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Simple and Mixed Ligand Complexes of Ag(I) Involving Substituted Dithiocarbamic Acids, Triphenylphosphine and the Chelating Phosphine Diphos-A Synthetic and Spectrophotometric Study

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# SIMPLE AND MIXED LIGAND COMPLEXES OF Ag(I) INVOLVING SUBSTITUTED DITHIOCARBAMIC ACIDS, TRIPHENYLPHOSPHINE AND THE CHELATING PHOSPHINE DIPHOS – A SYNTHETIC AND SPECTROPHOTOMETRIC STUDY

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## ABSTRACT

Silver(I), being a soft acid shows a preference for P and S containing ligands. In the present study, simple and mixed ligand complexes of Ag(I) involving mono- and diethanoldithiocarbamates, Ag(MEADTC) and Ag(DEADTC), with triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (diphos) were synthesized. For a comparison, Ag(DEDTC), the diethyl analogue, was also synthesized and the properties studied with IR, UV-visible, TG, DT techniques. The mixed ligand complexes involving PPh<sub>3</sub> and diphos viz., Ag(DEDTC)(PPh<sub>3</sub>)<sub>2</sub>, Ag(DEDTC)(diphos), Ag(DEADTC)(PPh<sub>3</sub>)<sub>2</sub> and Ag(DEADTC)(diphos) (DEDTC<sup>-</sup> = diethyldithiocarbamate anion, DEADTC<sup>-</sup> = diethanoldithiocarbamate anion) showed very low conductivity indicating non-ionic character and ruled out possible ion pair formation such as  $[(PPh_3)_2Ag]^+DEDTC^-$  or  $[(diphos)Ag]^+DEDTC^$ proposed earlier. In addition, the isolated Ag(MEADTC) complex was found to be highly unstable and, hence, an equilibrium study was made and the stability constant was determined to be 6.1  $\pm$  0.2 by the Harvey and Manning method.

## **INTRODUCTION**

Silver(I) ion is known to be a typical class b or soft acid. Therefore, Ag(I) ion shows a preference for P and S containing ligands over N and O containing ligands. In the present study, simple complexes involving Ag(I), mono- and diethanoldithiocarbamic acids were prepared. The simple complexes were then allowed to react with simple and chelating phosphines to give rise to mixed ligand complexes. A spectrophotometric study was also undertaken on the Ag(I) - MEADTC complex by the Harvey - Manning method. Fig. 1 shows the different ligands which were employed in the present study.

### **RESULTS AND DISCUSSION**

The following equations show the methods of preparation of the simple and mixed ligand complexes investigated in the present study:

Ethanol-water AgNO <sub>3</sub> + NaDEDTC	(1)							
$Ag(DEDTC) + 2PPh_3 \xrightarrow{CH_2Cl_2} > [Ag(DEDTC)(PPh_3)_2]$	(2)							
Ag(DEDTC) + diphos	(3)							
DEDTC = diethyldithiocarbamate anion								

The same methods of preparation were employed for the corresponding DEADTC<sup>-</sup> complexes also.

The infrared spectrum of the potassium salt of diethanoldithiocarbamic acid, KDEADTC, shows two characteristic absorptions due to  $\nu$ C-N and  $\nu$ C-S stretching modes at 1450 and 940 cm<sup>-1</sup>, respectively. It is interesting to note that the  $\nu$ C-N bands appear at 1477 and 1465 cm<sup>-1</sup> for sodium diethyldithiocarbamate and sodium piperidinedithiocarbamate, respectively<sup>1</sup>. The presence of two electron-withdrawing

#### SIMPLE AND MIXED LIGAND COMPLEXES OF Ag(I)



Fig. 1.

 $-C_2H_4OH$  groups in KDEADTC contributes little to the thioureide form. However, the infrared spectrum of Ag(DEADTC) shows vC-N at 1470 cm<sup>-1</sup> and vC-S at 960 cm<sup>-1</sup>. The shifts of these absorptions to higher wave number is normal, indicating an effective bonding between the dithiocarbamate and Ag(I) ion. The infrared spectra of the mixed ligand complexes involving phosphines show predominant absorptions due to the aromatic ring around 700 cm<sup>-1</sup>. The absorption bands due to the phosphine ligands obscure the vC-N absorptions of the dithiocarbamate moiety and only a shoulder appears around 1470 cm<sup>-1</sup>.

Both the simple and mixed ligand complexes showed poor solubility in common organic solvents and, hence, electronic spectrum could not be recorded. However, the simple Ag(I)-dithiocarbamate complexes dissolve in pyridine giving yellow coloured solutions.  $AgNO_3$  is known to form a tetrahedral complex,  $[Ag(py)_4]^+$ , which is yellow in colour<sup>2</sup>. In the present study, the complexes in pyridine also show a similar spectrum indicating the decomposition of the dithiocarbamate complexes.

Thermograms of Ag(DEADTC) and Ag(DEDTC) are similar and the decomposition is almost a single step process and is complete at around 600°C. The final product was identified<sup>3</sup> as  $Ag_2S$ . A comparison of the thermograms of PPh<sub>3</sub>, Ag(DEADTC) and [Ag(DEADTC)(PPh<sub>3</sub>)<sub>2</sub>] clearly shows a two-step

decomposition for the mixed ligand complex. The first step is the decomposition of the dithiocarbamate moiety and then the evaporation of PPh<sub>3</sub> leaving the final residue of  $Ag_2S$ . Similarly, the mixed ligand complexes involving diphos also gave  $Ag_2S$  as the final product as confirmed by the X-ray powder pattern. All the thermograms are in keeping with the proposed formulae of the compounds and the percentage values of residue (Table I) agree well for  $Ag_2S$ .

Ag(DEADTC) is insoluble in common solvents. Coordination through S is confirmed by a shift of v C-S frequency to a higher value by 20 cm<sup>-1</sup>. However, the fact that only pyridine dissolves the complex indicates the polymeric nature of the complex. The molar conductivity of the complex was found to be <4.0 for a 0.001 mol dm<sup>-3</sup> solution, which indicated the complex to be non-ionic. The structures of Ag(I) complexes with diethyldithiocarbamate and di-npropyldithiocarbamate were found to be hexameric<sup>4-6</sup> indicating the tendency of these type of complexes to be polymeric in nature. On the basis of poor solubility and similarities to Ag(DEDTC), Ag(DEADTC) should also be polymeric. The stoichiometry of the complexes is also supported by TG studies. Bis(phosphine) (PPh<sub>3</sub>),M(DEDTC) (DEDTC<sup>-</sup> complexes of the general formula diethyldithiocarbamate anion, M = Cu, Ag, Au) were shown to exhibit a stability order:  $Cu < Ag < Au^{7,8}$ . In the present work, Ag(I) is shown to form stable (PPh<sub>3</sub>)<sub>2</sub>Ag(DEADTC) complex and not an ion pair, such as [(PPh<sub>2</sub>)<sub>2</sub>Ag]<sup>+</sup>[(DEADTC)]<sup>\*</sup>, as shown by the low conductivity value (molar conductivity is less than 4.0 for a 0.001 mol dm<sup>-3</sup> solution) in CH<sub>2</sub>Cl<sub>2</sub>. However, earlier studies on  $AgX(PPh_3)$ , (X = Cl, Br) complexes showed them to be polymeric<sup>9</sup>. Based on the limited solubility of AgS<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> complexes and the established polymeric nature of  $AgX(PPh_3)_2$  complexes,<sup>9</sup> the present set of phosphine complexes should also be polymeric in nature. The absence of an ionpair type of interaction leads to a tetrahedrally coordinated AgS<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> species (Fig. 2) as observed earlier<sup>10,11</sup>, though the two Ag-S bonds must be quite weak.



Fig. 2. Coordination Environment Around Ag(I) in (PPh<sub>3</sub>)<sub>2</sub>Ag(DEADTC). S and S' are from two different dithiocarbamate units indicating the polymeric nature.

Similar tetrahedral coordination in  $[Ag(py)_4]^+$  is well established<sup>2</sup>. However, in the present study single crystals could not be obtained because of the solubility constraint and hence complete information on the structure is not available.

#### Spectrophotometric Study

Stability of Ag(I)-(MEADTC) Complex in 50:50 Ethanol-Water. The interaction ratio of Ag(I)-MEADTC was found to be 1:1 by Job's continuous variation plot. Equimolar concentrations of Ag(I) and MEADTC were taken in different ratios to the same total concentration of 5 X 10<sup>-4</sup> M. The optical density (O.D.) was measured at  $\lambda = 450$  nm and the maximum O.D. value of 0.525 was observed for the 1:1 ratio of metal to ligand.

The formation constant of the Ag(I)-MEADTC complex was also determined by the Harvey-Manning<sup>12</sup> method. In the present study, the concentration of Ag(I) was kept constant and the ligand concentration was varied. The O.D's were measured for different mole ratios of the ligands to metal at  $\lambda = 450$  nm. A plot of mole ratio versus O.D. showed a break at 1:1 ligand to metal ratio. The stability of the Ag(MEADTC) complex was calculated from the plot. Measurements were made for three different concentrations of metal ions viz., 2 x 10<sup>-4</sup>, 4 x 10<sup>-4</sup>, 8 x 10<sup>-4</sup> M. The average logK value was found to be 6.1 ± 0.2 indicating moderate stability. Fig. 3 shows the mole ratio plot for the Ag(I) concentration of  $4 \times 10^{-4}$ M.

# EXPERIMENTAL

**Preparation of Potassium Salt of Bis(2-hydroxyethyl)dithiocarbamic acid** (KDEADTC). To a mixture of di(hydroxyethyl)amine (9.5 mL, 0.1 mol) and carbon disulphide (6 mL, 0.1 mol) in 40 mL of ether, potassium hydroxide (5.6 g, 0.1. mol) was added and the solution was cooled to  $5^{\circ}$ C. After 10 minutes a pale yellow solid separated out, which was filtered, washed with ether and dried under vacuum.

# Preparation of (Dialkyldithiocarbamato)silver(I) [Ag(DEDTC), Ag(DEADTC),

**Ag(MEADTC)]**. Silver nitrate (1.6 g, 0.01 mol) in 15 mL of water was added to a solution of the corresponding sodium or potassium salt of the dithiocarbamate (0.01 mol) in 1:1 ethanol - water (20 mL) with continuous stirring. Yellow coloured solids separated out, which were filtered, washed with ethanol and then dried. The complex involving the diethyl analogue was stable but the di(hydroxyethyl)dithiocarbamate complex showed signs of decomposition after about 30 minutes after its separation. This complex was preserved under vacuum. In the case of mono(hydroxyethyl)dithiocarbamic acid, the ligand was prepared fresh by combining equimolar quantities of the amine and carbon disulphide in alcohol and then adding to Ag(I). The complex was highly unstable and could not be separated at all.

# <u>Preparation of Mixed Ligand Complexes Involving Silver(I) Dithiocarbamate</u> and PPh<sub>3</sub>, Diphos. Solid Ag(DEADTC) (2.5 g, 0.01 mol) was treated with a solution of triphenylphosphine (5.2 g, 0.02 mol) in dichloromethane (25 mL). On continuous stirring a clear solution resulted which was filtrated and set aside. Colourless needles separated after 12 hours. The solid was filtered and dried under



Fig. 3. Mole Ratio Plot for the Ag(I) - MEADTC Complex

vacuum. A similar procedure was followed for the preparation of the mixed ligand complexes involving diphos. In the case of [Ag(DEADTC)(diphos)], a dirty white crystalline material resulted. [Ag(DEDTC)(diphos)] was a colourless crystalline material.

All the prepared complexes and the ligands analysed well in agreement with the proposed formulae. The analytical results are presented in Table I.

<u>Physical Measurements</u>. A JASCO IR-700 infrared spectrophotometer was used to record IR spectra. TG studies were made using a Stanton Redcraft instrument at a heating rate of 6°/min.

For the spectrophotometric studies,  $1 \ge 10^{-4}$  M to  $9 \ge 10^{-4}$ M dithiocarbamic acid solutions were prepared by standard methods and the concentration of Ag(I) ion

Compound	Empirical Formula	м.Р °С	Yield %	% TG residue	XC Found (Calcd)	%H Found (Calcd)	XN Found (Calcd)	% Ag Found (Calcd)
(Ag(DEADTC))	C H NO S Ag 5 10 2 2	a	70	43.1	20.6 (20.8)	3.4 (3.5)	4.6 (4.9)	37.0 (37.7)
(Ag(DEADTC)(PPh_3)2)n	C H NO P S Ag	160	70	15.3	60.5 (60.6)	4.8 (4.9)	1.9 (1.7)	13.0 (13.3)
(Ag(DEDTC)(diphos)) n	C_H_NP_S_Ag 31 34 2 2 2	210	64	18.9	56.9 (56.9)	5.2 (5.2)	2.0 (2.1)	16.3 (16.5)
(Ag(DEADTC)(diphos)) n	C H NO P S Ag 31 34 2 2 2	201	60	18.1	59.1 (59.2)	4.8 (4.9)	2.2 (2.0)	13.5 (13.7)

# Table I. Physical and Analytical Data of Complexes

\* decomposes immediately on separation.

was kept constant at 4 x  $10^{-4}$ M. The optical density was measured at 450 nm. The ionic strength was maintained constant with 0.1 M KNO<sub>3</sub>. The interaction ratio was found by Job's continuous variation method and the formation constant was determined by the Harvey-Manning method<sup>12</sup>.

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