

Synthesis and Characterization of Four New Complexes of Cu(I), Cu(II), Ir(III) and Pd(II) Formed by CS₂ Insertion in L₂MX_n (L = PPh₃ and Imidazole, X = Cl, n = 2,3)

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Four new complexes [L₂Cu(S₂COC₂H₅)] {L=PPh₃ (**A**), C₃H₄N₂ (**B**)}, [L₂IrCl₂(S₂COC₂H₅)] (L=PPh₃) (**C**) and [L₂Pd(S₂COC₂H₅)] (L=PPh₃) (**D**) have been synthesized by the insertion of CS₂ in L₂CuCl₂, L₃IrCl₃ and L₂PdCl₂, respectively in mixed solvent of dichloromethane and ethanol at room temperature. The complexes have been characterized by FTIR, UV-visible and ESR spectroscopy. All the complexes have been found to be air-stable. Complexes (**A**), (**B**) and (**D**) are distorted square planar while complex (**C**) is of distorted octahedral geometry.

Keywords: Metal complexes, Cu(I,II), Ir(III), Pd(II), Imidazole, Triphenylphosphine.

INTRODUCTION

Carbon disulphide, a versatile ligand with the potential to form complexes with most of the transition metals have the ability to insert into a variety of M-X bonds (X = H, C, N, P, S, Cl or O), of which its insertion into M-O bonds of alkoxides is specific leading to the formation of metal *O*-alkyl thiocarbonates or dithiocarbonates [1]. Insertion of carbon disulphide into M-H and M-P bonds leading to the formation of dithioformate and phosphoniodithiocarboxylate ligands is common [2]. The complexation of transition metals with σ -donors like phosphines, arsine and stibines having empty *d*-orbitals of proper symmetry is also known [3]. Moreover, in recent years, research in the area of carbon rich ligands with appreciable π -electron density are gaining more attention because of their good optoelectronic property which take an active part in tuning the electronic properties and stabilizing the complexes. The antioxidant and biological activities of transition metal compounds with dithio-ligands are also known, which can be synthesized by insertion of CS₂ into transition metal centers containing carbonyls, arsine, phosphine and cyclopentadienyls. CS₂, being an unsaturated electrophile and an abundant source of C₁ chemistry, is a useful reagent for insertion into transition metal complexes in presence of other donor ligands producing new and exciting derivatives. It can bond to metal centres in various modes such

as η^1 -end on, η^2 -bridging and η^2 -side on coordination modes (Fig. 1), which can be distinguished from FTIR spectra and therefore has versatile coordination chemistry which provides an attractive entry into the chemistry of sulphur containing coordinated ligands. Some examples of CS₂ insertion reaction yielding η^3 -S₂CR ligand systems also exist. The insertion of CS₂ generally takes place to a metal in a low valency state [3,4].

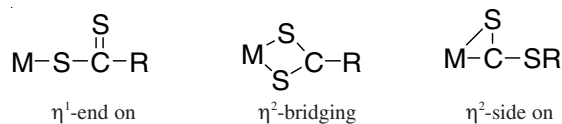


Fig. 1. Various bonding modes of CS₂ to metal centre

Triphenylphosphine (PPh₃) receives wide attention as a ligand due to its good σ -donating and π -accepting nature. It can also bind strongly to transition metals with low oxidation state and can stabilize organometallic and hydride derivative of the elements [5]. Moreover, imidazole derivatives play significant role in medicinal chemistry such as antifungal, antibacterial, anti-inflammatory, analgesic, antitubercular, antidepressant, anticancer, antiviral and antileishmanial activities [6]. It can function as both an acid and as a base and hence is amphoteric. Many studies on insertion of CS₂ have been reported so far using various transition metals complexes such as Ru

[4,7], Cu [5], Mn, Re [8], Ni [9], Pt, Pd [10], Rh, Ir [10-12], Au [13], U [14], *etc.* All these transition metals are remarkable in the sense that they display several oxidation states.

Herein, we reported the synthesis and characterization of four new complexes formed by insertion of CS₂ into CuL₂Cl₂ (L = PPh₃ and imidazole), IrL₃Cl₃ and PdL₂Cl₂ (L = PPh₃) in mixed solvent of dichloromethane and ethanol at room temperature.

EXPERIMENTAL

The chemicals used for the synthesis were mostly of AR grade (Ranbaxy) and procured from Sigma-Aldrich and Fluka. Carbon disulphide (CS₂) was purchased from E. Merck. Cupric chloride pentahydrate (CuCl₂·5H₂O, Fluka A.G. grade), iridium chloride trihydrate (IrCl₃·3H₂O, Arora Mathey Ltd., Kolkata) and palladium chloride dihydrate (PdCl₂·2H₂O, Arora Mathey Ltd. Kolkata) were digested with conc. HCl for several times before use. The complexes were synthesized according to the literature method [4].

The FTIR spectra (4000-250 cm⁻¹) of the complexes were obtained as KBr disc using Shimadzu-Prestige-21 FTIR spectrometer. Electronic spectra (250-1100 nm) of the complexes were obtained by using Shimadzu-Graphicord UV-1700 spectrometer with 1 cm³ quartz cell. ESR spectrum at liquid N₂ temperature in DMSO was recorded at SAIF, IIT Bombay, India on E-112 ESR spectrometer.

Synthesis of [(PPh₃)₂Cu(S₂COC₂H₅)] (A): The digested CuCl₂·5H₂O (4.417 g, 25.91 mmol) was dissolved in a mixture of ethanol and dichloromethane (1:1) to which triphenylphosphine (13.591 g, 51.82 mmol) dissolved in a mixture of ethanol and dichloromethane (1:1) was added dropwise with constant stirring. After 2 h, white precipitate of (PPh₃)₂CuCl₂ was observed. It was filtered off, washed with ethanol, recrystallized with CH₂Cl₂:CHCl₃ (1:1) and then dried. The (PPh₃)₂CuCl₂ (3 g, 4.55 mmol) was added to a mixture of CH₂Cl₂ and ethanol (2:1). CS₂ (1 mL) was added dropwise and the mixture was stirred for more than 2 days at room temperature. The resulting mixture was exposed to air at room temperature for slow evaporation to reduce the volume upto 10-15 mL. White precipitate of complex (PPh₃)₂Cu(S₂COC₂H₅) was formed. It was then filtered off, washed with a mixture of ethanol:water (2:1), recrystallized from CH₂Cl₂:C₂H₅OH (1:1) and then dried. The compound was air-stable, soluble in chloroform and dichloromethane but sparingly soluble in dimethyl sulphoxide. Yield: 73.43 %. Elemental analysis (%) calcd. for [(PPh₃)₂Cu(S₂COC₂H₅)]: C, 66.0410; H, 4.974; S, 9.025; Cu, 8.9527. Found: C, 66.1101; H, 4.0901; S, 9.205; Cu, 9.0012. IR (KBr, ν_{max}, cm⁻¹): 3057 (C-H), 1185 (C-O), 1097 (C-S), 287 (Cu-S), 280 (Cu-P).

Synthesis of [(C₃H₄N₂)₂Cu(S₂COC₂H₅)] (B): The digested CuCl₂·5H₂O (4.092 g, 24 mmol) was dissolved in a mixture of ethanol and dichloromethane (1:1) to which imidazole (3.268 g, 48 mmol) dissolved in 20 mL ethanol was added dropwise with constant stirring. After stirring about 2 h, green precipitate of (C₃H₄N₂)₂CuCl₂ was observed. It was filtered off, washed with ethanol, recrystallized with CH₂Cl₂:CHCl₃ (1:1) and dried. The (C₃H₄N₂)₂CuCl₂ (3.5 g, 12.94 mmol) was added to a mixture of CH₂Cl₂ and ethanol (2:1) followed by the dropwise addition of 1 mL of CS₂ and the resulting mixture was stirred continuously at room temperature for more than 2 days. It was exposed to

air at room temperature for slow evaporation to reduce its volume to 10-15 mL. Brownish green precipitate of [(C₃H₄N₂)₂Cu(S₂COC₂H₅)] was formed which was filtered off, washed with a mixture of C₂H₅OH:H₂O (2:1), recrystallized from CH₂Cl₂:C₂H₅OH (1:1) and then dried. The compound is air-stable, soluble in dimethyl sulphoxide but sparingly soluble in dichloromethane. Yield: 76.92 %. Elemental analysis (%) calcd. for [(C₃H₄N₂)₂Cu(S₂COC₂H₅)]: C, 33.6899; H, 4.0841; N, 17.4617; S, 19.966; Cu, 19.7908. Found: C, 33.5991; H, 4.0798; N, 17.5121; S, 20.11; Cu, 19.8101. IR (KBr, ν_{max}, cm⁻¹): 1499, 1424, 1067 (C-S), 1172, 1258 (C-O), 441 (Cu-N), 310, 326 (Cu-S).

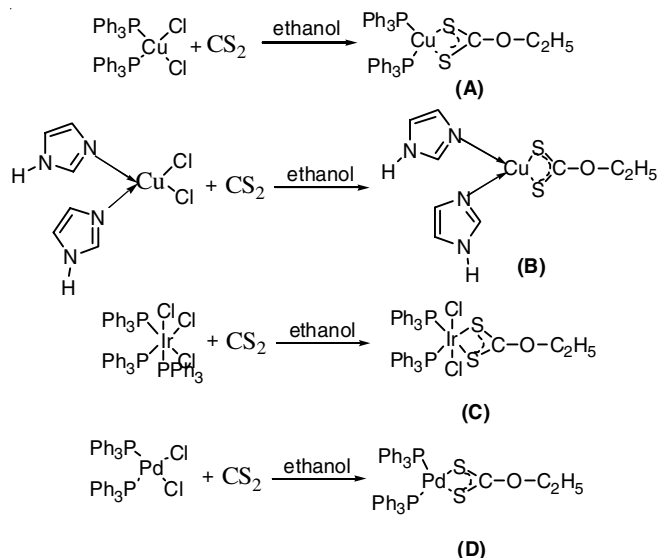
Synthesis of [(PPh₃)₂IrCl₂(S₂COC₂H₅)] (C): The digested IrCl₃·3H₂O (0.571 g, 1.91 mmol) was dissolved in CH₂Cl₂, ethanol and DMSO (3:1:1) to which triphenylphosphine (1.503 g, 5.73 mmol) dissolved in 30 mL dichloromethane was added dropwise with constant stirring. After stirring about 2 h, brown precipitate of (PPh₃)₃IrCl₃ was observed. It was filtered off, washed with ethanol, recrystallized with CH₂Cl₂:CHCl₃ (1:1) and then dried. The (PPh₃)₃IrCl₃ (2 g, 1.84 mmol) was added to a mixture of CH₂Cl₂ and ethanol (2:1) followed by the dropwise addition of 1 mL of CS₂. The resulting mixture was stirred for more than 2 days at room temperature and then exposed to air for slow evaporation at room temperature to reduce the volume upto 10-15 mL. Brown precipitate of [(PPh₃)₂IrCl₂(S₂COC₂H₅)] was formed which was filtered off, washed with a mixture of C₂H₅OH:H₂O (2:1), recrystallized from CH₂Cl₂:C₂H₅OH (1:1) and then dried. The compound is air-stable and soluble in dimethyl sulphoxide. Yield: 56.64 %. Elemental analysis (%) calcd. for [(PPh₃)₂IrCl₂(S₂COC₂H₅)]: C, 51.5364; H, 3.8816; S, 7.05; Ir, 21.1482. Found: C, 51.7435; H, 3.7981; S, 7.15; Ir, 21.0213. IR (KBr, ν_{max}, cm⁻¹): 3060 (C-H), 1480, 1431, 1099 (C-S), 1321 (C-O), 320, 329 (Ir-P), 300 (Ir-S).

Synthesis of [(PPh₃)₂Pd(S₂COC₂H₅)] (D): The digested PdCl₂·2H₂O (0.532g, 3 mmol) was dissolved in a mixture of ethanol and dichloromethane (1:1) to which triphenylphosphine (1.574 g, 6 mmol) dissolved in a mixture of ethanol and dichloromethane (1:1) was added dropwise with constant stirring. After stirring about 2 h, brownish yellow coloured precipitate of (PPh₃)₂PdCl₂ was observed. It was filtered off, washed with ethanol, recrystallized with CH₂Cl₂:CHCl₃ (1:1) and then dried. The (PPh₃)₂PdCl₂ (2 g, 2.849 mmol) was added to a mixture of CH₂Cl₂ and ethanol (2:1). CS₂ (1 mL) was added dropwise and the resulting mixture was stirred for more than 2 days at room temperature. It was then exposed to air at room temperature for slow evaporation to reduce the volume to 10-15 mL. Brownish yellow precipitate of [(PPh₃)₂Pd(S₂COC₂H₅)] was formed which was filtered off, washed with a mixture of ethanol:water (2:1) and recrystallized from dichloromethane:ethanol (1:1) and then dried. The compound is air-stable and soluble in benzene, ethanol, dichloromethane and dimethylsulphoxide. Yield: 73.91 %. Elemental analysis (%) calcd. for [(PPh₃)₂Pd(S₂COC₂H₅)]: C, 62.2728; H, 4.6902; S, 8.51; Pd, 14.1478. Found: C, 62.4102; H, 4.722; S, 8.68; Pd, 14.1321. IR (KBr, ν_{max}, cm⁻¹): 3057 (C-H), 1307 (C-O), 1096 (C-S), 324, 361 (Pd-P), 270 (Pd-S).

RESULTS AND DISCUSSION

At room temperature, reaction of CS₂ with the compounds [(PPh₃)₂CuCl₂] (I), [(C₃H₄N₂)₂CuCl₂] (II), [(PPh₃)₃IrCl₃] (III)

and $[(PPh_3)_2PdCl_2]$ (**IV**) in mixed solvent of dichloromethane and ethanol results in the formation of new compounds $[(PPh_3)_2Cu(S_2COC_2H_5)]$ (**A**), $[(C_3H_4N_2)_2Cu(S_2COC_2H_5)]$ (**B**), $[(PPh_3)_2IrCl_2(S_2COC_2H_5)]$ (**C**) and $[(PPh_3)_2Pd(S_2COC_2H_5)]$ (**D**), respectively as shown in **Scheme-I**.



Scheme-I: Synthetic route of the complexes $[(PPh_3)_2Cu(S_2COC_2H_5)]$ (**A**), $[(C_3H_4N_2)_2Cu(S_2COC_2H_5)]$ (**B**), $[(PPh_3)_2IrCl_2(S_2COC_2H_5)]$ (**C**) and $[(PPh_3)_2Pd(S_2COC_2H_5)]$ (**D**)

The FTIR spectrum of compound (**A**) shows a sharp bands at 1097.54 and 3057.30 cm^{-1} due to stretching frequency of $\nu(C-S)$ and aromatic $\nu(C-H)$ stretching frequency, respectively. A weak band at 1185.31 cm^{-1} due to $\nu(C-O)$ stretching frequency is also observed. Other sharp bands at 747.45 and 287.41 cm^{-1} due to aromatic C-H bending frequency and $\nu(Cu-S)$ stretching frequency, respectively and a weak band at about 280 cm^{-1} is due to $\nu(Cu-P)$ stretching vibration. For compound (**B**), the FTIR spectrum shows sharp peaks at 1067.65, 1499.72, 1424.49 cm^{-1} and a weak peak at 1172.77 cm^{-1} due to $\nu(C-S)$ stretching frequency. The sharp peak at 1258.61 cm^{-1} and a weak peak at 1172.77 cm^{-1} is due to $\nu(C-O)$ stretching frequency. Two sharp peaks were observed at about 310 and 326.95 cm^{-1} due to $\nu(Cu-S)$ stretching vibration, and a medium peak at 441.72 cm^{-1} is due to $\nu(Cu-N)$ stretching vibration. In the compound (**C**), it shows broad peak at 1099.47 cm^{-1} , two sharp peaks at 1431.24 cm^{-1} and 1480.43 cm^{-1} are due to $\nu(C-S)$ stretching vibration. The sharp peak at 3060.20 cm^{-1} is due to aromatic C-H stretching vibration. The broad peak at 1321.30 cm^{-1} is due to $\nu(C-O)$ stretching vibration. A sharp peak at 747.45 cm^{-1} is due to aromatic C-H bending vibration. The sharp peak at 300 cm^{-1} corresponds to $\nu(Ir-S)$ stretching vibration and two sharp peaks at about 320 and 329.84 cm^{-1} are due to $\nu(Ir-P)$ stretching vibration. For compound (**D**), FTIR spectra shows sharp peak at 1096.58 cm^{-1} is due to $\nu(C-S)$ stretching frequency. A sharp peak at 3057.30 cm^{-1} is due to aromatic $\nu(C-H)$ stretching vibration. A broad peak at 1307.79 cm^{-1} is due to $\nu(C-O)$ stretching vibration. The sharp peak at 748.41 cm^{-1} is due to aromatic $\nu(C-H)$ bending vibration. A sharp peak at about 270 cm^{-1} is due to $\nu(Pd-S)$ stretching vibration and two sharp peaks at 324.05 and 361.67 cm^{-1} are due to $\nu(Pd-P)$ stretching vibration.

Since triphenylphosphine is a strong σ -donor and hence more basic than imidazole it stabilizes low oxidation state; therefore, Cu in complex (**A**) is in +1 oxidation state while with imidazole in complex (**B**) is in +2 state. Moreover, ESR spectrum of compound (**B**) at liquid nitrogen temperature shows that compound has characteristic of tetragonal distortion (Fig. 2) showing two g-values ($g_{||} = 2.20$ and $g_{\perp} = 2.04$) with hyperfine coupling constant ($A = 160$ G). Hence, Cu metal in this complex is in +2 state with ground state term symbol is $^2D_{5/2}$. In the electronic spectrum of compound (**C**), the broad peak at around 888 nm shows that Ir metal is in +3 oxidation state while in compound (**D**), the weak peak at around 360 nm of wavelength indicates L $\rightarrow$ M charge transfer transition with Pd in +2 oxidation state [15,16].

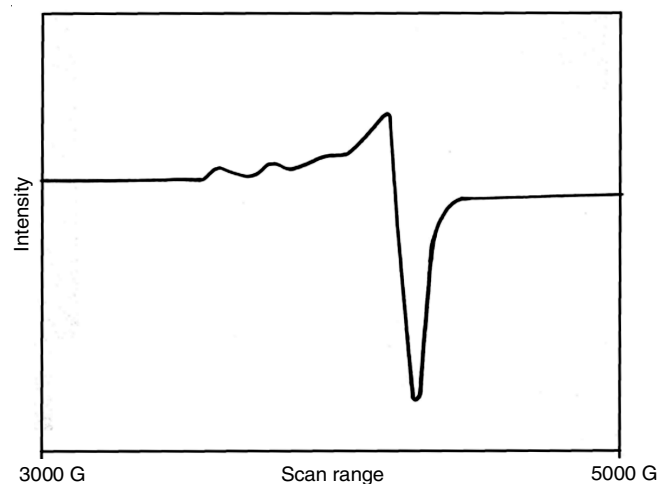
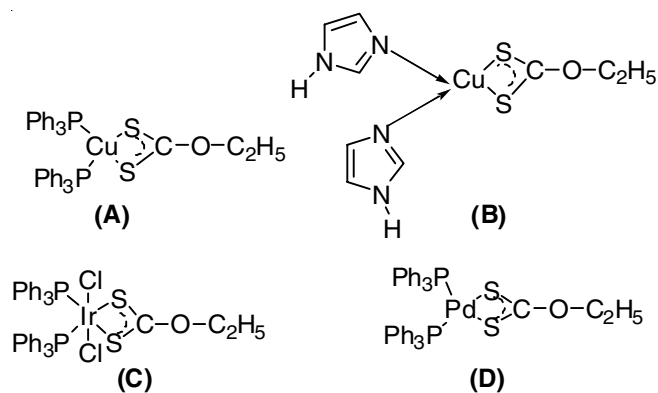


Fig. 2. ESR spectrum of the compound $[(C_3H_4N_2)_2Cu(S_2COC_2H_5)]$ (**B**)

The tentative structures of the complexes have shown below:



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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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