*Pakistan Journal of Pharmaceutical Sciences*
*Vol.15, No.2, July 2002, pp.69-79*

# SYNTHESIS AND CHARACTERIZATION OF COPPER(I) TRIPHENYLPHOSPHINE COMPLEXES WITH ETHYLPYRIDINE

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## ABSTRACT

Copper(I) complexes of the type $[CuX(PPh_3)n(L)_n]_n$ {where X = $Cl^-$, $Br^-$ $I^-$, $NO_3$, $SCN^-$; $PPh_3$ = triphenylphosphine and L = 4-ethylpyridine} have been prepared and characterized on the basis of their molecular weight, magnetic susceptibility, conductance, infrared studies and elemental analysis. Ethylpyridine behaved as monodentate ligand. The variation in stoichiometry and the probable structures of these complexes have been discussed.

## INTRODUCTION

Copper(I) complexes of the types $[CuX(PPh_3)]_4$, $[CuNO_3(PPh_3)_2]$ (Jardine *et al.,* 1971) $[CuI(n\text{-}Bu_3P)]_4$ (Mann *et al.,* 1936) have already been prepared and characterized. Some copper(I) and silver(I) complexes containing mixed ligands and bearing the general formula $[CuI(PPh_3)_2(Py)_2]$ (Vohra & Jannat 1973), $[CuX(PPh_3)(HOx)]_2$ (Sultana & Irshad 1979), $[AgX(PPh_3)(HOx)]_2$ (Sultana *et al.,* 1980), $[CuX(PPh_3)(Pz)]$ (Sultana *et al.,* 1981), $[Cu_nX_n(PPh_3)_n(Mepy)]$ (Sultana *et al.,* 1994) have been prepared and studied. We also reported a number of other triphenylphosphine mixed ligand complexes with quinoline (Sultana *et al.,* 1988), dimethylaniline (Sultana *et al.,* 1994), aminopyridine (Sultana *et al.,* 1995), aminophenol (Sultana *et al.,* 1995$^a$) and methylpyridine (Sultana *et al.,* 1997) etc. The variation in stoichiometry and the probable structure of these complexes have been discussed in view of their chemical and spectral data in the above references. These complexes have been suggested to have dimeric structure and the experimental data are in support of bridging of halides, nitrates or thiocyanate groups between the two copper(I) atoms.

4-ethylpyridine forms different compounds with copper halotriphenylphosphine in variable ratios of 1:1, 1:2 and also in excess. Complexes of variable stoichiometry as $[CuX(PPh_3)(Ep)]_2$, $[CuX(PPh_3)_2(Ep)]$ $[CuX(PPh_3)(Ep)_2]_2$ and $[CuX(PPh_3)_2(Ep)_2]_2$ have been obtained. The infrared spectral data in the region 4000-700 $cm^{-1}$ suggest that copper(I) has variable coordination number 4, 5 and 6 in these complexes. They are sparingly soluble in common organic solvents, consistent with a polymeric character. They are shown to be non-ionic in character and diamagnetic in nature as shown by magnetic susceptibility studies.

## EXPERIMENTAL

### *Preparation of $[CuX(PPh_3)(Etpy)]_2$*

This was prepared by reacting one mMole of tetra[halogeno(triphenylphosphine)copper(I)] $[CuX(PPh_3)]_4$ (Vohra & Jannat 1973) with two millimoles of ethylpyridine in benzene and refluxing the whole mixture for 3-4 hrs. On crystallizing the product at room temperature the chloro complex gave gray powder m.p. 158°C 11B [$CuCl(PPh_3)(Etpy)]_2$; the bromo tetramer gave $[CuBr(PPh_3)(Etpy)]_2$ m.p. 148°C; and the iodo tetramer yielded $[CuI(PPh_3)(Etpy)]_2$ m.p. 260°C. When excess (1 ml) of the ligand was added, the chloro tetramer gave white crystalline compound $[CuCl(PPh_3)(Etpy)_2]$ m.p. 160°C; whereas the bromo and iodo complexes yielded the same $[CuX(PPh_3)(Etpy)]_2$ X = $Br^-$ m.p. 148°C and $I^-$ m.p. 260°C. There was no reaction in equimolar amounts.

### *Preparation of $[Cu_2X_2(PPh_3)_3(Etpy)]$, $[CuX(PPh_3)_2(Etpy)]_2$ and $[CuX(PPh_3)(Etpy)_2]_2$*

The reaction of di-[μ-halogenobis(triphenylphosphine)copper(1)] $[CuCl(PPh_3)_2]_2$ with ethylpyridine in equimolar ratios, gave no new product. When the concentration of ligand was doubled the chloro complex gave $[CuCl(PPh_3)_2(Etpy)]$ m.p. 220°C; whereas the bromo and iodo compounds obtained are $[CuX(PPh_3)(Etpy)]_2$.

When excess of the ligand was added, the chloro complex gave the compound $[Cu_2Cl_2(PPh_3)_3(Etpy)]$ m.p. = 208°C; the bromo compound yielded $[CuBr(PPh_3)_2(Etpy)]_2$ m.p. = 200°C; the iodo compound gave $[CuI(PPh_3)(Etpy)]_2$ 13Z m.p.= 192°C.

The di-[μ-nitrato and thiocyanatobis(triphenylphosphine)copper(1)] $[CuZ(PPh_3)_2]_2$ Z= $NO_3^-$ and $SCN^-$ on refluxing with excess of ethylpyridine in alcohol and chloroform respectively yielded compounds of the type $[CuNO_3(PPh_3)_2(Etpy)]$ m.p. = 220°C and $[CuSCN(PPh_3)(Etpy)_2]_2$ m.p. = 152°C. When equimolar, or double the amount of the ligand was taken in the above reactions, substitution of ethylpyridine did not occur.

## RESULTS & DISCUSSION

All the complexes synthesized with 4-ethylpyridine were further studied for their ionic or non-ionic character and magnetic susceptibility. Conductance measurements were carried out in nitrobenzene at 20°C. None of them showed any ionic character and hence all were non-ionic. Magnetic susceptibility measurements showed them to be diamagnetic. The solubility studies, elemental analysis and infrared spectra are given in tables 1-4.

From the infrared (table 3) studies and elemental analysis (table 4) the compound is shown to be a dimer having the formula $[CuX(PPh_3)(Etpy)]_2$ where halogen is forming bridge between the two copper(I) atoms. Complexes having different stoichiometry were obtained for different halogens, this may be due to the difference in the reactions of the halogens.

### *Infrared studies of copper triphenylphosphine ethylpyridine complexes*

Infra red studies (table 3) of the complexes proved the presence of the ligands, triphenylphosphine and ethylpyridine. Two different linkages which constitute the IR spectrum are metal phosphorous and metal nitrogen linkage of aromatics moieties. The peaks due to the aromatic and aliphatic groups in the compounds are sharp, well defined as these groups are well isolated free from internal or external influences and the recorded peaks in this region are quite consistent with the standard peaks given by these groups. The peaks due to metal-phosphorous and metal-nitrogen are also true reflection of their characteristic bonding in the complexes. There is a reasonable close analogy between the ring vibration of benzene and those of pyridine and quinoline and difference in the hydrogen deformation. However, the out of plane hydrogen deformation vibration appear to be like those of benzene compounds containing an additional substituents.

**Table 1**

Physical characteristics of copper triphenylphosphine complexes with 4-ethylpyridine

| Serial No. | Code No. | Complex [Parent: ligand] | % Yield | M.P. °C | Colour & Appearance |
|---|---|---|---|---|---|
| 1. | 11B | $[CuCl(PPh_3)]_4:[C_7H_9N]_2$ | 45 | 158 | Gray powder |
| 2. | 11C | $[CuCl(PPh_3)]_4:[C_7H_9N]n$ | 50 | 160 | Green crystals |
| 3. | 12B | $[CuBr(PPh_3)]_4:[C_7H_9N]_2$ | 50 | 148 | Green crystals |
| 4. | 12C | $[CuBr(PPh_3)]_4:[C_7H_9N]_n$ | 45 | 148 | Green crystals |
| 5. | 12CF | $[CuBr(PPh_3)]_4:[C_7H_9N]_n$ | 12 | 148 | Dark green crystals |
| 6. | 1B | $[CuI(PPh_3)]_4:[C_7H_9N]_2$ | 45 | 260 | Yellow crystals |
| 7. | 13C | $[CuI(PPh_3)]_4:[C_7H_9N]_n$ | 55 | 260 | Pale crystals |
| 8. | 11Y | $[CuCl(PPh_3)_2]_2:[C_7H_9N]_2$ | 45 | 220 | White crystals |
| 9. | 11Z | $[CuCl(PPh_3)_2]_2:[C_7H_9N]_n$ | 55 | 208 | Cream crystals |
| 10. | 12Y | $[CuBr(PPh_3)_2]_2:[C_7H_9N]_2$ | 55 | 148 | Light green |
| 11. | 12Z | $[CuBr(PPh_3)_2]_2:[C_7H_9N]_n$ | 50 | 200 | White crystals |
| 12. | 13Y | $[CuI(PPh_3)_2]_2:[C_7H_9N]_2$ | 46 | 260 | Pale crystals |
| 13. | 13Z | $[CuI(PPh_3)_2]_2:[C_7H_9N]_n$ | 25 | 192 | Pale crystals |
| 14. | 14Z | $[CuNO_3Cl(PPh_3)_2]_2:[C_7H_9N]_n$ | 25 | 220 | Yellow crystals |
| 15. | 15Z2 | $[CuSCN(PPh_3)_2]_2:[C_7H_9N]_n$ | 45 | 152 | White crystals |
| $C_7H_9N$ = 4- Ethylpyridine | | | | | |

Band absorptions in the region 1118 - 1090 $cm^{-1}$ are attributed to VP-C modes. The shift to higher frequency of VP-C at 1089 $cm^{-1}$ indicates coordination of triphenylphosphine. In the synthesized compounds, these bands are observed at 1445, 1150 and 990-1000 $cm^{-1}$ in case of halo complexes and 1430, 1095-1120 and 1010-1000 $cm^{-1}$ in nitrato and thiocyanato compounds respectively. The shifts may be attributed to the coordination of triphenylphosphine as a monodentate or as a bridging ligand.

Presence of medium absorption peak in the region 1600-1585 $cm^{-1}$ along with the sharp peaks with high intensity in the 1500-1400 $cm^{-1}$ region, corresponds to the skeletal vibration, involving C-C stretching vibration in the ring, these are singlets and not doublets, which is in the case of substituents on benzene ring is another proof of the purity of the compounds. The broad and weak bands in the region 2000-1650$cm^{-1}$ are effect of overtone and combination peaks is the characteristic of ring substituents.

A number of workers (Allen *et al.,* 1964; Lobana & Bhatia 1990; Engelhardt *et al.,* 1989; Afridi & Sultana 1983 and Satoh *et al.,* 1988) studied and showed close resemblance in the absorption bands of coordinated pyridine and free pyridine. Sharp distinct peaks are observed in the region 900-675 $cm^{-1}$ is characteristic nature of compound. Gill (Gill *et al.,* 1961) reported that vibration frequencies of pyridine do not change greatly when pyridine is coordinated to a metal. Each band in the spectrum of pyridine is faithfully reproduced with only minor shifts in the spectra of the complexes.

**Table 2A**

Solubility data of copper triphenylphosphine complexes with 4-ethylpyridine in various organic solvents

| Solvent → Sample code↓ | MeOH 1 | EtOH 2 | BuOH 3 | EtOAC 4 | Acetone 5 | $CHCl_3$ | $CCl_4$ |
|---|---|---|---|---|---|---|---|
| 11A | - | - | 2 | 4 | 2 | 3 | 3 |
| 11C | 2 | 1 | - | 4 | 3 | 4 | 1 |
| 12CF | 2 | 3 | 3 | 2 | 3 | 1 | 2 |
| 13C | 1 | 1 | ? | 1 | 2 | 2 | 2 |
| 11Z | 2 | 2 | 2 | 2 | 3 | 2 | 1 |
| 13X | 2 | 1 | ? | 1 | 2 | 1 | 1 |
| 13Y | 1 | 1 | ? | 2 | 2 | 2 | 1 |
| 13Z2 | - | 1 | 2 | ? | 3 | 3 | 1 |
| 15Z2 | 1 | 2 | ? | 1 | 1 | 2 | 1 |

**Table 2B**

Solubility data of copper triphenylphosphine complexes with 4-ethylpyridine in various organic solvents

| Solvent → Sample code↓ | Benzene 8 | Nitrobenzene 9 | DMF 10 | DMSO 11 | THF 12 | Ether* 13 |
|---|---|---|---|---|---|---|
| 11A | 1 | 4 | 3 | 3 | 1 | 2 |
| 11C | 4 | 4 | 1 | 4 | 4 | 3 |
| 12CF | 1 | 2 | 2 | 2 | 3 | 2 |
| 13C | 1 | 2 | 2 | 2 | 3 | 2 |
| 11Z | 2 | 4 | 3 | 3 | 3 | 2 |
| 13X | 2 | 1 | 2 | 1 | 3 | 1 |
| 13Y | 1 | 2 | 1 | 1 | 1 | 2 |
| 13Z2 | 1 | - | 1 | 2 | 2 | 1 |
| 152 | 1 | 2 | 2 | 2 | 3 | 1 |

1= Slightly soluble, 2=50% soluble, 3=75% soluble, 4=completely soluble, - = completely insoluble, ? = sample not checked in this solvent.

*Diethylether

All these samples were insoluble in hexane and ethylene glycol except sample 11Z which had solubility 1 in hexane.

**Table 3**
IR absorption bands of copper triphenylphosphine 4-ethylpyridine complexes

| Sample Code | Compound | Main IR absorption |
|---|---|---|
| | Ethylpyridine | 415(m) 700(s) 750(m) 1090(sm) 1320(db,m) 1390(s) 1440(s) 1485(m) 1615(m) 1670(br) 1825(m) 1900(m) 1970(m) 2980(m) 3050(sm) 3450(br). |
| 11B | $[CuCl(PPh_3)(C_7H_9N]_2$ | 435(m) 510(s) 570(sm) 620(sm) 700(s) 750(s) 790(m) 830(s) 855(m) 985(sm) 1000(s) 1030(db,s) 1070(s) 1100(s) 1115(sm) 1160(m) 1185(s) 1225(s) 1315(db,m) 1440(s) 1485(db,s) 1560(sm) 1590(m) 1615(s) 1670(br) 1770sm) 1825(m) 1900(m) 1970(m) 2940(m) 2980(s) 3050(s) 3450(sm) and 3520(sm). |
| 11C | $[CuCl(PPh_3)(C_7H_9N]_n$ | 435(m) 510(s) 570(sm) 620(sm) 700(s) 750(s) 785(m) 830-845(db,s) 985(sm) 1000(s) 1020(m) 1030(s) 1070(s) 1100(s) 1115(sm) 1160(m) 1185(s) 1225(s) 1315(db,m) 1440(s) 1485(db,s) 1560(sm) 1590(m) 1615(s) 1670(br) 1770(sm) 1825(m) 1900(m) 1970(m) 2880(sm) 2940(m) 2980(s) db 3050(s) and 3450(br). |
| 12B | $[CuBr(PPh_3)(C_7H_9N]_2$ | 435(m) 510(s) 570(sm) 620(sm) 700(s) 750(s) 785(m) 830-845 (db,s) 985(sm) 1000(s) 1020(m) 1030(s) 1070(s) (m) 1100(s) 1115(sm) 1160(m) 1185(s) 1225(s) 1315(db,m) 1440(s) 1485(db,s) 1560(sm) 1590(m) 1615(s) 1670(br) 1770(sm) 1825(m) 1900(m) 1970(m) 2880(sm) 2940(m) 2980(s) db 3050(s) and 3450(br). |
| 13B | $[CuI(PPh_3)(C_7H_9N]_2$ | 510(s) db 700(s) 750(s) 830(s) 1000(s) 1020(s) db 1070(s) 1100(s) 1110(sm) 1160(m) 1190(s) 1220(db,s) 1315(s) 1335(m) 1390(sm) 1425-1440(db,s) 1465(s) 1485-1500(db,s) 1555(s) 81575(sm) 1590(s) 1610(s) 1670(m) 1710(m) 1780(db,m) 1830(db, m) 1900(m) 1975(db,m) 2880(m) 2940(m) 2975(m) and 3050(m). |
| 11Y | $[CuCl(PPh_3)_2(C_7H_9N]$ | 280(s) 440(s) 500(s) 620(m) 700(s) 750(s) 855(m) 925(m) 985(m) 1000(s) 1030(s) 1070(s) 1100(s) 1160(m) 1185(m) 1210(m) db 1435(s) 1480(s) 1570(db,m) 1670(sm) 1770(sm) 1820(m) 1895(m) 1970(m) and 3050(s). |
| 11Z | $[Cu_2Cl_2(PPh_3)]_3(C_7H_9N)]_2$ | 430(m) 510(s) 620(m) 700(s) 840(s) 1000(s) 1015(m) 1030(s) 1070(s) 1095(s) 1155(s) 1185(s) 1220(s) 1280(sm) 1310(db,s) 1435(db,s) 1480(s) 1560(m) 1590(s) 1610(s) 1670(sm) 1770(sm) 1820(m) db 1890(m) 1940(m) 2930(sm) 2980(db,sm) 3050(m) and 3420(br) |
| 12Z | $[CuBr(PPh_3)_2(C_7H_9N)]_2$ | 435(m) 510(s) 620(m) 700(s) 750(s) 850(s) 920(m) 975(m) 1000(s) 1030(s) 1070(m) 1090(s) 1155(s) 1185(s) 1280(sm) 1310(m) 1435(s) 1470(s) 1580(db,m) 670(sm) 1770(sm) 1820(sm) 1890(m) 1920(m) and 3050(m) |

*Table 3 continued*

| Sample Code | Compound | Main IR absorption |
|---|---|---|
| 13Z | $[CuI(PPh_3)(C_7H_9N)]_2$ | 10(s) db 570(sm) 700(s) 750(s) 790(m) 830(s) 1000-1030(trp,s) 1070(m) 1100(s) 1160(m) 1185(m) 1220(db,s) 1310(db,m) 1435(db,s) 1480(db,s) 1550(m) 1590(m) 1610(s) 1670(sm) 1770(sm) 1825(m) 1900(m) 1970(m) 2880(sm) 2930(m) 2980(m) 3050(s) and 3450(br). |
| 14Z | $[CuNO_3(PPh_3)_2(C_7H_9N)]_2$ | 430(m) 510(s) db 700(s) 750(s) 790(m) 815(m) 1000(m) 1030(s) 1070(m) 1100(s) 1160(m) 1185(m) 1230(s) 1310(m) 1330(m) 1440(s) 1470(s) 1485(s) 1570(m) 1590(m) 1610(m) 1670(m) 1770(sm) 1825(m) 1970(m) 3050(s) and 3450(m). |
| 15Z | $[CuSCN(PPh_3)(C_7H_9N_2]_2$ | 430(sm) 510(s) 620(sm) 700(s) 750(s) 1000(m) 1030(m) 1100(s) 1190(m) 1385(m) 1435(s) 1480(s) 1590(m) 1610(sm) 1670(sm) 1770(sm) 1825(sm) 1900(m) 1970(m) 2100(s) 2880(sm) 2930(m) 2980(m) 3050(s) and 3450(br). |

[sm = small, s = sharp, w = weak, m = medium, br = broad, db = doublet, trp = triplet]

Pyridine and the picolines all show CH absorption in the range 3070-3020 $cm^{-1}$ (Marion *et al.,* 1951; Coulson *et al.,* 1951) which appear as a series of multiple absorptions under high resolutions (Finnegan *et al.,* 1955). Marion *et al.,* (Marion *et al.,* 1951) have noted a band near 3030 $cm^{-1}$ in anabasine which is assigned to the C-H stretching mode of the pyridine ring. Pyridine (Coulson *et al.,* 1951) appears to have small absorptions as high as 3420 $cm^{-1}$ which is in the NH stretching frequency region.

### *C = C and C = N Vibrations*

Pyridine absorbs at 1580, 1570 and at 1485 $cm^{-1}$; the position of these absorptions in a series of alkyl pyridines have also been studied by Lobana & Bhatia (1990), Barron *et al.* (1985) and by Yamamoto *et al.* (1980), who have commented on the changes in the relative intensities which follow alterations in the position of the substituent groups.

### *Ring vibration and hydrogen deformation*

Pyridine shows a strong band near 1200 $cm^{-1}$ and another between 1100 $cm^{-1}$ and 1000 $cm^{-1}$. The remaining characteristic region is that between 900 and 700 $cm^{-1}$ in which CH deformations occur. Pyridine (Deacons & Green 1965) with five free hydrogen atoms corresponding to monosubstituted benzenes absorb at 750 $cm^{-1}$. A series of eight variously substituted ethylpyridine nineteen substituted methylpyridines have also been shown to follow this correlation with slightly wider divergencies. Satoh *et al.* (1988) report similar findings and note that characteristics patterns appear in the 2080-1650 $cm^{-1}$ region as with benzene systems.

All these compounds show sharp absorption in the 3020-3040 $cm^{-1}$ region which is due to C-H absorption as a band near 3030 $cm^{-1}$ have been noted in anabasine (Marion *et al.,* 1951) which is absent in piperidine, this band is assigned to C-H stretching mode of pyridine ring. The other peak appears at 3400 ± 50 $cm^{-1}$ which is due to N-H stretching.

**Table 4**
Elemental analysis of copper triphenylphosphine 4-ethylpyridine complexes

| No. | Compound | Elements | C | H | N | X | P | Cu |
|---|---|---|---|---|---|---|---|---|
| 11B | $[CuCl(PPh_3)(C_7H_9N]_2$ | Calculated | 64.10 | 5.1 | 2.99 | 7.57 | 6.61 | 13.57 |
| | | Found | 64.23 | 4.9 | 2.86 | 7.49 | 6.63 | 13.60 |
| 11C | $[CuCl(PPh_3)(C_7H_9N)_2]_n$ | Calculated | 66.77 | 5.78 | 4.87 | 6.16 | 5.38 | 11.04 |
| | | Found | 66.86 | 5.48 | 4.88 | 6.09 | 5.39 | 10.96 |
| 12B | $[CuBr(PPh_3)(C_7H_9N)]_2$ | Calculated | 58.55 | 4.72 | 2.73 | 15.58 | 6.04 | 12.39 |
| | | Found | 58.71 | 4.73 | 2.75 | 15.46 | 6.0 | 12.21 |
| 13B | $[CuI(PPh_3)(C_7H_9N)]_2$ | Calculated | 53.67 | 4.33 | 2.51 | 22.70 | 5.54 | 11.26 |
| | | Found | 53.63 | 4.32 | 2.50 | 22.67 | 5.54 | 11.35 |
| 11Y | $[CuCl(PPh_3)_2(C_7H_9N)]$ | Calculated | 70.68 | 5.38 | 1.92 | 4.85 | 8.48 | 8.70 |
| | | Found | 70.45 | 5.31 | 1.89 | 4.80 | 8.50 | 8.63 |
| 11Z | $[CuCl(PPh_3)_3(C_7H_9N)]$ | Calculated | 70.58 | 5.21 | 1.35 | 6.846 | 8.96 | 12.2 |
| | | Found | 70.69 | 5.31 | 1.23 | 6.79 | 8.85 | 12.01 |
| 12Z | $[CuBr(PPh_3)_2(C_7H_9N)]_2$ | Calculated | 66.63 | 5.07 | 1.81 | 10.31 | 7.99 | 8.20 |
| | | Found | 66.74 | 5.08 | 1.78 | 19.21 | 8.01 | 8.14 |
| 13Z | $[CuI(PPh_3)(C_7H_9N)]_2$ | Calculated | 53.67 | 4.33 | 2.51 | 22.70 | 5.54 | 11.26 |
| | | Found | 53.63 | 4.32 | 2.50 | 22.67 | 5.54 | 11.35 |
| 14Z | $[CuNO_3(PPh_3)_2(C_7H_9N)]_2$ | Calculated | 68.24 | 5.20 | 3.70 | - | 8.19 | 8.32 |
| | | Found | 68.03 | 5.14 | 3.79 | - | 8.23 | 8.14 |
| 15Z | $[CuSCN(PPh_3)(C_7H_9N)_2]_2$ | Calculated | 66.32 | 5.57 | 7.04 | 5.35 | 5.19 | 10.54 |
| | | Found | 66.14 | 5.56 | 7.22 | 5.41 | 5.23 | 10.62 |

The absorption in 1580, 1480 $cm^{-1}$ region is assigned to C-C and C-N vibrations. These bands are also absent in piperidine spectrum (Thangadurai & Natarajan 2001); the absorption at 1430-1438 $cm^{-1}$ and 738-745 $cm^{-1}$ are due to triphenylphosphine and confirm its coordination on complex formation. The peaks observed in 1250-1300 and 1000-1100 $cm^{-1}$ regions are due to the ring vibration or the hydrogen deformation. All the absorptions below 700 to 1000 $cm^{-1}$ are assigned to C-H deformation of both the ligands. The sharp peaks in 400-450 $cm^{-1}$ region show the M-X linkages.

### *Nitrato Complexes*

In the nitrato compound $[CuNO_3(PPh_3)_2(Etpy)]_2$ there is a sharp doublet at 720 $cm^{-1}$ for $NO_2$ bending vibration while the N-O stretching vibrations are observed in 1390-1370 $cm^{-1}$ region and two sharp peaks at 1550 $cm^{-1}$ for N=O stretching band. It has been noted that the absorptions at 1360 and 810 $cm^{-1}$ are an indication of the presence of a bidentate nitrate group which appeared at 1390-1370 and 850 $cm^{-1}$ in our compounds showing that $NO_3$ ion is acting as a bridging group, using its N and O terminal (Sultana *et al.,* 1994; Sultana *et al.,* 1995 and Sultana *et al.,* 1995[a]).

***Thiocyanato Compounds***

The SCN group may coordinate to the metal through nitrogen or sulfur or both (M-NCS-M'). In general, class A metals (first transition series such as Cr, Mn, Fe, Co, Ni, Cu and Zn) form M-N bonds, whereas class B metals (second half of the second and third transition series, such as Rh, Pd, Ag, Cd, Ir, Pt, Au and Hg) form M-S bonds (Thangadurai & Natarajan 2001).

The CN stretching frequencies are lower in N-bonded complexes (near and below 2050 cm-1 than in S-bonded complexes (near 2100 $cm^{-1}$) (Mitchell & Williams 1960). The bridging complexes exhibit v(CN) well above 2100 $cm^{-1}$; however, this rule must be applied with caution as v(CN) are affected by many other factors (Barron *et al.,* 1985 and Yamamoto *et al.,* 1980).

Several workers (Turco & Pecile 1961; Lewis *et al.,* 1961) considered V(CS) as a structural diagnosis: 780-860 $cm^{-1}$ for N-bonded, and 720-690 $cm^{-1}$ for S-bonded complexes. However, this band is rather weak and is often obscured by the presence of other bands in the same region. It was suggested by these authors that the N-bonded complex exhibits a single sharp δ(NCS) near 480 $cm^{-1}$, whereas the sulfur bonded complex shows several bands of low intensity near 420 $cm^{-1}$; however, these bands are also weak and tend to be obscured by other bands. In our complex this band appears as a sharp band at 510 $cm^{-1}$ showing the coordination through the nitrogen of the SCN group.

Lobana & Bhatia (1990) measured the IR spectra of tetrahedral $[M(NCS)_2L_2]$, monomeric octahedral $[M(NCS)_2L_4]$, and polymeric octahedral $[M(NCS)_2L_2]$ type complexes where M = Fe, Co, Ni etc.; L = py, α-picoline, etc), and found that v(CS) are higher by 40-50 $cm^{-1}$ for tetrahedral than for octahedral complexes for the same metal, although v(CN) are very similar to both.

Turco and Pecile (1961) noted that the presence of other ligands in a complex influences the mode of the N-C-S bonding. For example, in $[Pt(NCS)_2L_2]$, the NCS is N-bonded if L is a phosphine (π-acceptor), and is S-bonded if L is an amine. For $[Cr(NCS)_4L_2]_n^-$ ions. The NCS group also forms a bridge between two metal atoms. CN stretching frequency of a bridging group is generally higher than that of a terminal group. According to Chatt and Duncanson (1956) the CN stretching frequencies of Pt(II) complexes are in the region 2150-2182 $cm^{-1}$ for the bridging and 2100-2120 $cm^{-1}$ for the terminal NCS group.

Both N-bonded and S-bonded NCS groups have been found in [Pd(4,4'-dimethylbipy) (NCS)(SCN)] and $[Pd\{Ph_2P(CH_2)_3NMe_2\}$-(NCS)(SCN)]. Similar mixed NCS-SCN bonding was found for [PdL(NCS)(SCN)], where L is $Ph_2P(o\text{-}C_6H_4)AsPh_2$ and $[Ph_2P(CH_2)_2NMe_2]$ (Meek *et al.,* 1970). These bidentate ligands contain two different donor atoms which give different electronic effects on the NCS groups trans to them. Thus, the trans effect together with the steric effect of these ligands, may be responsible for the mixing of the N- and S-bonding. Example includes $[Ni(DPEA)(NCS)_2]_2$ (DPEA= di(2-pyridyl-α-ethyl)amine] where terminal N-bonded and bridging NCS groups are mixed [V(CN): 2094 and 2128 cm-1 respectively].

Thiocyanate absorbs in the 2020-2090 $cm^{-1}$ and silver thiocyanate (Afridi & Sultana 1983) has a strong band at 2170 $cm^{-1}$. The range 2200-2000 $cm^{-1}$ can be regarded as covering all the various forms in which –C≡N grouping occurs in inorganic compounds.

The infrared studies of these compounds show the coordination of both the ligands triphenylphosphine and ethylpyridine as has been discussed by selecting individual various functional peaks as C=C, C=N and N-H vibrations which clearly indicate the coordination of ethylpyridine through its nitrogen atom; whereas the presence of triphenylphosphine has been shown by P-C modes and its shifting on coordination.

## CONCLUSION

Elemental analysis and IR studies revealed the fact that the complexes so formed have the structures $[CuX(PPh_3)(Etpy)]_2$, $[CuX(PPh_3)2(Etpy)]_2$, $[CuX(PPh_3)(Etpy)_2]_2$, $[Cu_2Cl_2(PPh_3)_3(Etpy)]$ and $[CuCl(PPh_3)(Etpy)_2]$.

Complexes having different stoichiometry were obtained for different halogens, this may be due to the differences in the reactivities of the halogens. The halo compounds of phosphine copper(I) behave similarly with organic ligand in general. The nitrato anion act as a bidentate ligand in copper(I) complexes. All the complexes maintain their diamagnetic ability and do not go to high oxidation state satisfying the phenomenon that phosphine lowers as well as stabilizes the low oxidation states of the transition metals.

In conclusion, the present study leads to the fact that ethylpyridine act as a monodentate ligand, with halogen bridging the two copper(I) atoms which are in unit positive oxidation states. The trans position for triphenylphosphine is suggested because of its bulky size so as to avoid steric hindrance.

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