

Mixed ligand complexes of silver (I) metal salts of some organic acids with 1-nitroso-2-naphthol

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ABSTRACT

A series of new mixed ligand complexes of silver(I) metal salts of organic acids such as o-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2,4,6-trinitrophenol(TNP), 8-hydroxyquinoline (8HQ), 2-methyl-8-hydroxyquinoline (Me^{*}hQ), 5,7-dinitro-8-hydroxy-quinoline (DN8HQ), 1-nitroso-2-naphthol (1N2N), 2-nitroso-1-naphthol (2N1N), o-amino-benzoic acid (OABA), o-nitrobenzoic acid (ONBA), salicylic acid (SalA), acetylsalicylic acid (AcSalA) with N and O donor ligand 1-nitroso-2-naphthol have been synthesized and characterized. IR-spectra indicate the presence of hydrogen bonding in these complexes, which may be one of the stabilizing them.

Key words: Silver (I) metal salt, Mixed ligand complex, 1-Nitroso-2-naphthol, Infrared spectra, Electronic absorption spectra.

INTRODUCTION

1-Nitroso-2-naphthol has been extensively used in analytical chemistry¹⁻³. Complexes of 1-nitroso-2-naphthol with alkali metals, alkaline earth metals transition metals as well as rare earth metals are well investigated⁴⁻⁹. The present investigation describes the synthesis and characterization of number mixed ligand complexes of silver(I), having general formula ML₂. HL, where M = Ag(I), L = deprotonated organic acids viz., ONP, DNP, TNP, 8HQ, 1N2N, SalA, OABA etc., HL = 1-nitroso-2-naphthol. Characterization involves elemental analysis, melting point, conductivity measurements, infrared spectra and electronic absorption spectra.

EXPERIMENTAL

o-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 5, 7-dinitro-8-hydroxyquinoline, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, o-aminobenzoic acid, o-nitrobenzoic acid, salicylic acid and acetylsalicylic acid of AnalaR quality were used.

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 absolute ethanol on hot plate of magnetic stirrer at 80°C for about one hour. 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.

Again sodium salt of organic acid was dissolved in 90% ethanol and an alcoholic solution of AgNO₃ (in molar proportion) then added. The mixture was refluxed on hot plate of magnetic stirrer at 80°C about half an hour, when characteristic colour 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

0.001 mole of silver (I) salt of organic acid dissolved in 25 ml 95% ethanol in clean and dry conical flask and 0.173g (0.001 mole) of 1-nitroso-2-naphthol was added in slight excess. The mixture was refluxed with constant stirring on hot plate of magnetic stirrer at 75-80°C for about 30 minutes.

The solution was concentrated, cooled to give characteristic colour precipitate. The precipitate was filtered, washed with 95% ethanol and dried in an electric oven at 100°C.

RESULTS AND DISCUSSION

Some physical properties of the second ligand (1-nitroso-2-naphthol) and its mixed ligand complexes obtained are listed in Table 1.

The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, DMF etc., partly soluble in ethanol and insoluble in non polar solvents like benzene, CCl₄, 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

Molar conductance of all the compounds were measured in methanol at 27°C at concentration of 10⁻³ M. The values are given in Table-1. The value of about 35-40 ohm⁻¹cm²mole⁻¹ appears and characteristics of 1:1 electrolyte¹⁰ whereas ideally molar conductance of a neutral compound should be zero. However, significantly low values (7.2 – 11.0) of molar conductance of the compounds indicate them to be non-electrolyte or covalent nature.

Infrared Spectra

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 show in Table 2.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Cond.	Analysis % found/(calcd.)			
				C	H	N	Ag.
1-Nitroso-2-naphthol(1N2N)	Blackish brown	109m.	-	-	-	-	-
AgONP. 1N2N	Deep brown	225t	7.2	44.78 (44.82)	2.52 (2.62)	6.53 (6.68)	25.61 (25.77)
AgDNP. 1N2N	Deep brown	>280	9.0	41.32 (41.38)	2.09 (2.15)	9.00 (9.05)	23.14 (23.27)
AgTNP.1N2N	Greenish Yellow	278d	8.3	37.61 (37.72)	1.01 (1.10)	10.85 (11.07)	21.02 (21.22)
Ag8HQ.1N2N	Deep Brown	200d	7.5	46.89 (48.92)	3.01 (3.12)	6.66 (6.91)	25.72 (25.90)
AgDN8HQ.1N2N	Brown	210t	9.3	44.21 (44.27)	2.09 (2.14)	10.72 (10.87)	20.84 (20.97)
AgMe8HQ.1N2N	Deep Brown	108d	10.0	54.61 (54.67)	3.38 (3.42)	6.21 (6.38)	24.42 (24.60)
Ag1N2N.1N2N	Deep grey	>280	9.8	52.89 (52.98)	2.72 (2.87)	6.15 (6.18)	23.76 (23.84)
Ag2N1N.1N2N	Grey	260t	8.7	52.92 (52.98)	2.81 (2.87)	6.13 (6.18)	23.68 (23.84)
AgOABA.1N2N	Grey	278d	11.0	46.89 (46.92)	2.38 (2.46)	6.66 (6.26)	24.01 (24.16)
AgONBA.1N2N	Light brown	145d	10.5	45.61 (45.64)	2.38 (2.46)	6.18 (6.26)	24.01 (24.16)
AgsalA.1N2N	Brown	>300	9.8	48.78 (48.80)	2.81 (2.87)	3.29 (3.35)	25.62 (25.16)
AgAcSalA.1N2N	Teak brown	290d	7.8	49.46 (49.46)	2.96 (3.04)	8.94 (9.04)	23.32 (23.48)

Table 2:

Compound	ν_{O-H}	$\nu_{N=O}$	ν_{C-O}	$\nu_{M-O/M-N}$
1-nitroso-2-naphthol(aN2N)	3500-1800br	1640	1175	-
AgONP.1N2N	No of variable bands occur between 3500-1800	1605, 1580	1170	615, 580, 487, 445
AgTNP.1N2N'	Variable bands occur between 3500-1800	1623, 1560	1154	613, 537, 425
AgDN8HQ.1N2N	3500-3300br, 3100br	1547	1109	616, 530, 425
AgMe8HQ.1N2N	Variable band occur between 3500-1800	1610, 1569	1196	610, 570, 465, 448
AgSalA.1N2Nl	2700br	1615, 1590	1101	617, 543, 504, 470, 425
AgAcSalA.1N2N	No of variable bands occur between 3500-1800	1625, 1535	1112	651, 581, 488

Mixed ligand complexes of 1-nitroso-2-naphthol show multiple medium strong absorption bands over a wide range 3500 – 1800 cm^{-1} . The observed absorption features in this region point to the presence of strong hydrogen bonding.

The sharp band at 1640 cm^{-1} , possibly N=O frequency of 1-nitroso-2-naphthol, has been found to be metal sensitive in the complexes. This absorption shifts considerably (15-45 cm^{-1}) in all the mixed ligand complexes, suggesting coordination of silver metal ion through N=O group.

The spectra of the ligand, i.e. 1N2N shows characteristic absorption of C-O stretching vibration at 1175 cm^{-1} . In all the mixed ligand complexes except AgMe8HQ.1N2N, this band has shifted towards lower frequency by ~ 5-80 cm^{-1} . In AgMe8Hq.1N2N, this band has shifted to higher frequency at 1196 cm^{-1} . This also supports the coordination of metal through hydroxyl oxygen atom.

The band in the region 516-425 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium bands in the region 651-530 cm^{-1} is assigned to M-N band frequency¹¹. These bands are not present in the corresponding ligand. These assignment are based on the assumption¹² 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

Table 3: Major diffuse reflectance bands (in nm) for mixed ligand complexes of Ag(I) with 1-nitroso-2-naphthol (1N2N)

Compound	Diffuse reflectance (in nm)
1-Nitroso-2-naphthol (1N2N)	210, 256, 362, 653
AgONP.1N2N	220, 360, 545
AgDNP.1N2N	220, 340, 365, 380, 400
AgTNP.1N2N	220, 350, 360
Ag8HQ. 1N2N	230, 375, 500
AgDN8HQ.1N2N	210, 275, 420
AgMe8HQ.1N2N	240, 370
AgOABA.1N2N	220, 290, 360, 510
AgONBA.1N2N	220, 260, 350
AgSalA.1N2N	220, 260, 300, 380

appear at lower frequencies. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of nitroso group to silver metal in all the complexes.

Electronic Spectra

Electronic spectra were recorded on UV-VIS CINTRA-10 and PERKIN-ELMER LAMBDA-15 spectrophotometer in methanol solvent. The band observed in electronic spectra of the ligand and complexes are given in Table 3.

Ligand (1N2N) exhibits sharp intense band at 210nm, 256nm, 362nm and 653 nm. These bands indicate π - π^* transition as well as charge transfer in aromatic ring.

Electronic absorption band of these complexes are observed in the region 220-260 nm and 275-340 nm which indicate the formation of π - π^* complexes.

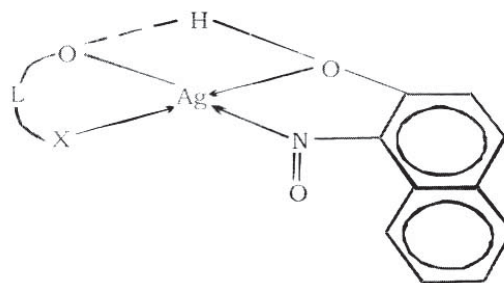
The electronic spectra of mixed ligand complexes show a charge transfer band in the region 350 -545 nm.

The shift in position of δ - δ^* and charge transfer bands of the ligand in the complexes show that there is a δ -interaction between metal and ligand orbital.

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_2HL' , where $M = Ag(I)$, $L =$ deprotonated ONP, DNP, TNP, 8HQ, DN8HQ, Me8HQ, OABA, ONBA, 2N1N, 1N2N, SalA, AcSalA and $HL' = 1$ -nitroso-2-naphthol (1N2N).

Their IR spectra suggested the coordination of the ligand (1N2N) with Ag(I) through the nitrogen atom of nitroso ($N=O$) group and oxygen atom of $-OH$ (phenolic) group. This leads to the following probable structure for these complexes (Fig. 1).



(Where L = deprotonated ONP, DNP, TNP, 8HQ, DN8HQ, Me8HQ, OABA, ONBA, 2N1N, 1N2N, SalA, AcSalA; X = O or N)

Fig.1:

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