

Mixed Ligand Complexes of Silver(I) Metal Chelates of Some Organic Acids With Derivatives of 5,7-Dinitro-oxine

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A series of some mixed ligand silver(I) complexes having the general formula $ML.HL'$, where $M = Ag(I)$, $L =$ deprotonated *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 8-hydroxyquinoline(oxine), *o*-aminobenzoic acid, salicylic acid or acetylsalicylic acid, $HL' = 5,7$ -dinitro-oxine have been synthesized. The structure of these complexes were confirmed by analytical and spectral data.

Key Words: Mixed ligand complex, Silver(I) metal chelate, 5,7-Dinitro-oxine.

INTRODUCTION

Schraufstatter¹ has investigated the behaviour of 2-methyl oxine towards certain bacteria. Albert *et al.*² pointed out bacteriostatic action of certain drugs arises from their ability to chelate with certain trace metals present in the bacterial cell. 5,7-Dinitro-oxine and 2-methyl-oxine have been extensively investigated their possible use in analytical determination of metal ions³⁻⁵. The complexing ability of derivatives of oxine with alkali metals^{6,7}, alkaline earth metals⁸, *p*-block elements (*viz.*, Sn, Pb)^{9,10} well established. In view of above reported work, it was decided to extend and examine the complexing ability of the derivative *e.g.*, 5,7-dinitro-oxine as second ligand with silver(I) metal salts of organic acids.

EXPERIMENTAL

Preparation of silver(I) metal salts: 1:1 Stoichiometric proportion of organic acid (HL) and sodium hydroxide were taken in a clean and dry conical flask and refluxed in 90 % ethanol on hot plate of magnetic stirrer at 80 °C for about 1 h. The solution was concentrated and cooled, when the coloured sodium salt precipitated out. It was filtered, washed with absolute ethanol and dried in an electric oven at 100 °C.

The sodium salt of organic acid was dissolved in 90 % ethanol and an alcoholic solution of $AgNO_3$ (in molar proportion) then added. The mixture was refluxed on hot plate of magnetic stirrer at 80 °C for 0.5 h, when characteristic coloured precipitate of silver(I) metal chelate was obtained. It was filtered, washed with 90 % ethanol and dried in an electric oven at 100 °C.

Preparation of mixed ligand silver(I) complexes: Silver(I) metal chelate of organic acid and 5,7-dinitro-oxine were taken in 1:1 (mol ratio) in 95 % ethanol. The content was refluxed on hot plate of magnetic stirrer at 80 °C with constant stirring for *ca.* 2-3 h. The solution was concentrated, cooled to give characteristic colour precipitate. It was filtered, washed with 95 % ethanol and dried in an electric oven at 100 °C.

RESULTS AND DISCUSSION

Some physical properties of the ligand (HL') and the new mixed ligand complexes (ML.HL') are listed in Table-1.

TABLE-1

Compound (colour)	m.p. (°C)	Molar conductance	Elemental analysis (%): Found (calcd.)			
			C	H	N	Ag
DN8HQ (Greenish yellow)	200d	–	–	–	–	–
AgONP.DN8HQ (Yellowish green)	> 280	8.7	37.40 (37.42)	1.81 (1.87)	11.52 (11.64)	22.35 (22.45)
AgSalA.DN8HQ (Deep yellow)	290d	9.7	39.95 (40.00)	1.98 (2.08)	8.66 (8.75)	22.37 (23.50)
AgAcSalA.DN8HQ (Deep yellow)	> 280	7.8	41.30 (41.38)	2.23 (2.30)	8.01 (8.05)	20.53 (20.69)
AgOABA.DN8HQ (Yellowish brown)	280d	9.2	40.01 (40.08)	2.22 (2.29)	1.61 (11.69)	22.44 (22.55)

d = decomposition.

The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, partly soluble in ethanol and insoluble in non-polar solvents like benzene, carbon tetrachloride, chloroform, *etc.* The complexes are stable under dry conditions. From Table-1, it is evident that most of complexes undergo a transformation at a higher temperature than the melting point of the ligand indicating their greater stability.

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 low values (7.0-9.7) of molar conductance of the compounds indicate them to be non-electrolyte or covalent nature¹¹.

Infrared spectra of the ligand and mixed ligand complexes of Ag(I) were recorded in KBr phase between 4000-400 cm^{-1} with the help of Bruker-Bertex-70 FTIR spectrophotometer. Selected absorption bands are shown in Table-2.

The spectra of 5,7-dinitro-oxine shows a medium broad absorption band over a wide range of 3650-3250 cm^{-1} . The presence of absorption features in this region points out to the presence of strong intramolecular hydrogen bonding involving hydroxyl hydrogen atom and nitrogen atom of the quinoline ring. The different bands

TABLE-2
KEY IR BANDS (cm^{-1}) OF MIXED LIGAND COMPLEXES OF
Ag(I) WITH 5,7-DINITRO-OXINE

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O/M-N})$
AgOABA.DN8HQ	3200-2600	1642, 1582, 1546	1110	658, 620, 516, 415
AgSalA.DN8HQ	3200-2700	1610, 1576, 1534	1176, 1154, 1112	671, 621, 516, 435
AgAcSalA.DN8HQ	3200-2500	1642, 1582, 1547	1109	658, 619, 515, 439

between 2925-1875 cm^{-1} in the spectra are attributed to C-H stretching vibrations and N---H hydrogen bonding. For weak hydrogen bonding, the bands appear above 2800 cm^{-1} and for strong hydrogen bonding the bands appear between 2800-1800 cm^{-1} . The bands at 1645, 1585 and 1110 cm^{-1} are respectively assigned to NO_2 , C=C/C=N and C-O stretching vibrations of the 5,7-dinitrooxine ligand.

In all the mixed ligand complexes, the stretching -OH vibrations bands appeared as a broad band in the range of 3200-2600 cm^{-1} which clearly indicate the presence of hydrogen bonding as well as the complexation of metal through the hydroxyl oxygen atom. The $-\text{NO}_2$ group frequency in all the mixed ligand complexes remain almost unchanged.

In the IR spectra of these complexes, the 1580 cm^{-1} band of the ligand [assigned to $\nu(\text{C=N})$] has appeared as split bands at *ca.* 1580 and 1546 cm^{-1} . The split band appear due to the presence of C=C, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{N=O}$ group, *etc.* in the various silver salts of organic acids (*i.e.*, first ligand). Shifting and splitting in this region in the stretching frequency of C=N suggest the coordination of the ligand with silver metal through nitrogen atom of quinoline ring. The C-O stretching frequency of ligand at 1110 cm^{-1} has appeared as split bands appear due to the presence of C-O group in the various salts of organic acids (*i.e.*, first ligand).

The band in the region 500-415 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium bands in the region 666-619 cm^{-1} is assigned to M-N band frequency¹². The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of derivative of 8-hydroxy-quinoline to metal in all the complexes.

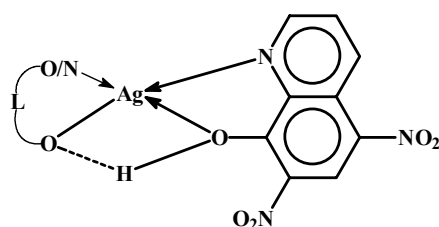
Electronic spectra were recorded on UV-Vis Cintra-10 and Perkin-Elmer Lambda-15 spectrophotometer in methanol. The band observed in electronic spectra of the ligand and complexes are given in Table-3.

TABLE-3
MAJOR DIFFUSE REFLECTANCE BANDS (nm) FOR LIGANDS (DN8HQ) AND
THEIR MIXED LIGAND COMPLEXES OF Ag(I)

Compound	Diffuse reflectance (nm)
5,7-Dinitrooxine (DN8HQ)	280, 404, 653
AgOABA.DN8HQ	220, 240, 335, 400
AgSalA.DN8HQ	210, 280, 400

The sharp intense band of 5,7-dinitro-oxine appears at 280, 404 and 653 nm. The band indicates π - π^* transition as well as charge transfer in aromatic ring. Electronic absorption bands of these complexes are observed in the region 210-280 nm and 335-653 nm which indicate the formation of π - π^* complexes and charge transfer. The shift in position of π - π^* and charge transfer bands of the ligand in the complexes show that there is a π -interaction between metal and ligand orbitals.

Structure and bonding: On the basis of elemental analysis, infrared, electronic spectra and conductivity measurements, the general formula of mixed ligand complexes of Ag(I) comes out to be $ML.HL'$, where $M = Ag(I)$, $L =$ deprotonated ONP, DNP, TNP, OABA, SalA and AcSalA and $HL' = DN8HQ$. Following probable structure for these complexes are given in Fig. 1.



(where L = deprotonated ONP, DNP, TNP, OABA, SalA or AcSalA)

Fig. 1

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