/M-N}$ |
|----------------------------------|-----------------|-------------------------------------|---------------------------------|--------------------------------|------------------------|---------------------|
| β -alanine (β -Ala) | 3409 | 1664 | 1594 | 1427 | 670 | |
| Al(ONP)2. β -Ala | 3431 | 1618 | 1520 | 1422 | 671 | 580,500 |
| Al(DNP)2. β -Ala | 3433 | 1625 | 1522 | 1432 | 672 | 570,521 |
| Al(TNP)2. β -Ala | 3452,3387,3322 | 1652 | 1521 | 1435 | 674 | 548,512 |
| Al(8HQ)2. β -Ala | 3386 | 1604 | 1579,1500 | 1470,1386 | 669 | 546,495 |

In the mixed ligand complexes this band appears in the region $1386\text{--}1470\text{ cm}^{-1}$. Except few mixed ligand complexes the shifting of this band to lower frequency by upto 41 cm^{-1} clearly indicates the involvement of $-\text{COOH}$ group of the ligand in complex formation and coordination of Al(III) ion through oxygen atom of $-\text{COOH}$ group of the ligand (β -alanine).

The strong band at 670 cm^{-1} in the spectra of the ligand (β -alanine) may be due to $-\text{COO}^-$ bending vibration. In the mixed ligand complexes this band appears in the region of $669\text{--}674\text{ cm}^{-1}$. The shifting of this band by a very low frequency, suggests that $-\text{COO}^-$ bending vibration is not metal sensitive.

A weak asymmetrical ($-\text{NH}_3^+$) N-H bending band in the spectra of ligand(β -alanine) appears at 1664 cm^{-1} . In the mixed ligand complexes this band appears in the region $1604\text{--}1652\text{ cm}^{-1}$.The shifting of these bands indicates the metal–nitrogen interaction and these bands are metal sensitive.

The bands in region $495\text{--}521$ & $546\text{--}580\text{ cm}^{-1}$ in the spectra of all the mixed ligand complexes may be assigned to M-O/M-N band frequency.

Electronic spectra: The ultraviolet-visible spectral data were recorded on SHIMADZU UV-Vis 160A spectrophotometer in paraffin solvent. The bands observed in the UV-Vis spectra of the ligand (glycine) and the mixed ligand complexes of Al(III) are given in Table-3.

Table -3

**Major diffuse reflectance bands (in nm) for mixed
ligand complexes of Al(III)**

| Compound | Diffuse reflectance |
|----------------------------------|---------------------|
| Al(ONP) ₂ .β- alanine | 649 |
| Al(DNP) ₂ .β- alanine | 650 |
| Al(TNP) ₂ .β- alanine | 652 |
| Al(8HQ) ₂ .β- alanine | 652 |

STRUCTURE & BONDING

On the basis of quantitative analysis, the molecular formula of the mixed ligand complexes of aluminium metal salts of some organic acids with β-alanine is found to be $ML_2.L'$, where $M = Al(III)$, $L =$ deprotonated ONP, DNP, TNP, 1N2N or 8HQ; $L' =$ deprotonated β-alanine. Infrared spectra indicate that the aluminium metal replaces the H-atom of the hydroxyl or carboxyl group and through the N/O-atom of the $-NO_2$ /-NO/-NH₂ group or quinoline ring of the first ligand(L) forming two five/six membered chelates. The coordination of second ligand(β-alanine) through nitrogen atom of -NH₂ group and oxygen

atom of -COOH group with metal ion forming a six membered chelates. The probable structures of the complexes are shown in Fig 1.

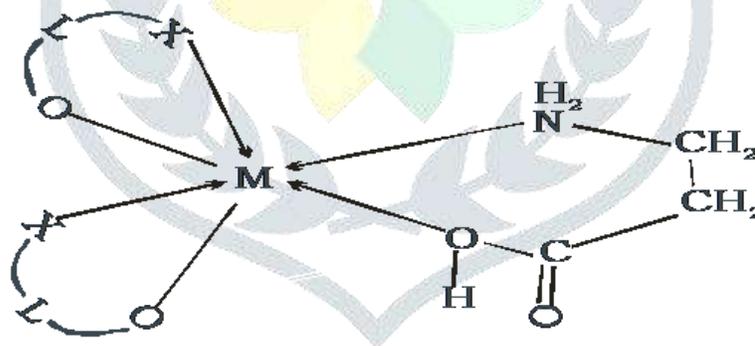


Figure-1

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