

## **MIXED LIGAND COMPLEXES OF Ag(I) METAL SALTS OF SOME ORGANIC ACIDS WITH GLYCINE**

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RECEIVED : 23 June, 2015

A number of novel mixed ligand complexes of type ML.HL' have been synthesized and characterized, where M = Ag(I), L = deprotonated o-nitrophenol (ONP), 2, 4-dinitro-phenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline-(8HQ) or salicylic acid(SalA); HL' = Glycine (Gly). All the complexes have been found to be coloured, fairly stable in dry conditions and decompose at a temperature higher than the melting point of the ligand. 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**

**G**lycine, an amino derivative of acetic acids 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 glycine have been well investigated earlier [1-8]. In this communication, we have taken the glycine 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 Glycine (Gly). 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.

Table 1

Compound	Colour	M.P./ Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	Ag
Glycine(Gly)	White	233m	---	---	---	---	---
AgONP.Gly	Yellow	245d	7.1	26.66 (26.81)	2.69 (2.80)	8.60 (8.72)	33.41 (33.60)
AgDNP.Gly	Yellowish brown	252d	8.1	26.16 (26.24)	2.09 (2.18)	11.35 (11.48)	29.31 (29.46)
AgTNP.Gly	Pale yellow	280d	8.8	23.26 (23.36)	1.64 (1.70)	13.50 (13.63)	26.11 (26.24)
Ag1N2N.Gly	Brown	250d	10.5	40.46 (40.58)	3.02 (3.10)	7.74 (7.89)	30.21 (30.38)
Ag8HQ.Gly	Deep brown	200m	7.9	40.30 (40.39)	3.31 (3.37)	8.45 (8.57)	32.84 (32.99)
AgSalA.Gly	Cream	235m	9.5	33.66 (33.77)	3.04 (3.13)	4.25 (4.38)	33.56 (33.71)

Table 2. Pertinent IR data for ligand (Glycine) &amp; its mixed ligand Ag(I) complexes

Compound	$\nu_{N-H}$	$\delta_{asym}NH_3^+$	$\nu_{asym}COO^-$	$\delta_{sym}NH_3^+$	$\nu_{sym}COO^-$	$\delta_{COO^-}$	$\nu_{M-O/M-N}$
Glycine(Gly)	3022-2358	1664	1591	1526, 1480	1421	672	---
AgONP.Gly	3499, 3276	1651	1606	1522, 1481	1423	669	565, 527, 505
AgDNP.Gly	3480, 3280	1645	1600	1509, 1475	1425	670	517, 475
AgTNP.Gly	3506, 3238	1651	1612	1562, 1488	1426	669	555, 515
Ag8HQ.Gly	3441, 3250	1639	1596	1503, 1470	1425	669	570, 501, 476
Ag1N2N.Gly	3429	1640	1612	1518, 1473	1430	670	560, 500

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  $80^\circ C$  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  $100^\circ C$ .

#### 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 glycine. The mixture was refluxed on magnetic hot plate with constant stirring at  $70-80^\circ C$  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  $100^\circ C$ .

## RESULTS & DISCUSSION

**S**ome physical properties of the second ligand (Gly) and the mixed ligand complexes (ML.HL') obtained are listed in Table-1.

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 [9] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (7.1-10.5) of molar conductance of the compounds indicate them to be non-electrolyte.

**Infrared Spectra :** Infrared measurements for compounds were made between  $4000-450 \text{ cm}^{-1}$  in KBr disc with the help of FTIR spectrophotometer, Shimadzu 8201 PC. Pertinent infrared spectral data for these compounds are shown in Table – 2.

The broad, strong  $^+\text{NH}_3$  stretching band in the region  $3022-2358 \text{ cm}^{-1}$  observed in the ligand. Multiple combination and overtone bands extend the absorption to about  $2000 \text{ cm}^{-1}$ . This overtone regions usually contains a prominent band near  $2300-2200 \text{ cm}^{-1}$  assigned to a combination of asymmetrical  $^+\text{NH}_3$  bending vibration and the torsional oscillation of  $^+\text{NH}_3$  group. Above observation is due to free glycine exists in zwitter ion ( $^+\text{NH}_3 - \text{CH}_2\text{COO}^-$ ) form<sup>10</sup>.

In the spectra of the mixed ligand complexes, two medium or weak absorption bands: one in the region  $3506-3429 \text{ cm}^{-1}$  and the other in the region  $3280-3238 \text{ cm}^{-1}$  are observed. These bands represent respectively, the free asymmetrical and symmetrical N–H stretching modes [11]. This observation is probably inversion of zwitter ion form into original form after the formation of mixed ligand complexes.

The strong band at  $1421 \text{ cm}^{-1}$  in the spectra of ligand is in all probably due to the symmetric  $\text{cm}^{-1}$  stretching vibration. In the mixed ligand complexes, the broad appear in the region  $1430-1423 \text{ cm}^{-1}$ . The shifting of the band upto  $9 \text{ cm}^{-1}$ , suggest the participation of oxygen atom of  $-\text{COOH}$  group. Further asymmetric  $\text{COO}^-$  stretching frequency appears at  $1591 \text{ cm}^{-1}$  found that the carboxylic oxygen in the ligand and in all the mixed ligand complexes the bands appear in the region  $1612-1596 \text{ cm}^{-1}$ . The shifting of the band by  $5-21 \text{ cm}^{-1}$  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.

The strong band at  $672 \text{ cm}^{-1}$  in the ligand of the ligand may be due to  $\text{COO}^-$  bending vibration. In the mixed ligand complexes this band appears in the region of  $670-669 \text{ cm}^{-1}$ . 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 spectra of the ligand appears at  $1664 \text{ cm}^{-1}$ . In the mixed ligand complexes this band appears in the region  $1651-1639 \text{ cm}^{-1}$ . The fairly strong symmetrical ( $^+\text{NH}_3$ ) N–H bending bands in the spectra of ligand appear in the region  $1526-1460 \text{ cm}^{-1}$ . 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  $570 - 527 \text{ cm}^{-1}$  and  $517 - 475 \text{ cm}^{-1}$  are tentatively assigned to M–O and M–N modes [12] respectively. These bands are not present in the ligand. These assignments are based on the assumption [13] that since oxygen atom 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 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 Glycine(Gly)**

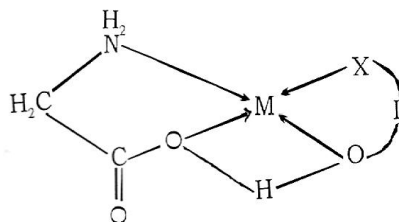
Compound	Diffuse reflectance ( in nm)
AgONP.Gly	242, 398
AgDNP. Gly	235, 350, 378
AgTNP. Gly	229, 315, 341, 378
Ag1N2N. Gly	242, 350, 379
Ag8HQ. Gly	238, 288, 405

The electronic spectra of the mixed ligand complexes show bands at the region 229-341 nm, which indicate  $\pi-\pi^*$  transition in the complexes. The mixed ligand complexes show charge transfer bands in the region 350-405 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 = Ag(I); L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N or SalA; X = O or N

Fig. 1

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