

## **MIXED LIGAND COMPLEXES OF Ag (I) METAL SALTS OF SOME ORGANIC ACIDS WITH $\beta$ -ALANINE**

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A number of novel mixed ligand complexes of type  $ML.HL'$ , where  $M = Ag(I)$ ,  $L =$  deprotonated *o*-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) or salicylic acid (SalA);  $HL' = \beta$ -Alanine ( $\beta$ -Ala) have been synthesized. These complexes have been characterized by analytical data, IR, UV-VIS spectral analysis and molar conductance measurements. IR spectral data show that the hydrogen bonding in these complexes is a dominant factor for their stability. Low value of their molar conductance would suggest them to be non-electrolyte.

### **INTRODUCTION**

**T** $\beta$ -Alanine, an amino derivative of propanoic acid has two different coordinating sites : N-atom of  $-NH_2$  group and O-atom of  $-COOH$  group. Compounds have analytical and technical importances. Transition metal and non-transition metal complexes with  $\beta$ -Alanine have been well investigated earlier [1-6]. In this communication, we have taken the  $\beta$ -Alanine as a secondary ligand to investigate the coordination behaviour towards Ag (I) and metal salts of some organic acids and also to study whether it is selective in comparison to the other amino acid complexes.

### **EXPERIMENTAL**

**O**-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), salicylic acid (SalA); and  $\beta$ -Alanine ( $\beta$ -Ala) of AnalaR grade were used as such.

**Preparation of Silver (I) metal salts of organic acids :** 0.01mole of organic acid and 0.01 mole of sodium hydroxide were mixed in 90% ethanol. The mixture was refluxed on magnetic hot plate with constant stirring at 80°C for about one hour. The solution was concentrated and cooled to give characteristic colour precipitate of sodium salt. It was filtered, washed with 90% ethanol and dried in an electric oven at 100°C.

Again, 0.01 mole sodium salt of organic acid was dissolved in 90% ethanol and an alcoholic solution of 0.01 mole  $AgNO_3$  then added. The mixture was refluxed on magnetic hot plate with constant stirring at 80°C for about half hour when characteristic colour precipitate

of silver salt of organic acid was obtained. It was filtered, washed with solvent and finally dried in an electric oven at 100°C.

#### Preparation of Mixed ligand complexes :

The suspension of 0.001 mole of silver salt of organic acid in 95% ethanol was mixed with 0.001 mole of  $\beta$ -alanine. The mixture was refluxed on magnetic hot plate with constant stirring at 70-80°C for 2-3 hours and cooled. The characteristic colour precipitate of adduct got separated. It was filtered, washed with absolute ethanol and finally dried in an electric oven at 100°C.

## RESULTS & DISCUSSION

Some physical properties of the second ligand ( $\beta$ -Alanine) and the mixed ligand complexes (ML.HL') obtained are listed in Table 1.

**Table 1**

Compound	Colour	M.P./ Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
$\beta$ -Alanine( $\beta$ -Ala)	White	236m	---	---	---	---	
Ag(ONP). $\beta$ -Ala	Light yellow	245d	10.0	32.15 (32.25)	3.19 (3.28)	8.22 (8.36)	32.03 (32.19)
Ag(DNP). $\beta$ -Ala	Yellow	264d	9.0	28.32 (28.43)	2.55 (2.63)	10.91 (11.05)	28.18 (28.38)
Ag(TNP). $\beta$ -Ala	Yellow	250m	9.5	25.36 (25.42)	2.05 (2.11)	13.02 (13.18)	25.22 (25.37)
Ag(1N2N). $\beta$ -Ala	Green	280d	9.2	42.16 (42.29)	3.45 (3.52)	7.45 (7.59)	29.06 (29.22)
Ag(8HQ). $\beta$ -Ala	Cream	240m	8.9	42.15 (42.25)	3.78 (3.81)	8.15 (8.21)	31.55 (31.63)
Ag(SalA). $\beta$ -Ala	Light brown	260d	7.6	35.85 (35.94)	3.48 (3.59)	4.11 (4.19)	32.13 (32.29)

**Table 2. Pertinent IR data for ligand( $\beta$ -Alanine) & its mixed ligand Ag(I) complexes**

Compound	$\nu_{N-H}$	$\delta_{asym}NH_3^+$	$\nu_{asym}COO^-$	$\delta_{sym}NH_3^+$	$\nu_{sym}COO^-$	$\delta_{COO^-}$	$\nu_{M-O/M-N}$
$\beta$ -Alanine( $\beta$ -Ala)	3410	1665	1595	1526, 1480	1425	670	---
Ag(ONP). $\beta$ -Ala	3420	1690	1609	1535, 1455	1408	670	554, 532
Ag(DNP). $\beta$ -Ala	3434	1670	1620	1515, 1470	1420	670	520, 495
Ag(TNP). $\beta$ -Ala	3490, 3225	1690	1612	1545, 1475	1427	670	590, 515, 450
Ag(1N2N). $\beta$ -Ala	3428, 3312	1685	1597	1550, 1480	1413	669	585, 517, 465
Ag(8HQ). $\beta$ -Ala	3395	1695	1598	1505, 1469	1415	671	540, 511
Ag(SalA). $\beta$ -Ala	3437	1675	1619	1517, 1470	1425	670	570, 512

Glycine is a white crystalline solid, highly soluble in cold water, ethanol but sparingly soluble in ether, chloroform, benzene etc. The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but sparingly soluble in non-polar solvents, viz., chloroform, *n*-hexane, benzene, dioxane etc.

**Molar Conductance :** Molar conductance of all the compounds were measured in methanol at 27°C at a concentration of  $10^{-3}$  M. The values are given in Table-1. The value of about 35-40  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  appears and characteristics of 1 : 1 electrolyte [7] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (7.6-10.0) of molar conductance of the compounds indicate them to be non-electrolyte.

**Infrared Spectra :** Infrared measurements for compounds were made between 4000-4500  $\text{cm}^{-1}$  in KBr disc with the help of FTIR spectrophotometer, Shimadzu 8201 PC. Pertinent infrared spectral data for these compounds are shown in Table 2.

A broad, strong ( $^+\text{NH}_3$ ) N-H stretching band in the region 3410-2360  $\text{cm}^{-1}$  observed in the ligand ( $\beta$ -Alanine). Multiple combination and overtone bands extend the absorption to about 2000  $\text{cm}^{-1}$ . Above observation is due to free  $\beta$ -alanine exists in zwitter ion ( $^+\text{NH}_3 - \text{CH}_2\text{COO}^-$ ) form [8].

In the spectra of the mixed ligand complexes, two medium or weak absorption bands : one in the region 3490-3420  $\text{cm}^{-1}$  and the other in the region 3395-3312  $\text{cm}^{-1}$  are observed. These bands represent respectively, the free asymmetrical and symmetrical N-H stretching modes. This observation is probably inversion of zwitter ion form into original form after the formation of mixed ligand complexes.

The strong band at 1595  $\text{cm}^{-1}$  in the spectra of ligand is in all probably due to the symmetric  $\text{cm}^{-1}$  stretching vibration. In the mixed ligand complexes, the bands appear in the region 1620-1597  $\text{cm}^{-1}$ . The shifting of the band to higher frequency upto 25  $\text{cm}^{-1}$ , suggest the interaction of oxygen atom of  $-\text{COOH}$  group with the silver metal. Further asymmetric  $\text{COO}^-$  stretching frequency appears at 1595  $\text{cm}^{-1}$  found that the carboxylic oxygen in the ligand. The weak band at 1425  $\text{cm}^{-1}$  in the spectrum of the ligand represents symmetric  $-\text{COO}^-$  stretching vibration. In the mixed ligand complexes, this band appears in the region 1427-1405  $\text{cm}^{-1}$ . Shifting of this band to higher frequency by upto 20  $\text{cm}^{-1}$  clearly indicates the involvement of  $-\text{COOH}$  group of the ligand in complex formation and coordination of Ag(I) ion through O-atom of  $-\text{COOH}$  group of  $\beta$ -Alanine.

The strong band at 670  $\text{cm}^{-1}$  in the spectrum of the ligand may be due to  $-\text{COO}^-$  bending vibration. In the mixed ligand complexes, this band appears in the region of 671-669  $\text{cm}^{-1}$ . 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 spectrum of the ligand appears at 1665  $\text{cm}^{-1}$ . In the mixed ligand complexes, this band appears in the region 1695-1670  $\text{cm}^{-1}$ . The fairly strong symmetrical ( $^+\text{NH}_3$ ) N-H bending bands in the spectrum of ligand appear in the region 1526-1480  $\text{cm}^{-1}$ . In the mixed ligand complexes, these bands appear in the region 1569-1440  $\text{cm}^{-1}$ . The shifting of these bands indicates the metal-nitrogen interaction and these bands are metal sensitive.

In all the mixed ligand complexes, the bands with medium to strong absorption in the far infrared region 590-532  $\text{cm}^{-1}$  and 520-465  $\text{cm}^{-1}$  are tentatively assigned to M-O and M-N modes [9, 10] respectively. The above data confirm the coordination of oxygen/-nitrogen atom of first ligand to silver metal in all the mixed ligand complexes.

**Electronic spectra :** Electronic spectra were recorded on Systronics Double Beam UV-VIS Spectrophotometer-2201 in methanol. The bands observed in electronic spectra of the mixed ligand complexes of Ag (I) are given in Table-3.

**Table 3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Ag (I) with  $\beta$ -Alanine**

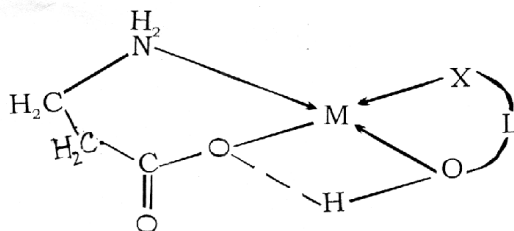
Compound	Diffuse reflectance ( in nm)
AgONP. $\beta$ -Ala	238, 389
AgDNP. $\beta$ -Ala	222, 354
AgTNP. $\beta$ -Ala	245, 344, 395
Ag1N2N. $\beta$ -Ala	235, 344, 376
Ag8HQ. $\beta$ -Ala	232, 408

The electronic spectra of the mixed ligand complexes show bands at the region 222-245 nm, which indicate  $\pi$ - $\pi^*$  transition in the complexes. The mixed ligand complexes show charge transfer bands in the region 344-408 nm.

The shift in position of  $\pi$ - $\pi^*$  transition and charge transfer bands in the complexes show that there is a  $\pi$ -interaction between metal and ligand orbitals.

## STRUCTURE & BONDING

On the basis of quantitative analysis, IR, UV-VIS spectral data and conductivity measurements suggest the probable structure for these complexes (Fig. 1).



where  $M = \text{Ag (I)}$ ;  $L = \text{deprotonated ONP, DNP, TNP, 8HQ, 1N2N or SalA}$ ;  $X = \text{O or N}$

Fig. 1

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