Synthesis, Spectroscopic, Thermogravimetric and Electrochemical Characterization of Triphenylphosphineoxide Complexes of the type [MCl$_x$ (Ph$_3$PO)$_{6-x}$] (M = Cu(II), Co(II), x = 2; M = Fe(III), x = 3)

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Triphenylphosphineoxide (PPh$_3$O) complexes of the type [MCl$_x$(Ph$_3$PO)$_{6-x}$] (**1**, M = Cu(II), x = 2; **2**, M = Co(II), x = 2; **3**, M = Fe (III), x = 3) were synthesized. The complex **1** and **2** were synthesized by the solid state melt down reaction between MCl$_2$.nH$_2$O (M = Cu, n = 2; M = Co, n = 6) and four molar equivalent of PPh$_3$O ligand whereas the complex **3** was synthesized by refluxing anhydrous FeCl$_3$ with four molar equivalents of PPh$_3$O in acetonitile. The complexes were characterized by melting point determination, elemental analysis, conductivity measurement, FAB-Mass, FTIR, UV-Vis, DTA-TGA, cyclic voltammetry (complex **1** and **2**) and ESR analysis. The molecular stoichiometry of the complexes was established on the basis of elemental analysis and the TGA weight loss patterns and the molecular mass were determined by FAB-mass spectra. The complex **1** and **2** show a molecular ion peak at m/z 1245 and at 1241, respectively corresponding to [M-1]$^+$ peak, whereas the complex **3** shows a peak at m/z 961 due to [M-Cl]$^+$. The molecular geometries of the complexes were proposed on the basis of UV-Vis and ESR analysis. The cyclic voltammetric study of the Cu(II) complex, **1**, shows a quasi-reversible redox peak for the Cu(II)/Cu(III) couple whereas the Co(II) complex **2** shows an irreversible peak due to oxidation of Co(II) to Co(III).

Key Words: Phosphine oxide, Transition metal complex, Spectroscopic, DTA-TGA and ESR analysis.

INTRODUCTION

The coordination chemistry of tertiaryphosphines, in particular, triphenylphosphine, is well established because of the strong σ-donor as well as π-acceptor capacities of the phosphorous atom to form strong metal-phosphorous linkage[1]. Till date, several thousands of such phosphine complexes were reported, with almost all transition metals. The chemistry of these phosphines also gained much attention because some of the phosphine complexes (particularly platinum metal complexes) were found to be successful homogeneous catalyst for a range of reactions like hydrogenation,

carbonylation, hydroformylation reaction, *etc*. On contrary, complexes with phosphineoxides, a class of σ-donor ligand have got comparatively less attention; perhaps due to the lack of π-accepting properties as these ligands form only very weak coordination. Though, a considerable number of such phosphineoxide complexes with different transition metals[2-13] were reported but their numbers in comparison with the tertiaryphosphine complexes are negligible.

In phosphineoxide, the donor oxygen atom being "Hard" in nature prefers to form complexes with hard metal centre, *i.e.* Cr(III), Co(III), Mn(III), Fe(III), *etc.* Nevertheless, there exists some reports[2-4,11-13] on phosphineoxide complexes with some soft metal center *e.g.* Co(II), Ni(II), Ru(II), Rh(I), *etc*. but in majority of the cases the complexes are not stable either in solution or in solid state. Through literature survey it has been found that there are some reports on PPh_3O complexes of Cu(II)[4-7], Co(II)[4,9] and Fe(III)[10]. Surprisingly, most of the Cu(II) and Co(II) complexes reported so far possessing a coordination number four and five, having either a tetrahedral or planner geometry. In contrast, complexes of phosphineoxides with coordination number six with Cu(II) and Co(II) remain unexplored.

In this work, two new six coordinated complexes, $[Cu(PPh_3O)_4Cl_2]$ (**1**) and $[Co(PPh_3O)_4Cl_2]$ (**2**) were synthesized by solid-state melt down reaction between $MCl_2 \cdot nH_2O$ with PPh_3O and another complex, $[FeCl_3(Ph_3PO)_3]$ (**3**), by reacting anhydrous $FeCl_3$ with PPh_3O in acetonitrile solution. It might be interesting to point out that from the environmental point of view, the solid-state method for synthesis of transition metal complexes has got several advantages over solution media *e.g.* easy handling, less pollution, lesser energy requirement, *etc*. All the complexes have been characterized by melting point determination, conductivity measurement, elemental analysis (C, H), FAB-Mass, FTIR, UV-Vis, ESR, DTA-TGA and cyclic voltammetry (complex **1** and **2**).

EXPERIMENTAL

All the solvents used were distilled prior to use. The chemicals used were mainly of analytical grade. Other laboratory chemicals such as PPh_3, H_2O_2, metal salts $MCl_2 \cdot nH_2O$ and anhydrous $FeCl_3$ were purchased from RANKEM chemicals, India and were used without further purification. The ligand PPh_3O was prepared by oxidizing PPh_3 with H_2O_2 by following literature procedure[14]. Melting points of the complexes were determined by Raaga melting point apparatus. Molar conductances were measured in a 10^{-3} M acetonitrile solution at room temperature by using Elico (India) conductivity bridge (type 032). Elemental analysis (C and H) were recorded using Perkin-Elmer 2400 elemental analyzer. The FAB mass spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer/data system using

argon (6 kV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol was used as the matrix. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. FTIR spectra (4000-400 cm^{-1}) were recorded in KBr by using a Perkin Elmer (model-883) spectrophotometer. The UV-Vis spectra of the complexes were recorded both in solid state and in solution (acetonitrile) in the visible region (400-800 nm) on a Shimadzu, Graphicord UV-240 spectrophotometer. DTA-TGA of the complexes were recorded in a Perkin Elmer DTA-TGA instrument (Model: Pyris Diamond) under air at a heating rate of 20 ºC/min. The ESR spectra were recorded in solid state at liquid nitrogen temperature using TCNE as reference at SAIF, IIT Bombay. Cyclic voltammetric study of the complexes **1** and **2** were performed in CH instruments, USA, in acetonitrile solution using Pt as working electrode and Ag/AgCl as the reference electrode with tetrabutylammoniumperchlorate (TBAP) as the supporting electrolyte.
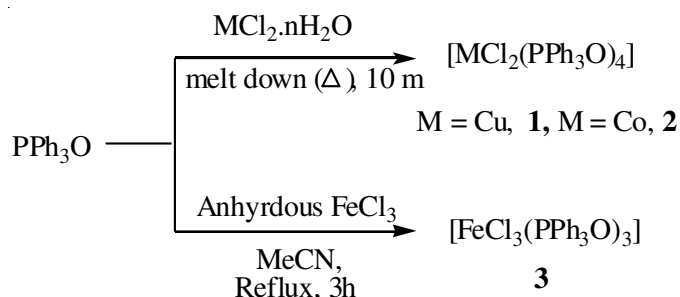
Synthesis of complexes 1 and 2: $MCl_2 \cdot nH_2O$ (0.002 M) and PPh_3O (0.008 M) were taken in a porcelain bowl and grinded to fine powder. The bowl was then heated at 250 ºC for 10 min during which all the metal salt and PPh_3O were melted. It was noticed that while heating, an immediate colour change was observed from deep blue to bright yellow in case of copper and from pink to deep blue in case of cobalt. After completion of each reaction, the mixture was cooled and treated with benzene so that all the unreacted metal salts get precipitated. After evaporating benzene from the solution a bright yellow coloured complex, **1**, was obtained in case of copper and deep blue colour complex, **2** was obtained in case of cobalt. Both the complex **1** and **2** were purified by column chromatography using dichloromethane as elutant. Complex **1**, yield 80 %; m.p. 128 ºC; Complex **2**, yield 90 %; m.p. 220 ºC.

Synthesis of [Fe(Ph₃PO)₃Cl₃]: Anhydrous $FeCl_3$ (0.002 M) was dissolved in 15 mL of acetonitrile and to this a solution of Ph_3PO (0.008 M) in 15 mL of acetonitrile was added. The reaction mixture was refluxed for 3 h during which the colour of the solution changed from brown to deep violet. After evaporating the solvent to dryness, the dark brown solid mass thus obtained was washed with chloroform. The compound was purified by column chromatography using dichloromethane as elutant. Yield 85 %; m.p. 96 ºC.

RESULTS AND DISCUSSION

The phosphineoxide complexes of Cu, **1** and Co, **2** were synthesized by the solid state reaction of $MCl_2 \cdot nH_2O$ with 4 molar equivalent of the Ph_3PO ligand by following a strategy shown in reaction **Scheme-I**. It might be interesting to point out that to the best of our knowledge, the other phosphineoxide complexes of Cu and Co reported so far are all synthesized

in solution media. It is noteworthy to mention here that the solution state reactivity, between the metal chloride and Ph_3PO resulted in the formation of four coordinated tetrahedral complexes $[CuCl_2(Ph_3PO)_2]^5$ and $[CoCl_2(Ph_3PO)_2]^6$. Unfortunately, the solid state reaction does not work for the reaction of $FeCl_3$ with Ph_3PO. However, the Fe complex was synthesized by treating anhydrous $FeCl_3$ with 4 molar equivalents of the ligand. Though, 4 molar equivalents of the ligand were used for the reaction but elemental analysis, DTA-TGA and molecular mass determination (FAB mass), confirms only three molecules of phosphineoxide get involved in coordination with the Fe atom, leading to formation of the complex **3**.

$$PPh_3O \longrightarrow \begin{array}{c} \underset{\text{melt down } (\Delta),\ 10\ m}{\overset{MCl_2.nH_2O}{\longrightarrow}} [MCl_2(PPh_3O)_4] \\ \\ M = Cu,\ \mathbf{1},\ M = Co,\ \mathbf{2} \\ \\ \underset{\substack{MeCN,\\ Reflux,\ 3h}}{\overset{Anhyrdous\ FeCl_3}{\longrightarrow}} [FeCl_3(PPh_3O)_3] \\ \mathbf{3} \end{array}$$

Scheme-I: Synthesis of triphenylphosphineoxide complexes

The elemental analysis, conductivity and FAB mass fragmentation of complexes were shown in the Table-1. In all the complexes, the observed values of the C and H percentage are very close to the calculated value which is in well agreement with the above formulation of the complexes. The molar conductances of the complexes indicate that they are non-ionic

TABLE-1
ELEMENTAL ANALYSIS, MOLAR CONDUCTANCE, FAB-MASS, FTIR AND
VISIBLE SPECTRAL DATA OF THE COMPLEXES **1-3**

Comp.	Mol. Cond. (mho)*	Elem. Anal. (%): Found (Calcd.)		FAB-mass m/z- (% intens.)	Peak assign.	IR ν(PO) (cm^{-1})	Visible spectra	
		C	H				Solid	Sol^n (MeCN)
1	27.2	67.97 (67.34)	4.92 (4.99)	1245 (5 %) 1211 (90 %) 1176 (53 %)	[M-1]$^+$ [M-Cl]$^+$ [M-2Cl]$^+$	1189	420, 848	450
2	38.0	68.17 (67.55)	4.94 (5.00)	1241 (10 %) 1207 (66 %) 1172 (43 %)	[M-1]$^+$ [M-Cl]$^+$ [M-2Cl]$^+$	1152	640, 580, 500	670, 578, 562
3	134.1	63.45 (62.76)	4.62 (4.74)	961 (95 %) 924 (44 %)	[M-Cl]$^+$ [M-2Cl-1]$^+$	1145	492	492

*Recorded in 10^{-3} M MeCN.

as solids. The molar conductance of complex **3** is much higher compared to complex **1** and **2** which might be attributed to the fact that in **3** the metal atom is in +3 state where as in **1** and **2** the metal atoms are in +2 state. The FAB mass spectra of the complex **1** shows a very less intense molecular ion peak at m/z 1245 due to $[M-1]^+$ ion along with other peaks at m/z 1211 and 1176 corresponding to $[M-Cl]^+$ and $[M-2Cl]^+$ ions respectively. Similar to complex **1**, the complex **2** also shows peaks at m/z 1241, 1207 and 1172 due to $[M-1]^+$, $[M-Cl]^+$ and $[M-2Cl]^+$ ions, respectively. Unlike, complex **1** and **2**, the molecular ion peak in complex **3** is absent but the peaks due to $[M-Cl]^+$ and $[M-2Cl-1]^+$ are observed at m/z 961 and 924, respectively.

The FTIR spectra of the complexes show all the characteristics bands of the ligands *e.g.* aromatic -C-H stretching in the region 3050-2980 cm^{-1}, C=C stretching in the region 1480-1440 cm^{-1} *etc.*, in almost at the same position, but the striking feature has been observed in the stretching frequency ν(P-O) bands. The ν(P-O) bands of the complexes **1**, **2** and **3** are observed at 1189, 1152 and 1145 cm^{-1} (Table-1), respectively. Compared to the free ligand ν(P-O) stretching at 1200 cm^{-1} these values are 11, 48 and 55 cm^{-1} lower for copper, cobalt and iron complexes, respectively which indicates coordination of the Ph$_3$PO ligand through oxygen atom. It might be worth to mention here that compared to complex **1** and other reported triphenylphosphine oxide complexes of 1st row transition metals, the ν(P-O) stretching frequencies of complexes **2** and **3** are much higher, which indicates a linear arrangement of the P-O-M unit in those two complexes[6,7].

The electronic absorption spectra are often helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereo chemistries of metal ions in the complexes based on the positions and number of *d-d* transition peaks. The spectral data along with peak assignment of the complexes **1**, **2** and **3** are shown in Table-1. In case of Cu(II) complex **1**, in solid state, a broad band centered around 848 nm was observed which can be attributed to $^2E_g \rightarrow {}^2T_{2g}$ transition. The broadness of the peak may be due to Jahn-Teller effect and consequent lowering of symmetry from octahedral to tetragonally distorted geometry[6]. The bright yellow colour of the complex **1** might be assigned to the ligand to metal charge-transfer (Cl $\rightarrow$ Cu^{2+}) transition occurring[15] at 420 nm. The solution spectra of the copper complex **1** in acetonitrile are quite different from that of the solid state spectra. The band at 420 nm in solid state was shifted to 450 nm in solution which is a characteristic of a charge transfer band. The spectra of both the complexes **2** and **3** are consistent with distorted octahedral geometry. The solid state reflectance spectra of the cobalt complex **2** exhibit three peaks at 640, 580 and 500 nm attributed to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively. However, as expected, the measuring of

the spectra of the same complex in solution shows considerable shifting of band positions (Table-1). The visible spectrum of the Fe(III) complex **3**, in solution and also in solid state exhibits a weakly intense peak at 492 nm assigned to $^6A_1$-($^1E,^4A_1$), ligand field transition in high spin Fe(III) complex[16]. The high-spin nature of the Fe(III) complex was also anticipated from the ligand field strength of the Ph_3PO ligand.

Thermal behaviour of the complexes **1-3** were studied in the temperature range of 40-750 ºC, using a combined thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA). The observed wt. loss was measured from the TGA curve with the help of its 1st derivative (DTG). The thermogram of the Cu complex **1**, shows that weight loss corresponds to the decomposition of the complex in two successive steps. The 1st wt. loss (3.5 %) occurs in the temperature range *ca.* 80-135 ºC is consistent with the loss of two molecules of water (calculated wt. 2.8 %) physically associated with the complex as indicated by the endothermic peak of DTA curve. The major decomposition *i.e.* the 2nd wt. loss starts at *ca.* 227 ºC and continues till *ca.* 518 ºC, with three exothermic inflections observed by the DTA curve and is attributed to the gradual loss of ligand units from the complex. The final residue of 7.48 % corresponds to the remaining weight of CuO (calculated 6.31 %). Such type of thermal decomposition of a Cu(II) complex to CuO was also reported[17]. Like copper complex **1**, the thermogram of the cobalt complex **2** and iron complex **3** shows that decompositions occurs in two steps. In complex **2**, the 1st wt. loss (2.5 %) occurs in the temperature ranges of 70-130 ºC and is consistent with the loss of two molecule of water physically associated with the complex (calculated wt. 2.8 %). It has also been observed that in **2**, the major wt. loss (85.2 %) occurs in the temperature range of 226-582 ºC, which corresponds to the decomposition of the phosphineoxide and chloride from the metal center. The final residue (12.3 %) corresponds to the weight of two molecules of CoO (11.7 %). The thermogram of iron complex **3**, also show a weight loss in the temperature range of 60-130 ºC and 248-570 ºC, indicating loss of water molecule and decomposition of ligand moiety around the metal ion in the complex. The final residue (14.4 %) corresponds to the remaining weight as Fe_2O_3 (calcd. wt. 15.5 %). The DTA-TGA weight loss patterns are in well agreement with the proposed formulation of the complexes. It could be important to note here that the number of water molecule determined from thermogram for all the complexes confirm the data obtained by elemental analysis.

The X band ESR spectrum of the Cu(II), Co(II) and Fe(III) complexes recorded at liquid nitrogen temperature is shown in Fig. 1. The spectrum of **1** (Cu) shows (Fig. 1a) two absorption bands with corresponding $g_\parallel$ and $g_\perp$ value at 2.27 and 2.11, respectively and these g values can be used to evaluate the ground state term of the complex. Since $g_\parallel > g_\perp < 2$, a tetragonally

elongated structure of the complex is proposed with the unpaired electron occupying the dx^2-y^2 orbital giving $^2B_{1g}$ as the ground state[18]. The spectrum of the cobalt complex also shows two absorption bands with corresponding $g_{\parallel}$ and $g_{\perp}$ value at 2.08 and 2.52 indicating distorted octahedral geometry of the complex. The ESR spectrum of the Fe(III) complex shows three absorption bands with three corresponding g values as 3.61, 2.44 and 2.01, respectively. The three unequal g values *i.e.* $g_x \neq g_y \neq g_z$, clearly indicate a rhombic symmetry[19]. The difference between g_{max} and g_{min} is 1.50 and this large spread of g value indicates a high spin nature of the Fe(III) complex[20].
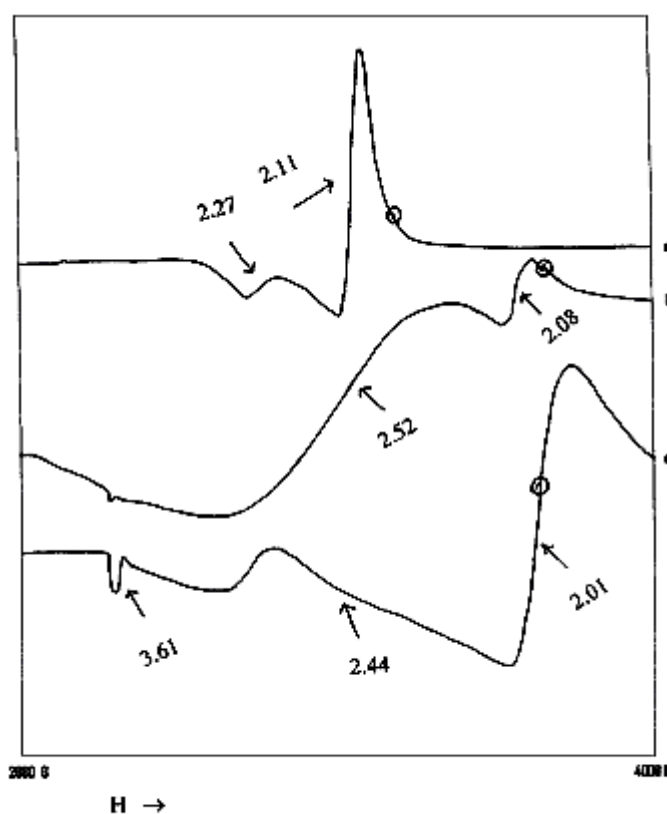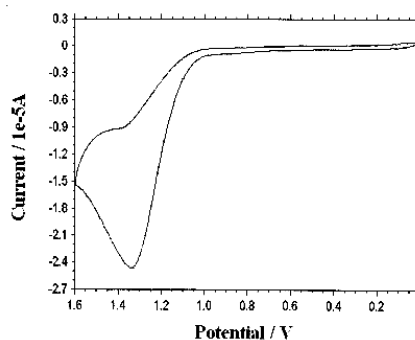

Fig. 1. ESR spectra: (a) complex **1**, (b) complex **2**, (c) complex **3**

The cyclic voltammetric studies of the Cu complex **1** and cobalt complex **2** were recorded in CH_3CN solution using TBAP as the supporting electrolyte. The complex **1** displays a well defined redox process (in the potential range 0-1.6 V) corresponding to the formation of the Cu(II)/Cu(III) couple at Ep_a = 0.498 V and the associated cathodic peak, Ep_c = 0.408 V. The couple is

found to be only quasi-reversible as indicated by the ΔEp value of 88 mV and the ratio of anodic to cathodic peak current ($Ip_a/Ip_c = 1.22$). Such type of electrochemical oxidation of Cu(II) to Cu(III) system was also reported for other Cu(II) complexes[18,21]. The poor reversibility of the complex might be due to the decomposition of the complex in acetonitrile solution in the cyclic voltammetry time scale. The cyclic voltammetric study of the Co(II) complex (in the potential range 0-1.6 V) shows a well defined irreversible oxidation peak at 1.34 V attributed to the oxidation of Co(II) to Co(III). The higher electrochemical irreversibility of the complex **2** over **1** indicates higher stability of the complex **1** over **2** in acetonitrle solution which is consistent with the theoretical stability of the complexes as indicated by hard-soft nature of the metal ligand interaction *i.e.* Cu(II) being relatively harder than Co(II) forms a more stable complex with phosphine oxide.
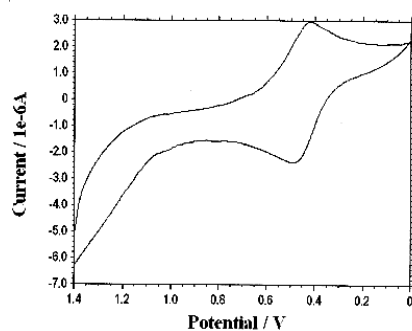
Fig. 2a. CV of complex **1**;   Fig. 2b. CV of complex **2**

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