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Synthesis and Characterization of Some Copper(I) Complexes Formed by the Insertion of Carbon Disulfide in L_2CuCl ($L = PPh_3$, $AsPh_3$ and $SbPh_3$)

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Insertion reaction of carbon disulfide with *bis*(triphenyl phosphine), *bis*(triphenyl arsine) or *bis*(triphenyl stibine) copper(I) chloride in a mixed solvent of dichloromethane and ethanol results in the formation of new class of copper (I) complexes of the type $[L_2Cu(S_2COEt)]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$). These three new complexes have been characterized by chemical analysis, DTA, TGA and infrared spectroscopic method. The molar conductances of these complexes are measured in dichloromethane (10^{-3} M) at room temperature.

Keywords: Carbon disulphide, Insertion, Copper complexes, Ligand, Coordination compound.

INTRODUCTION

Insertion reactions are of profound interest because of their major role in synthetic chemistry. A number of insertion reactions show promising importance in catalytic system involving transition metal-carbon bond. As an unsaturated electrophile and potentially a most abundant source of C_1 chemistry, carbon disulphide has proved to be a significant tool for insertion reactions of transition metal complexes [1], leading to a new class of compounds, often called organometalllic compound. Carbon disulfide has rather versatile coordination chemistry with a number of bonding modes to metal centres. It is widely accepted that CS_2 bonds in η^1-end on, η^2-side on and bridging coordination modes.

Besides, there exist some examples of CS_2 insertion reactions yielding η^3-S_2CR ligand system. Carbon disulfide inserts readily to a transition metal in low valency state. Dong *et al.* [2] have reported insertion reaction of CS_2 into a Cu(I) compound $[(PPh_3)_2CuNO_3]$ in a mixed solvent of CH_2Cl_2 and CH_3OH at room temperature. Copper(I) is found to display wide diversity in structural chemistry, the coordination number ranging from 2 to 6. The Cu(I) complexes with d^{10} configuration provide no optical absorption band. Copper(I) complexes are important in coordination chemistry and catalytic reactions. They are of significant importance in oxygen transfer oxidative addition and homogeneous hydrogenation.

There is an extensive chemistry of Cu(I) complexes with PPh_3 ligand [3]. In modern co-ordination chemistry, PPh_3, $AsPh_3$ and $SbPh_3$ ligands have aroused great attention as π-acceptor ligand. They bind strongly to many transition metals in low oxidation state and are used to stabilize organometallic and hydride derivative of the elements, either in isolated compounds or as intermediate in homogeneous catalytic reaction. Dong *et al.* [2] and Gogoi *et al.* [4] reported the synthesis and X-ray structure of $[(PPh_3)_2CuS_2COMe]$. Similarly, another few reports are available in this regard [5-10]. In particular, the complexes of the type $[L_2CuCl]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) are excellent starting material for the synthesis of new Cu(I) complexes of the type $[L_2Cu(S_2COEt)]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) which are obtained by treating L_2CuCl and with CS_2 in a mixed solvent of CH_2Cl_2 and C_2H_5OH at room temperature.

In this report, we describe the synthesis and characterization of three new Cu(I) complexes of the type $[L_2Cu(S_2COEt)]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) where L act as monodentate ligand and $EtOCS^{2-}$ anion acts as bidentate ligand. A study of their thermal stability as well as spectroscopic properties has been described through this article.

EXPERIMENTAL

All the chemicals used in the synthesis of the complexes were of AR grade (Ranbaxy, India) and used as such. Triphenyl phosphine, triphenyl arsine and triphenyl stibine were of Fluka A. G. made. Carbon disulphide was of E. Merck (India) made.

Synthesis of $[(PPh_3)_2Cu(S_2COEt)]$: The compound $(PPh_3)_2CuCl$ was prepared by treating CuCl (0.5 g, 5.05 mmol) and triphenyl phosphine (2.6 g, 9.9 mmol) in dichloromethane at room temperature. 0.5 g of $(PPh_3)_2CuCl$ (0.8 mmol) was added to a mixture of CH_2Cl_2 (20 mL), CS_2 (1.2 mL) and ethanol (10

TABLE-1
ELEMENTAL ANALYSIS DATA OF THREE COMPLEXES

Compound	Elemental analysis (%): Found (calcd.)			
	Cu	S	C	H
[$(PPh_3)_2Cu(S_2COEt)$]	9.17 (8.96)	8.91 (9.03)	69.65 (71.07)	4.48 (4.93)
[$(AsPh_3)_2Cu(S_2COEt)$]	8.10 (7.97)	8.13 (8.02)	59.77 (58.71)	3.87 (4.39)
[$(SbPh_3)_2Cu(S_2COEt)$]	6.90 (7.11)	7.03 (7.17)	51.91 (52.48)	3.38 (3.92)

mL). The mixture was stirred for 24 h at room temperature. The resulting solution was exposed to air for evaporation at room temperature to 10-15 mL, yellow crystals of [$(PPh_3)_2Cu(S_2COEt)$] was precipitated. It was filtered off, washed with ethanol and dried. It is air stable, yellow crystalline material, insoluble in water, chloroform, ether, slightly soluble in ethanol, toluene and readily soluble in dichloromethane, acetonitrile, dimethyl sulphoxide and benzene.

Synthesis of [$(AsPh_3)_2Cu(S_2COEt)$]: 0.5 g of CuCl (5.05 mmol) was treated with 3.09 g of triphenyl arsine (10.09 mmol) in dichloromethane solvent at room temperature to give $(AsPh_3)_2CuCl$. 0.861 g of $(AsPh_3)_2CuCl$ (1.2 mmol) was added to a mixture of CH_2Cl_2 (20 mL), CS_2 (1.2 mL) and ethanol (10 mL). The mixture was stirred for 24 h at room temperature. When the resulting mixture was exposed to air for evaporation to 10-15 mL, yellowish white crystals of [$(AsPh_3)_2Cu(S_2COEt)$] was precipitated. It was filtered off, washed with ethanol and dried. It is slightly soluble in chloroform, toluene, ethanol, but readily soluble in dichloromethane and dimethyl sulphoxide. It is insoluble in water, benzene and not very stable in air.

Synthesis of [$(SbPh_3)_2Cu(S_2COEt)$]: The compound $(SbPh_3)_2CuCl$ was prepared by adding CuCl (1 g, 10.1 mmol) to triphenyl stibine (7.13 g, 20.1 mmol) in dichloromethane solvent at room temperature. $(SbPh_3)_2CuCl$ (2.578 g, 3.2 mmol) was added to a mixture of CH_2Cl_2 (20 mL), CS_2 (1.2 mL) and ethanol (10 mL). The mixture was stirred for 24 h at room temperature. When the resulting solution was allowed for evaporation to 10-15 mL, yellowish white crystals of [$(SbPh_3)_2Cu(S_2COEt)$] was obtained. It was filtered off, washed with ethanol and dried. It is slightly soluble in chloroform, ethanol *etc.*, but readily soluble in dichloromethane and dimethyl sulphoxide. It is insoluble in water and benzene and not very stable in air.

The IR spectra of these compounds were recorded in a Perkin-Elmer spectrophotometer (Model No. 883) in the Department of Chemistry, Dibrugarh University. The molar conductivity measurement was carried out in 10^{-3} M CH_2Cl_2 solution at 25 °C using a digital conductance bridge, (Model: 180). The melting point of the compounds was determined on an electro thermal apparatus (Model: Raaga). Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of the compounds were performed in Department of Chemistry, Dibrugarh University by using Perkin Elmer DTA-TGA instrument (Model: Pyris Diamond). The chemical analysis of the compounds was expressed in terms of weight percentages of C, H, Cu and S. Copper and sulphur were analyzed as per known procedure. Copper was estimated iodometrically and sulphur was estimated gravimetrically. Carbon and hydrogen were analyzed at Central Drug Research Institute (CDRI), Lucknow.

RESULTS AND DISCUSSION

At room temperature, reaction of CS_2 with the compounds of the type [L_2CuCl] (L = PPh_3, $AsPh_3$, $SbPh_3$) in mixed solvent of dichloromethane and ethanol results in the formation of a new series of the compounds of the type [$L_2Cu(S_2COEt)$] (L = PPh_3, $AsPh_3$, $SbPh_3$). The mechanism of the reaction is attributed to the insertion of CS_2 in the O-H bond of ethanol to give HS_2COEt which in a subsequent reaction with [L_2CuCl] results in a mononuclear copper(I) complex [$L_2Cu(S_2COEt)$]. The reaction can be depicted as:

$$L_2CuCl + CS_2 + EtOH \longrightarrow [L_2Cu(S_2COEt)] + HCl$$

where L = PPh_3, $AsPh_3$ and $SbPh_3$.

Chemical analysis: The data of chemical analysis for the compounds are listed in the Table-1.

From the elemental analysis, it is seen that the compounds give satisfactory C, H, Cu and S analysis. Thus, the chemical analysis agrees well with their formulation. The melting point data shows that the stability of the compounds decreases in the order of the ligands: $PPh_3 > AsPh_3 > SbPh_3$.

The molar conductance data of the compounds in 10^{-3} M CH_2Cl_2 solution show them to be non-electrolyte in the view of established ranges for such compounds. The non-electrolyte behaviour of the compounds confirms their mononuclear nature and co-ordination character of the ligands PPh_3, $AsPh_3$ and $SbPh_3$. The molar conductivity and melting point data are shown in Table-2.

TABLE-2
MOLAR CONDUCTIVITY AND MELTING POINT DATA OF THE THREE COMPLEXES

Compound	Molar conductivity ($S\ mol^{-1}\ cm^2$)	m.p. (°C)
[$(PPh_3)_2Cu(S_2COEt)$]	4.6	155
[$(AsPh_3)_2Cu(S_2COEt)$]	5.4	145
[$(SbPh_3)_2Cu(S_2COEt)$]	3.8	141

An important characteristic of this compound is that they exhibit photoluminescence behaviour at room temperature. When the compounds were irradiated with an ultraviolet radiation source, they exhibit photoluminescence of the following types (Table-3).

TABLE-3
PHOTOLUMINESCENCE DATA OF THREE COMPLEXES

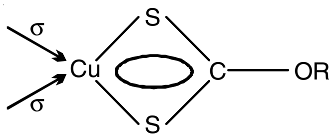
[$(PPh_3)_2Cu(S_2COEt)$]	Light green luminescence in short wave region (intense)
[$(AsPh_3)_2Cu(S_2COEt)$]	Violet luminescence in short wave region (less intense)
[$(SbPh_3)_2Cu(S_2COEt)$]	Red-pink luminescence in long wave region (most intense)

Infrared spectral analysis: The IR absorption spectrum of the compound $[(PPh_3)_2Cu(S_2COEt)]$ consist of a strong peak at 519 cm^{-1} corresponds to Cu-S asymmetric stretching vibration, while a weak IR absorption band at 1095 cm^{-1} is due to C-S stretching vibration. The spectrum also shows a weak absorption band at 3056 cm^{-1} owing to aromatic C-H stretching vibration. The strong peak at 743 cm^{-1} is due to aromatic C-H bending vibration.

Similarly, IR spectrum of the compound $[(AsPh_3)_2Cu(S_2COEt)]$ consist of a strong peak at 489 cm^{-1} which corresponds to Cu-S stretching vibration and a weak peak at 1080 cm^{-1} indicates C-S stretching vibration. The absorption band of 738 cm^{-1} is due to aromatic C-H bending vibration.

In the IR spectrum of the compound $[(SbPh_3)_2Cu(S_2COEt)]$, we observe a weak absorption band at 480 cm^{-1} which corresponds to the Cu-S stretching vibration and another weak absorption band at 1070 cm^{-1} arises from C-S stretching vibration. The weak absorption band at 3051 cm^{-1} is characteristic of aromatic C-H stretching vibration. The spectrum shows a strong band at 750 cm^{-1} owing to aromatic C-H bending vibration.

The IR spectral data shown in Table-4 indicated that the ν(Cu-S) and ν(C-S) decreases on going from PPh_3 to $SbPh_3$ derivatives in agreement with decreasing σ-donating capacity of the series in the order $PPh_3 > AsPh_3 > SbPh_3$. As the σ-donating capacity decreases there is corresponding decrease in the electron delocalization of the chelate ring (as shown below) with consequent decrease in the Cu-S and S-C force constant. Stronger the σ-donation, more prominent will be the partial double bond character of Cu-S and S-C bond.



The above trend is also reflected in the thermal stability of the complexes as obtained from DTA/TGA studies, which indicated the thermal stability order as $PPh_3 > AsPh_3 > SbPh_3$.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA): TGA-DTA studies of $[(PPh_3)_2Cu(S_2COEt)]$ shows (Fig. 1c) that the weight loss started at 160.18 °C and there is a gradual decline till 419.96 °C, indicating a continuous weight loss of the sample. Within the reported temperature range, 83.78 % of weight loss takes place. The first endothermic peak at 160.18 °C in the DTA curve is accompanied by 1.1 % weight loss, which indicates the loss of adsorbed moisture from the compound. The TGA thermogram shows 7 % weight loss at 250 °C, corresponds to an exothermic DTA peak between 225 and 305 °C, confirming the dissociation of $O-C_2H_5$ group (weight loss found = 7 % calculated = 6.345 %). At 419.96 °C, there was a weight loss of 84.4 %, corresponding to removal of two PPh_3 ligands and removal of CS_2 ligand. A weak exothermic peak in the DTA curve at 419.96 °C corroborates this decomposition and indicates the formation of CuO and some other products which is the final product of thermal decomposition of the sample (weight loss found = 84.4 % calculated = 91.03 %).

From TGA-DTA study of $[(AsPh_3)_2Cu(S_2COEt)]$, (Fig. 1b) it is seen that weight loss started at 149.41 °C and continues upto 496.91 °C. between 149.4-496.91 °C, there was a 81.66 % of weight loss. The first endothermic peak at 155 °C in the DTA curve shows 0.5 % weight loss, which corresponds to adsorbed moisture from the compound. The TGA curve shows 6 % weight loss at 230 °C. This corresponds to an exothermic peak between 220-260 °C, confirming the dissociation of $O-C_2H_5$ group (weight loss found = 6 % calculated = 5.6 %). At 496.91 °C, there was a weight loss of 81.77 %, corresponding to the removal of two $AsPh_3$ ligands and removal of CS_2 ligand (weight loss found = 81.77 % calculated = 92.02 %). This weight loss is indicative of formation of CuO and some other products.

Similarly TGA-DTA study of $[(SbPh_3)_2Cu(S_2COEt]$ shows (Fig. 1a) that the weight loss started at 148.84 °C and it continues up to 327.59 °C. Within the reported temperature 82.69 % of weight loss takes place. The first endothermic peak at 165 °C in the DTA curve is accompanied by 1.2 % weight loss, which indicates the loss of adsorbed moisture from the compound.

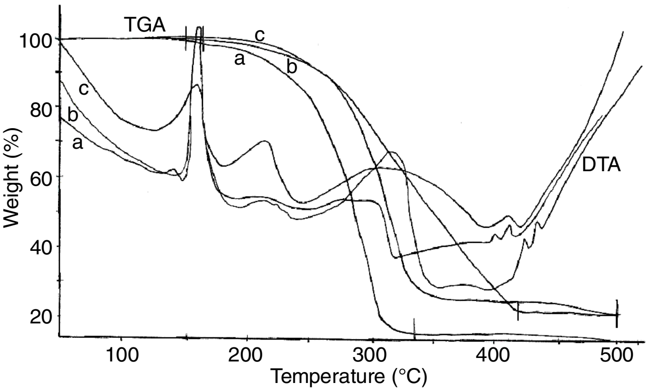


Fig. 1. TGA-DTA curve of (a) $[(SbPh_3)_2Cu(S_2COEt]$ (b) $[(AsPh_3)_2Cu(S_2COEt)]$ (c) $[(PPh_3)_2Cu(S_2COEt)]$

The TGA thermogram shows the weight loss (4.8 %) at 210 °C. This corresponds to an endothermic peak between 190 °C-220 °C, confirming the dissociation of $O-C_2H_5$ group (weight loss found = 4.8 % calculated = 5.04 %). At 327.59 °C, there was a weight loss of 83.3 %, corresponding to the removal of two $SbPh_3$ ligands and removal of CS_2 ligand. A weak exothermic peak in the DTA curve at 327.59 °C corroborates

TABLE-4
IR SPECTRAL DATA OF THE COMPLEXES

Compounds	$[(PPh_3)_2Cu(S_2COEt)]$	$[(AsPh_3)_2Cu(S_2COEt)]$	$[(SbPh_3)_2Cu(S_2COEt)]$	Assignment
Frequency (cm^{-1})	519(s)	489(w)	480(w)	Cu-S asymm. Stretching vibration
	1095(w)	1080(w)	1070(w)	C-S Stretching vibration
	3056(w)	3040(w)	3051(w)	Aromatic C-H Stretching vibration
	743(s)	738(w)	750(s)	Aromatic C-H bending vibration

this decomposition and indicates the formation of CuO and some other products like in earlier cases.

Conclusions

In coordination chemistry, because of their π-acceptor character the ligands PPh_3, $AsPh_3$ and $SbPh_3$ stabilize transition metals in lower oxidation state. Phosphorus, arsenic and antimony have empty *d*-orbital which are of proper symmetry to overlap with the metal orbital. The overlap facilities shift of electron density from the filled metal orbital to the ligand empty *d*-orbital through d_π-d_π back bonding. The π-acidic character of the ligands decreases in the order $PPh_3 > AsPh_3 > SbPh_3$. This order indicate that the smaller P-atom can participate more effectively in d_π-d_π back bonding.

The triaryl derivatives of P, As and Sb are stable with Cu(I) oxidation state (HSAB principle). The triaryls of P, As and Sb possess strong σ-donor capacity which decreases in the order P > As > Sb. The more σ-donor capacity, more stable is Cu(I) oxidation state. The stability of PPh_3, $AsPh_3$ and $SbPh_3$ derivatives follow the trend $PPh_3 > AsPh_3 > SbPh_3$. The PPh_3-derivative is found to be more stable than other two derivatives of As and Sb. It can also be visually noticed that comparatively less stable compounds of As and Sb are easily oxidized to blue colour in air.

The thermal characteristics of PPh_3, $AsPh_3$ and $SbPh_3$ derivatives have been studied by thermal gravimetric analysis and differential thermal analysis and it is found that PPh_3 derivatives is the most stable and stability trend is $PPh_3 > AsPh_3 > SbPh_3$. This trend can be explained from the σ-donor and π-acceptor property of the ligands corroborating the IR spectral results discussed earlier.

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