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# THERMOGRAVIMETRIC, $^{31}$P NMR AND MASS SPECTROMETRIC STUDIES OF Cu(I) AMINOPHOSPHINE COMPLEXES

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**ABSTRACT**

Different Cu(I) halides complexes of two different aminophosphines, *viz*, {Bis (*iso*propyl) amino}(morpholino)(Phenyl) phosphine (L) and Bis (morpholino) (phenyl) phosphine (L') have been reported earlier. Thermogravimetric studies of these metal complexes showed that the metal bound aminophosphine ligand is lost easily on heating, at moderate temperatures. In most cases, stepwise loss of the ligand is observed. Electrospray ionization mass spectroscopy (ESI MS), also confirms the easy loss of aminophosphine ligands. Mass spectra reveal ligand peak was observed with high intensity in all the cases. The isotopic pattern was also observed due to the presence of different isotopes ($^{63}$Cu, $^{65}$Cu, $^{35}$Cl, $^{37}$Cl, $^{79}$Br and $^{81}$Br). A comparison of donor-acceptor behavior of two ligands was also made from their $^{31}$P coordination chemical shifts. Initial results show promise for the use these complexes as precursors for chemical vapor deposition (CVD) for the production of thin metal/metal oxide layers.

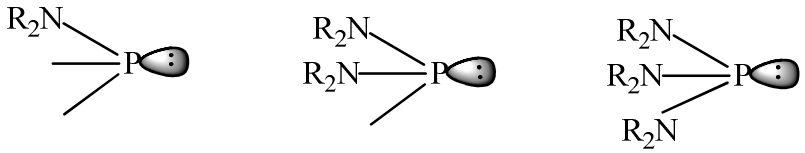
**Keywords:** Aminophosphines, Cu(I) complex, thermogravimetry, mass spectrometry



## INTRODUCTION

Chemistry of tertiary phosphines ($PR_3$, R= alkyl/aryl group) is well documented.[1-3] Phosphines are known to stabilize metal centers in low oxidation state by σ-donation and π-back donation. One of the most attractive features of phosphine ligand is accessibility for tuning their electronic properties and steric profiles by the suitable choice of the substituents on phosphorus. For example, phosphines containing hydrophilic functionality (groups like sulphonate, ammonium, and carboxyl) enhance their solubility in water. This modulation of steric and electronic factors provide the basis for the selection of a particular ligand for catalytic purposes.[4,5] Designing new, modified phosphine ligands have become an art, especially for the creation of highly effective and selective catalytic systems.[6] Apart from homogeneous catalysis, many metal phosphine complexes are known to show anticancer and anti tumor properties.

Aminophosphines are phosphorus (III) compounds with at least one P-N bond. Depending upon the number of amino substituents directly attached to the phosphorus, they can be termed mono, bis or tris aminophosphines (Fig.-1).




Mono(amino)phosphine Bis(amino)phosphine Tris(amino)phosphine

Fig.-1: Structural representation of aminophosphines

Aminophosphines manifests in large structural variety.[7,8] Cyclic, cage and polymeric P-N structures are known[7]. Nitrogen(s) adjacent to the phosphorus, also being potential ligand site(s) make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aminophosphines an interesting class of ligands for developing their coordination chemistry with transition metal substrates. Chemistry of aminophosphines has been well documented.[9] As mentioned earlier, by using suitable amino substituent, it is possible to change steric and electronic profiles of the phosphine ligand which finds application in the field of catalysis.

Coordination chemistry of phosphine with Cu(I) systems are well studied.[10,11] "Soft-Soft" interactions between Cu(I)- phosphine result in the formation of stable complexes of wide structural diversity. Though a variety of coordination number (two to six) are known, tetracoordinate tetrahedral geometry is most common. Many of these complexes are used as new precursors for chemical vapor deposition (CVD) of metallic thin layers.[12-13] Both copper and copper oxide thin films find applications in many areas. Thermal studies of copper(I) aminophosphines will throw more light on the thermal stability of the complexes and the ease of metal/metal oxide thin film production. Earlier we reported the synthesis and characterization of P* chiral aminophosphine and its coordination studies with metal centers and solid state $^{31}P$ NMR spectroscopic studies.[14-16] In this paper we report, the thermogravimetric analysis, $^{31}P$ NMR and mass spectrometric studies of these complexes.

## EXPERIMENTAL

Reactions were carried out under pure and dry nitrogen using standard Schlenk techniques.{Di (*iso*propyl) amino}(morpholino)(Phenyl) phosphine (L) and Bis (morpholino) (phenyl) phosphine (L') complexes of copper(I) were synthesized by literature methods.[13-14] Q-TOF-Mass Spectrometer equipped with a standard electro spray source (Q-TOF micro hybrid quadrupole time of flight mass spectrometer) was used for recording mass spectra. Thermogravimetric analyses were done using Perkin-Elmer TGA-7 thermogravimetric analyzer under an inert atmosphere. $^{31}P$ NMR spectra were recorded in $CDCl_3$ solutions using 85% $H_3PO_4$ as external standard on a JEOL 400 MHz NMR spectrometer.

## RESULTS AND DISCUSSION

Six copper(I) complexes two different aminophosphine, namely {Bis (*iso*-propyl) amino}(morpholino)(Phenyl) phosphine (L) and Bis (morpholino) (phenyl) phosphine (L') were used for the study (Fig.-2).

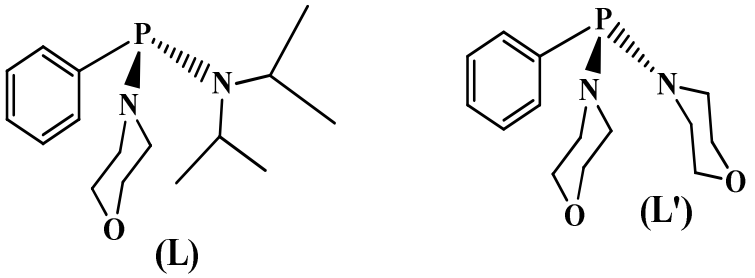



Fig.-2: Structural representation of aminophosphines ligands (L) and (L') used in the study

**Thermogravimetric analysis**

Thermal stability of aminophosphine copper(I) complexes were studied using thermogravimetry. Weight loss and temperature range are given in Table-1. Following observations were made.(i) Most of the copper(I) halide aminophosphine complexes did not show any decomposition below 90 °C (except the loss of solvent molecules in some cases). For example, compound **1** first weight loss (16.6%) at nearly 60°C corresponds to the loss of the solvent molecule dichloro methane (theoretical weight loss, 17.76 %) (Fig.-3). No weight loss responsible for solvent loss were seen for other samples. (ii) Single / multi-step decomposition was observed in different cases. In all the cases, the first significant weight loss corresponds to the loss of aminophosphine ligand. Loss of the ligand was observed around 125-150°C for the complexes except for complex **4.** Differential scanning calorimetric curves (DSC) also show sharp endothermal peaks corresponding to weight loss.

Table-1: Weight loss (observed and calculated) for the TGA profiles of Cu(I) aminophosphine complexes

| S. No. | Compound | Weight loss I | | Weight loss II | | Weight loss III | |
|---|---|---|---|---|---|---|---|
| | | Observed (Calculated) | Temp. (in °C) | Observed (Calculated) | Temp. (in °C) | Observed (Calculated) | Temp. (in °C) |
| 1. | $[CuClL]_2.2CH_2Cl_2$ **(1)** | 16.6 (17.7) | 50-90 | 42.0 (38.2) | 90-120 | 32.7 (30.8) | 120-320 |
| 2. | $[CuBrL]_2$ **(2)** | 34.9 (33.6) | 125-150 | 32.8 (33.6) | 150-280 | --- | --- |
| 3. | $[CuIL]_2$ **(3)** | 35.9 (37.3) | 130-170 | 38.2 (37.3) | 180-290 | --- | --- |
| 4. | $CuCl(L')_2$ **(4)** | 45.3 (42.4) | 120-140 | 43.2 (42.4) | 180-220 | --- | --- |
| 5. | $CuBr(L')_2$ **(5)** | 37.7 (39.8) | 110-140 | 41.2 (39.8) | 160-200 | --- | --- |
| 6. | $CuI(L')_2$ **(6)** | 58.5 (60.6) | 50-500 | --- | --- | --- | --- |

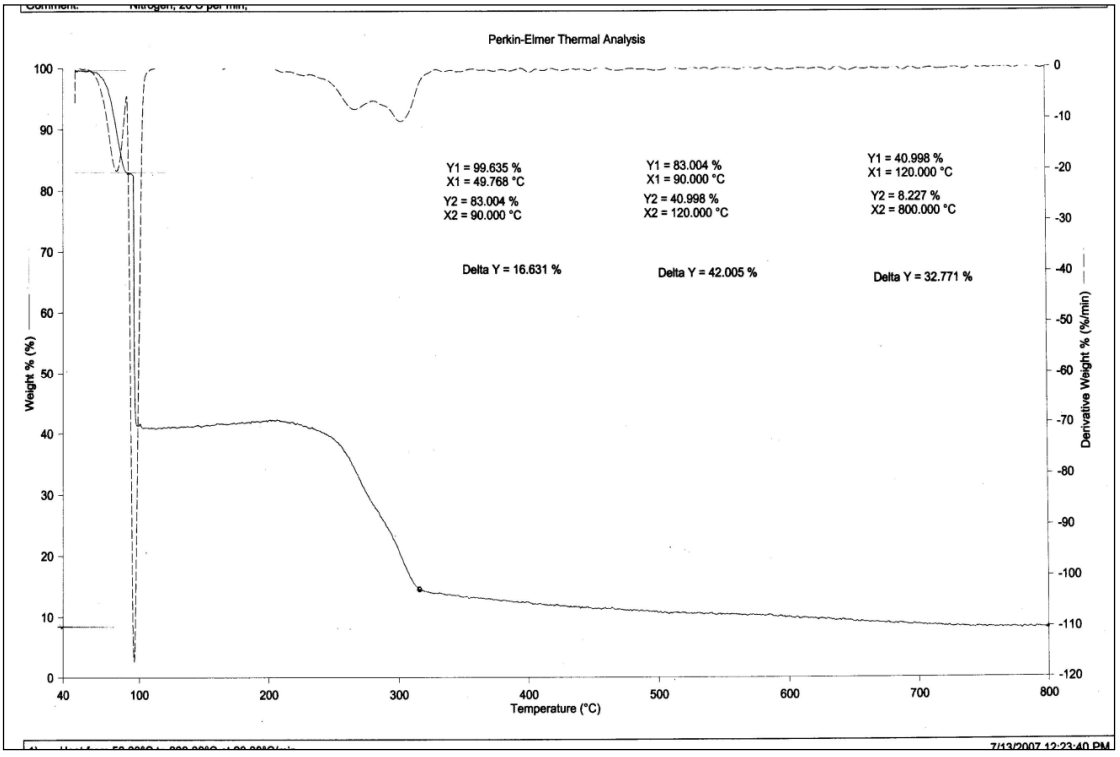



Fig.-3: TGA-DSC plot of $[CuClL]_2.2CH_2Cl_2$ (**1**)

**ESI-Mass spectrometry**

Electrospray ionization technique is a soft ionization technique, where ions are produced by an electrospray under less rigorous conditions and there is very little fragmentation. ESI MS spectra of the complexes gave peaks for molecular ion peaks. Most of the complexes of (L) and (L') showed peaks at 295 and 280 respectively, in varying intensity which corresponds to free aminophosphine ligand. This result is in accordance with thermogravimetric analysis which confirms the easy removal of aminophosphine ligand. Prominent mass spectral fragments observed for the complexes **1**-**6** are given in Table-2.

Possible fragmentation mechanism for dimeric copper(I) complexes (**1**-**3**) is given in the figure. It was observed that a number of fragments were more for theses complexes. In all cases, ligand

aminophosphine peaks are observed from moderate to high intensity (Fig.-4). A peak at 102 is observed in some cases due to the diisopropyl amine. "$Cu_2XL_2$" peaks were more prominent than molecular ion peak. Mass spectra revealed wide isotopic pattern due to the presence of different isotopes ($^{63}Cu$, $^{65}Cu$, $^{35}Cl$, $^{37}Cl$, $^{79}Br$ and $^{81}Br$). For monomeric complexes, molecular ion peak was observed with good intensity. Another prominent peak was "CuXL" obtained by the loss of one aminophosphine ligand. The possible fragmentation pattern for the complexes is given in the Scheme-1 and Scheme-2.

Table-2: Prominent mass spectral fragments of Cu(I) complexes of aminophosphine (L)

| S. No. | Copper(I) complex | L | CuXL | $Cu_2X_2L$ | $CuL_2$ | $CuXL_2$ | $Cu_2XL$ | $Cu_2XL_2$ |
|---|---|---|---|---|---|---|---|---|
| 1. | $[CuCl(L)]_2$ (**1**) | 295 (93) | ----- | 494(32), 496(26) | 651(30), 653(10) | ----- | | 749(60), 751(84), 753(18) |
| 2. | $[CuBr(L)]_2$ (**2**) | 295 (70) | 434(42), 436(26) | ----- | ----- | | 499(100), 501(66), 503(38) | 793(32), 795(40), 797(28) |
| 3. | $[CuI(L)]_2$ (**3**) | 295 (66) | ----- | ----- | ----- | | 549(100), 551(62) | 843(56), 845(44) |
| 4. | $CuCl(L')_2$ (**4**) | 281 (68) | 378(86), 380(100), 382(74) | ----- | ----- | 658(42), 660(48), 662(38) | ----- | ----- |
| 5. | $CuBr(L')_2$ (**5**) | 281 (100) | 422(42), 424(54), 426(40) | ----- | ----- | 702(56), 704(70), 706(52) | ----- | ----- |
| 6. | $CuI(L')_2$ (**13**) | 281 (100) | ----- | ----- | ----- | 752(68), 754(56) | ----- | ----- |

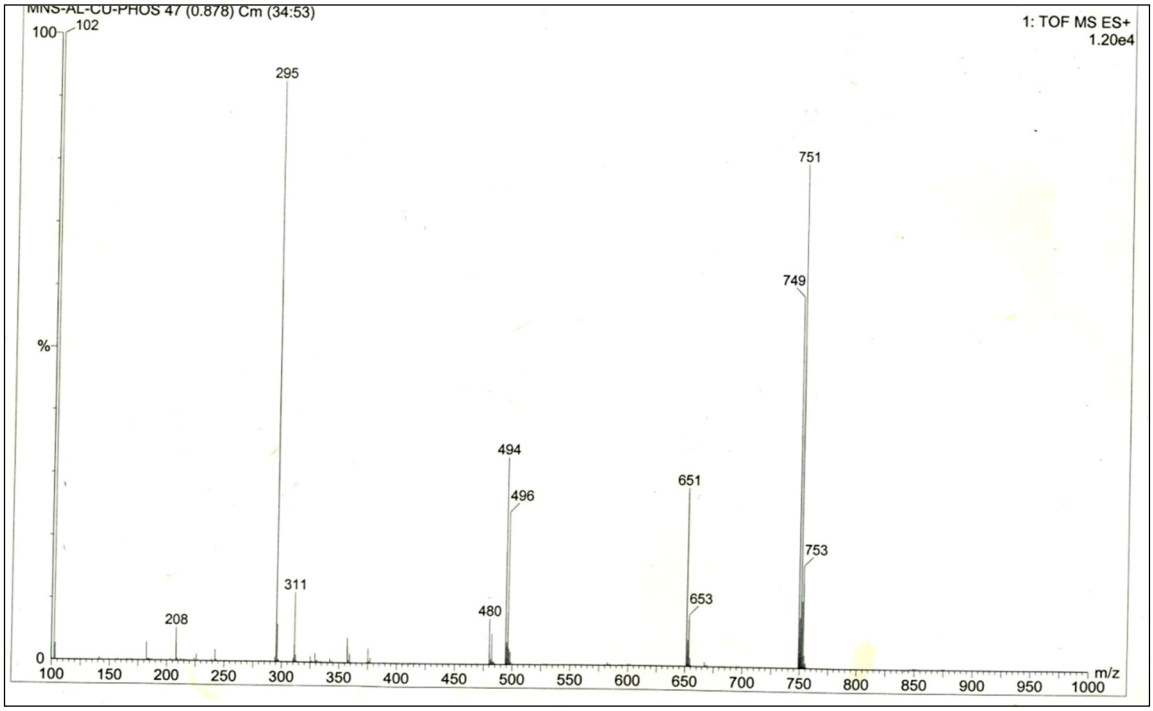
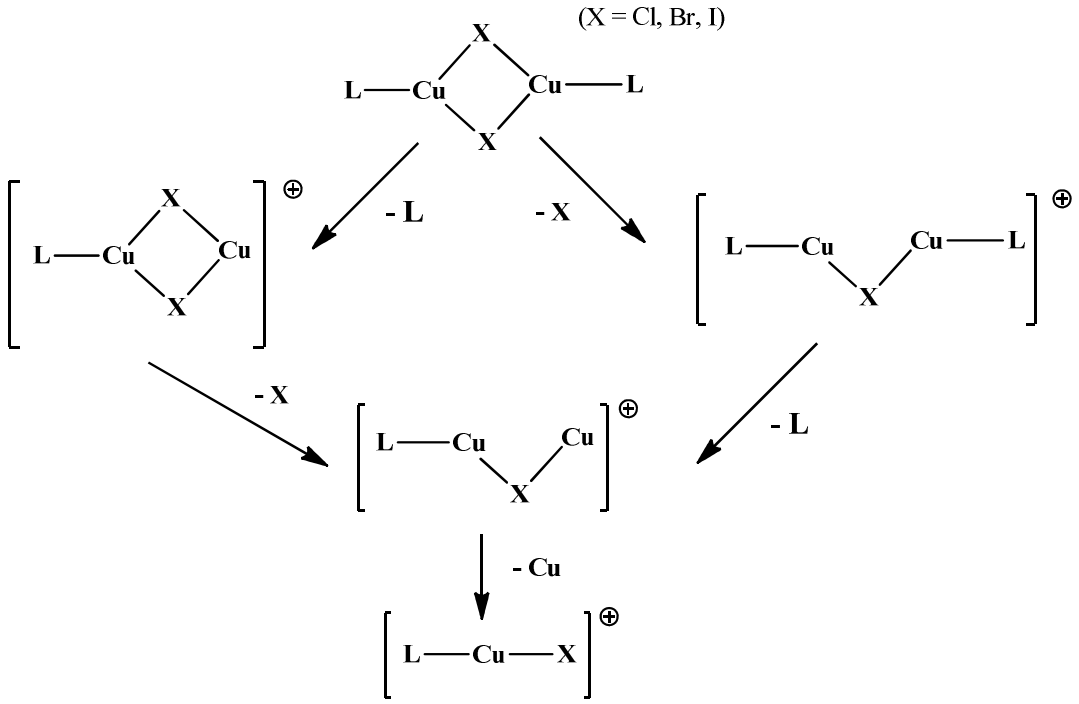
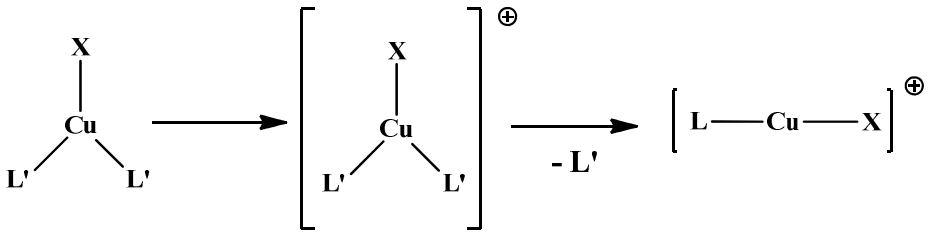



Fig.-4: ESI mass spectrum of $[CuCl(L)]_2$ (**1**)




**Scheme 1:** Fragmentation mechanism for dimeric copper(I) complexes **1-3**




**Scheme 2:** Fragmentation mechanism for monomeric copper(I) complexes **4-6**

**$^{31}$P NMR Studies**

Among the various NMR tools ($^{1}$H, $^{13}$C and $^{31}$P) available $^{31}$P NMR was found to be the most useful. Earlier we reported solid state $^{31}$P NMR (CPMAS) of aminophosphine complexes which showed quartet pattern which confirms direct Cu-P coupling[15]. For the complexes **1-6**, the following observations were made. (a) Sharp $^{31}$P signal of free aminophosphine ligand in gets slightly broadened after coordination with the metal center. The broadening of the signal is due to $^{1}J_{Cu\text{-}P}$ coupling. Copper is known to be a quadrupolar nucleus ($^{63}$Cu and $^{65}$Cu, I = 3/2). Figure-5 gives information about the nature of bonding in phosphine complexes can be obtained by comparing the phosphorus chemical shifts before and after coordination with the metal. Proton decoupled $^{31}$P NMR spectra of all the complexes are shielded after coordination when compared to the free aminophosphines. Aminophosphines accepts a part of electron density from the electron rich $d^{10}$ system, which results in shielding of signals. Coordination chemical shift ($\Delta\delta$), is defined as $\delta_{complex} - \delta_{free\ ligand}$, which is indicative of the donor-acceptor properties of the ligand. It is reported that a good σ-donor would produce a large coordination chemical shift, whereas a good π-acceptor would result in a small coordination chemical shift[5]. Coordination chemical shifts of the complexes are negative (Table-3). For aminophosphine (L) and (L'), coordination chemical shifts are found to be *ca.* -10 and -16 ppm respectively. A negative value for the coordination chemical shift implies

that aminophosphines can be a good π-acceptor ligand and its π-acceptor ability varies with amino substituents. Larger negative coordination chemical shift values for the complexes of (L') seem to suggest that (L') is a better π-acceptor than (L). (c) It was also observed that $^{31}P$ chemical shift values of the complexes are found to be independent of the structure (monomeric or dimeric) or the halogen atom (X= Cl, Br, I) present. For example, complexes **1**-**3** and **4**-**6** showed almost identical chemical shifts.

Table-3: Comparison of $^{31}P$ chemical shifts of aminophosphine ligands and its complexes

| S. No. | Aminophosphine | $^{31}P$ NMR (δ, ppm) | Compound | $^{31}P$ NMR (δ, ppm) | Coordination chemical shift |
|---|---|---|---|---|---|
| 1. | L | 76.4 | **1** | 66.5 | -9.9 |
| | | | **2** | 66.5 | -9.9 |
| | | | **3** | 66.7 | -9.7 |
| 2. | L' | 95.7 | **4** | 79.9 | -15.8 |
| | | | **5** | 80.2 | -15.5 |
| | | | **6** | 80.0 | -15.7 |

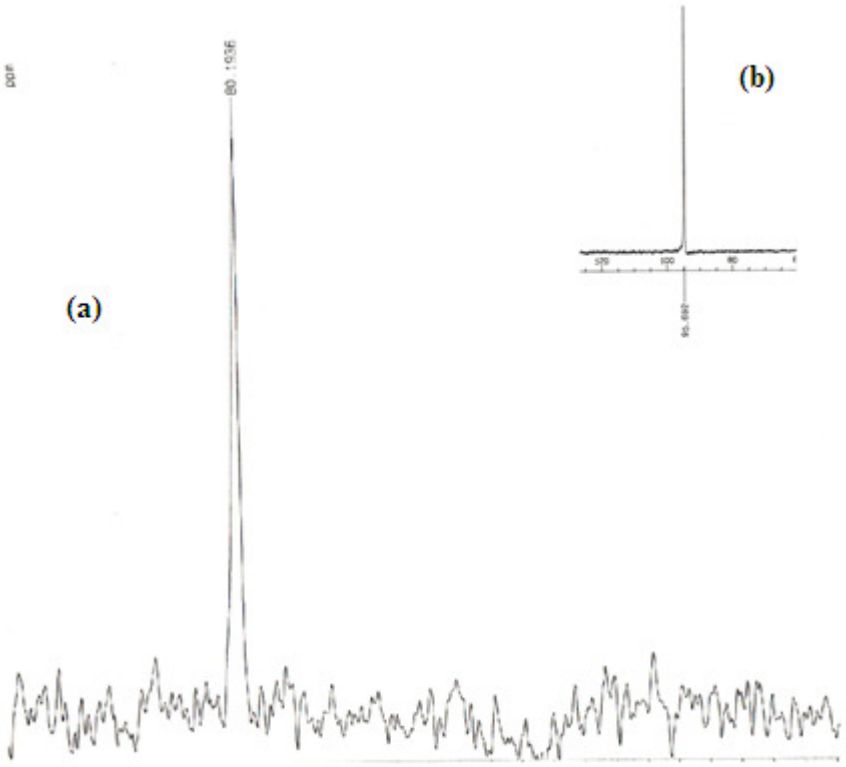



Fig.-5: Proton decoupled $^{31}P$ NMR spectrum of $CuCl(L')_2$ (**4**) in $CDCl_3$, ligand spectra in inset **(6b)**

## CONCLUSION

Thermogravimetric studies of Cu(I) aminophosphine complexes showed that aminophosphine ligand is lost easily on heating, at moderate temperatures. For complexes having more than one aminophosphine ligands, stepwise loss of the ligand is observed. Differential scanning calorimetric curves (DSC) also show sharp endothermal peaks corresponding to weight loss. Electrospray ionization mass spectroscopy (ESI MS), also confirms the elabile nature of aminophosphine ligands. Mass spectra reveal ligand peak was observed with high intensity in all the cases. Both ligands get shielded after coordination with the metal center and coordination chemical shifts were negative. On comparing $^{31}P$ coordination chemical

shifts, it was found that easy removal of the ligand on heating make these aminophosphine copper(I) complexes as potential precursors for chemical vapor deposition (CVD) for the production of thin metal/metal oxide layers.

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