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SILVER(I) COMPLEXES OF ANTHRANILIC ACID, *N*-PHENYLANTHRANILIC ACID, 1-NITROSO-2-NAPHTHOL AND 2-NITROSO-1-NAPHTHOL

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ABSTRACT. Silver(I) complexes of anthranilic acid, *N*-phenyl anthranilic acid, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol have been synthesized from $AgNO_3$ with > 90 % yields. The physical properties of the complexes have been studied. The solid complexes have been found to be non-conductors. The complexes were found to be free from nitrate ion with the stoichiometry AgL (where L = deprotonated ligand). The complexes have been characterized by partial elemental analysis, electronic, infrared, and nuclear magnetic resonance spectroscopy.

INTRODUCTION

Several complexes of silver(I) with different ligands have been synthesized and characterized, and their applications have been studied [1-14]. Many silver(I) complexes are of biological significance and have shown great potential as chemical disinfectants. In recent investigations silver(I) complexes of norfloxacin [3] and sulfadiazine [9] are found to be antibacterial and antifungal drugs. Silver(I) complexes of phosphino-hydrocarbons have shown significant cytotoxicity and are found to be tumor cell growth inhibitors [1]. Silver(I) complex of diphenyldithiocarbamate, is used as liquid membrane in ion selective electrode [14]. Therefore, it is worth synthesizing new silver complexes which may find important applications.

A large number of metal ion complexes of anthranilic acid and *N*-phenylanthranilic acid have been reported in the literature [15-18]. Some metal ion complexes of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol have also been reported [17,19-21]. The literature survey revealed that there is no report on the synthesis and characterization of silver(I) complexes of anthranilic acid, *N*-phenylanthranilic acid, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol. Hence silver(I) complexes of anthranilic acid, *N*-phenylanthranilic acid, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol have been synthesized and characterized in the present investigation.

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EXPERIMENTAL

Synthesis of silver(I)-anthranilic acid and silver(I)-N-phenylanthranilic acid complexes. Anthranilic acid (2.06 g, 15 mmol) and *N*-phenylanthranilic acid (3.20 g, 15 mmol) were dissolved or suspended in 10 mL of distilled water. The pH of the suspensions were brought to 6.8 and 10, respectively, with 2 M sodium hydroxide solution to get clear solutions. The solutions were heated to 70°. The solutions were added drop by drop to 7.5 mL of 2 M silver nitrate (15 mmol) solutions, respectively. The white precipitates obtained were filtered and washed thoroughly with ice water, ethanol, and diethyl ether, respectively. The precipitates were dried at room temperature in a light protected desiccator. The yields were > 90 %.

Synthesis of silver(I)-1-nitroso-2-naphthol and silver(I)-2-nitroso-1-naphthol complexes. 1-Nitroso-2-naphthol and 2-nitroso-1-naphthol (3.11 g, 18 mmol each) were suspended in 15 mL of distilled water. The pH of the suspensions were brought to 11 with 2 M sodium hydroxide solution to get clear solutions. The solutions were added drop by drop to 9.0 mL of 2 M silver nitrate (18 mmol) solutions, respectively. The brown precipitates obtained were filtered and washed thoroughly with water and diethyl ether, respectively. The precipitates were dried at room temperature in a light protected desiccator. The yields were > 90 %.

Analytical methods. The nitrogen contents of the silver(I) complexes were determined by the Kjeldahl method [22]. The complexes were decomposed with dilute nitric acid and the silver contents of the complexes were determined volumetrically [22].

Physical measurements. The visible electronic spectra of the ligands and their silver(I) complexes were recorded in DMSO solution on a Beckman Model 24 UV-Visible spectrophotometer in the spectral region of 700-350 nm. The infrared spectra of the ligands and the silver(I) complexes were recorded as solids (KBr discs) in the spectral range 4000-200 cm^{-1} on a PYE UNICAM SP3-300 Infrared spectrophotometer. The ^1H NMR spectra of the ligands and their silver(I) complexes were recorded in DMSO-d_6 solution at 90 MHz on a JOEL FX 90Q FT NMR spectrometer. The solid conductivities of the silver(I) complexes were measured as pellets pressed at a pressure of 6 MPa on a Philips PM2517E multimeter.

RESULTS AND DISCUSSIONS

Physical properties of silver(I) complexes. The solubility of the silver(I) complexes were examined in common organic solvents. The complexes were found to be insoluble in most of the common organic solvents such as ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, benzene, toluene, and dimethyl formamide. However, the complexes were found to be soluble in dimethyl sulphoxide. The complexes decomposed before melting. The physical properties of the complexes are summarized in Table 1.

Elemental analysis. The results of the partial elemental analysis are given in Table 2. These results clearly indicate the formation of complexes with the stoichiometry AgL (where L = deprotonated ligand). The absence of nitrate ion in the complexes was further confirmed by the ring test [23].

Table 1. Physical properties of silver(I) complexes.

Complex	Formula	Color	Yield (%)	Solubility in DMSO	Decomposition Temperature (°C)
Silver(I)-anthranilic acid	$Ag(C_7H_6NO_2)$	white	96	soluble	191
Silver(I)-*N*-phenylanthranilic acid	$Ag(C_{13}H_{10}NO_2)$	white	93	soluble	172
Silver(I)-1-nitroso-2-naphthol	$Ag(C_{10}H_6NO_2)$	brown	94	soluble	152
Silver(I)-2-nitroso-1-naphthol	$Ag(C_{10}H_6NO_2)$	dark brown	90	soluble	155

Table 2. Elemental analyses and electronic spectra of silver(I) complexes.

Complex		Silver (%)		Nitrogen (%)		λ_{max}
Name	Formula	Calculated	Found	Calculated	Found	nm
Silver(I)-anthranilic acid	$Ag(C_7H_6NO_2)$	44.20	43.76	5.73	5.66	460
Silver(I)-N-phenylanthranilic acid	$Ag(C_{13}H_{10}NO_2)$	33.69	33.08	4.37	4.28	450
Silver(I)-1-nitroso-2-naphthol	$Ag(C_{10}H_6NO_2)$	38.52	37.84	4.99	4.88	417
Silver(I)-2-nitroso-1-naphthol	$Ag(C_{10}H_6NO_2)$	38.52	37.42	4.99	4.86	447

Visible electronic spectra of the ligands and their silver(I) complexes. The spectra of all the four ligands did not show absorption maximum in the visible region. The spectra of silver(I) complexes of anthranilic acid and *N*-phenylanthranilic acid showed one broad absorption band around 460 and 450 nm, respectively, and that of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol showed one (relatively narrow) absorption band around 417 and 447 nm, respectively (Table 2). The absorption bands in the silver(I) complexes are most probably associated with the π-π^* electronic transition in the coordinated ligand molecules.

Infrared spectra of the ligands and their silver(I) complexes. The most significant infrared spectral data of the ligands and their silver(I) complexes are summarized in Table 3. The IR spectra of the silver(I) complexes were found to be different from that of their ligands and showed either a shift or disappearance of some characteristic frequencies and appearance of some new frequencies. The assignment of absorption bands in the IR spectra of the ligands and the silver(I) complexes have been made on the basis of the similar assignment in the organic compounds [24-26] and silver(I) complexes with other ligands [10,11,27-31] reported in the literature.

Ag(I)-anthranilic acid complex. The sharp and medium intensity bands at 3480 and 3370 cm^{-1} (due to N-H strechings in the ligand) disappeared in the spectrum of the complex. Instead a broad band between 3600-3000 cm^{-1} with maxima around 3420 and 3300 cm^{-1} due to N-H stretchings of amine salt appeared. This suggest that the NH_2 group is involved in coordination through its nitrogen atom. The broad band in the region 3100-2400 cm^{-1} with maxima around 3000 and 2600 cm^{-1} (due to O-H stretching in the ligand) also disappeared in the spectrum of the complex. The band at 1660 cm^{-1} (due to C=O stretching of carboxylic acid function in the ligand) disappeared in the spectrum of the complex. Instead a doublet at 1580 and 1380 cm^{-1}, which are characteristic of carboxylate ion, appeared in the spectrum of the complex. This suggest that the COO$^-$ group is involved in coordination through its oxygen atom. The band at 1162 cm^{-1} (due to C-N stretching of aromatic amine in the spectrum of the ligand) shifted to 1148 cm^{-1} in the spectrum of the complex. Further, the bands at 1410 and 920 cm^{-1} (due to O-H deformation and O-H out of plane bending, respectively) disappeared in the spectrum of the complex. These further suggest that both nitrogen (-NH$_2$) and oxygen(-OH) or (O=C-O$^-$) are involved in coordination. The appearance of two new bands at 420 and 390 cm^{-1} in the spectrum of the complex are assigned to Ag-O [28] and Ag-N [10,11,31] stretchings, respectively.

Table 3. Characteristic infrared frequencies (cm^{-1}) of the ligands and their silver(I) complexes.

Ligand and complex	$\nu_{N\text{-}H}$	$\nu_{O\text{-}H}$	$\nu_{C=O}$	$\nu_{N=O}$	ν_{COO^-}	$\delta_{O\text{-}H}$	$\nu_{C\text{-}O}$	$\nu_{C\text{-}N}$	$\delta_{O\text{-}H}$	$\nu_{Ag\text{-}O}$	$\nu_{Ag\text{-}N}$
Anthranilic acid (1) $C_6H_4(NH_2)COOH$	3480 *m* 3370 *m*	3100-2400 *vb* (3000,2600)	1660 *s*	–	–	1410 *s*	1300 *s*	1162 *m*	920 *m*	–	–
Ag-anthranilic acid (2) $Ag(C_6H_4.NH_2.COO)$	3420 *vb* 3300 *vb*	–	–	–	1580 *s* 1380 *s*	–	1310 *s*	1148 *m*	–	420 *w*	390 *w*
N-Phenylanthranilic acid (3) $C_6H_5NHC_6H_4COOH$	3320 *m*	3100-2400 *vb* (3000,2600)	1650 *s*	–	–	1408 *s*	1320 *s*	1160 *s*	900 *m*	–	–
Ag-*N*-phenylanthranilic acid (4) $Ag(C_6H_5NHC_6H_4COO)$	3600- 3000 *vb*	–	–	–	1572 *s* 1378 *s*	–	1285 *s*	1155 *w*	–	525 *w*	418 *w*
1-Nitroso-2-naphthol (5) $C_{10}H_6(NO)OH$	–	–	–	1520 *s*	–	1405 *m*	1215 *m*	1070 *s*	–	–	–
Ag-1-nitroso-2-naphthol (6) $Ag(C_{10}H_6NO.O)$	–	–	–	1280 *s*	–	–	1200 *s*	1080 *m*	–	520 *w*	435 *w*
2-Nitroso-1-naphthol (7) $C_{10}H_6(NO)OH$	–	3400-2800 *vb*	–	1660 *m*	–	1380 *m*	1310 *w*	1110 *m*	–	–	–
Ag-2-nitroso-1-naphthol (8) $Ag(C_{10}H_6NO.O)$	–	–	–	1270 *s*	–	–	1300 *m*	1140 *w*	–	470 *w*	368 *w*

Note. Ring vibrations are not listed. Since they were not affected by the complex formation, they appeared in the spectra of the ligands and complexes without significant shift. *s* = strong, *m* = medium, *w* = weak, *vb* = very broad.

Ag(I)-N-phenylanthranilic acid complex. The band at 3320 cm^{-1} (due to N-H stretching in the ligand) disappeared in the spectrum of the complex. Instead a broad band between 3600-3000 cm^{-1} with maxima around 3420 and 3300 cm^{-1} due to N-H stretching of amine salt appeared. This suggests that the N-H group is involved in coordination through its nitrogen atom. The broad band in the region 3100-2400 cm^{-1} (due to O-H stretching in the ligand) also disappeared in the spectrum of the complex. The band at 1650 cm^{-1} (due to C=O stretching of carboxylic acid function in the ligand) disappeared in the spectrum of the complex. Instead a doublet at 1572 and 1378 cm^{-1}, which are characteristic of carboxylate ion, appeared in the spectrum of the complex. This suggest that the COO$^-$ group is involved in coordination through its oxygen atom. The band at 1160 cm^{-1} (due to C-N stretching of aromatic amine in the spectrum of the ligand) shifted to 1155 cm^{-1} in the spectrum of the complex. Further, the bands at 1408 and 900 cm^{-1} (due to O-H deformation and O-H out of plane bending, respectively) disappeared in the spectrum of the complex. These further suggest that both nitrogen (-NH$_2$) and oxygen (-OH) or (O=C-O$^-$) are involved in coordination. The appearance of two new bands at 525 and 418 cm^{-1} in the spectrum of the complex are assigned to Ag-O [28] and Ag-N [10,11,31] stretchings, respectively.

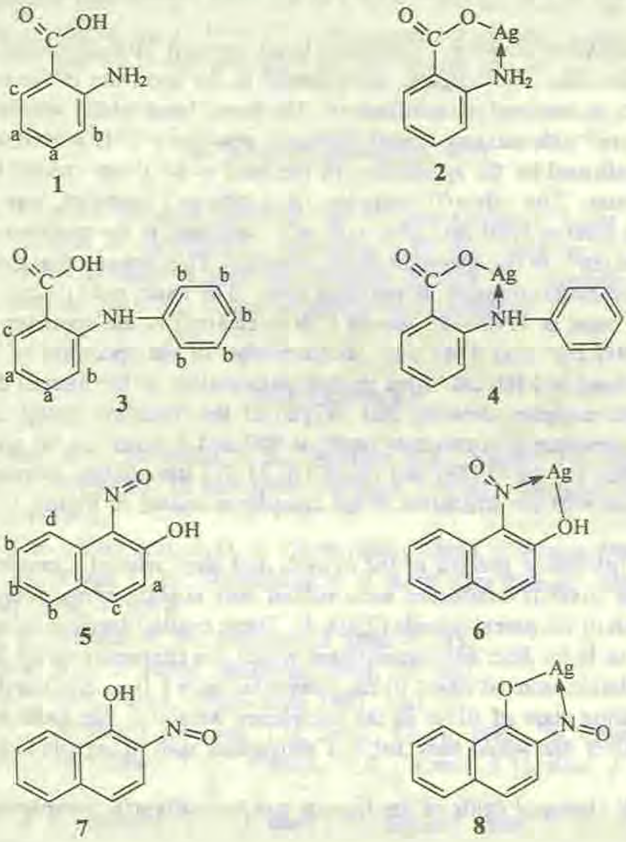

Figure 1. Structures of the ligands and their silver(I) complexes

Ag(I)-1-nitroso-2-naphthol complex. The band due to O-H stretching at 3200-2500 cm^{-1} was not observed in the spectrum of 1-nitroso-2-naphthol. This was also not observed by Amstutz *et al* [32]. The band due to O-H stretching at 3200-2500 cm^{-1} was also absent in the spectrum of the complex. Instead a broad band in the region 3600-3300 cm^{-1} with maxima around 3450 cm^{-1} was observed which is probably due to O-H stretching of absorbed water (this was confirmed by the appearance of the band at 1610 cm^{-1} which is due to O-H deformation of water, silver(I) complex of 1-nitroso-2-naphthol was found to be hygroscopic). The band at 1520 cm^{-1} (due to N=O stretching) in the spectrum of the ligand was shifted to 1280 cm^{-1}, in the spectrum of the complex. This suggest that the N=O group is involved in coordination through its nitrogen atom. Further more, the band at 1405 cm^{-1} (due to O-H deformation of the hydroxyl group in the ligand) disappeared in the spectrum of the complex. This suggest that the oxygen atom of the hydroxyl group is involved in coordination. The band at 1215 cm^{-1} (due to C-O stretching) and the band at 1070 cm^{-1} (due to C-N stretching) in the spectrum of the ligand were shifted to 1200 cm^{-1} and 1080 cm^{-1}, respectively, in the spectrum of the complex. The appearance of two new bands at 520 and 435 cm^{-1} in the spectrum of the complex are assigned to Ag-O [28] and Ag-N [10,11,31] stretchings, respectively.

Ag(I)-2-nitroso-1-naphthol complex. The broad band between 3400-2800 cm^{-1}, due to O-H stretching in the spectrum of the ligand, disappeared in the spectrum of the complex. This suggest that oxygen is involved in coordination. The broad band which was observed in the region 3600-3300 cm^{-1} with maxima around 3450 cm^{-1} was due to O-H stretching of absorbed water (this was confirmed by the appearance of the band at 1610 cm^{-1} which is due to O-H deformation of water. The silver(I) complex of 2-nitroso-1-naphthol was found to be hygroscopic). The band at 1660 cm^{-1} (due to N=O stretching) in the spectrum of the ligand was shifted to 1270 cm^{-1}, in the spectrum of the complex. This suggest that the N=O group is involved in coordination through its nitrogen atom. The band at 1310 cm^{-1} (due to C-O stretching) and the band at 1110 cm^{-1} (due to C-N stretching) in the spectrum of the ligand were shifted to 1300 cm^{-1} and 1140 cm^{-1}, respectively, in the spectrum of the complex. Further more, the band at 1380 cm^{-1} (due to O-H deformation in the ligand) disappeared in the spectrum of the complex showing that oxygen of the hydroxyl group is involved in coordination. The appearance of two new bands at 470 and 360 cm^{-1} in the spectrum of the complex are assigned to Ag-O [28] and Ag-N [10,11,31] stretchings, respectively. These results are consistent with the structures of the complexes shown in Figure 1.

Nuclear magnetic resonance spectra of the ligands and their silver(I) complexes. The ^{1}H NMR signals in the silver(I) complexes were shifted only slightly either down or up fields relative to the signals of the parent ligands (Table 4). These results clearly indicate the absence of unpaired electrons in the four silver complexes which is a characteristic of diamagnetism. Therefore, the oxidation state of silver in the complexes is +1 (i.e. Ag^+) and not +2 (i.e. Ag^{2+}). If the oxidation state of silver in the complexes were +2, the local magnetic field generated by the silver ion would have led to a substantial shift of signals [33].

Table 4. ^{1}H NMR chemical shifts of the ligands and their silver(I) complexes.

Ligand	Chemical shift (δ_{ppm})		
	Assignment*	In the ligand	In the complex
Anthranilic acid	a (2H) b (1H) c (1H)	6.6 7.2 7.7	6.6 7.1 7.8
N-Phenylanthranilic acid	a (1H) b (7H) c (1H)	6.75 7.25 7.90	6.70 7.15 7.97
1-Nitroso-2-naphthol	a (1H) b (3H) c (1H) d (1H)	6.4 7.6 7.8 8.8	6.6 7.55 7.82 9.3

* The assignment of protons in the ligands are shown in Figure 1.

The acid, hydroxyl, and amine protons were not observed.

Silver(I) complex of 2-nitroso-1-naphthol was not sufficiently soluble in DMSO-d_6. Hence its ^{1}H NMR spectrum was not recorded.

Solid conductivities of the complexes. The solid conductivities of the silver(I) complexes were measured as pellets pressed at a pressure of 6 MPa. All the complexes were found to be highly resistive (>100 M ohm). Hence the solid complexes are non-conductors. These results further confirmed that the complexes were neutral species and not ion pairs.

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