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## COPPER (I) COMPLEXES OF TRIPHENYLPHOSPHINE AND AMINOPHENOL

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Some new complexes of copper(I) containing mixed ligands having general formula  $[\text{CuX}(\text{PPh}_3)(\text{Amph})]$ ,  $[\text{Cu}_2\text{X}_2(\text{PPh}_3)_3(\text{Amph})]$  and  $[\text{Cu}_n\text{Z}_n(\text{PPh}_3)_2(\text{Amph})]$  [where  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$  and  $\text{Z} = \text{NO}_3^-$  or  $\text{SCN}^-$ ,  $n = 1, 4$  or  $5$  and  $\text{PPh}_3$  = triphenylphosphine and  $\text{Amph}$  = aminophenol] have been synthesized from  $[\text{CuX}(\text{PPh}_3)_4]$  and  $[\text{CuX}(\text{PPh}_3)_2]$  in benzene in variable ratios and characterized on the basis of infra red studies and elemental analysis. Magnetic susceptibility and conductivity measurements have also been carried out. These appear to be dimers and polymeric structures having bridging of halides, nitrate or thiocyanate groups between the two copper atoms.

**Key words:** Copper (I) Complexes. Mixed ligand of Triphenylphosphine, Aminophenol complexes.

### Introduction

A number of workers have prepared copper (I) halide [1-3], nitrate [4] and thiocyanate [5] complexes with triphenylphosphine bearing the formula  $[\text{CuX}(\text{PPh}_3)_4]$ ,  $[\text{CuX}(\text{PPh}_3)_3]$ ,  $[\text{CuX}(\text{PPh}_3)_2]$  and  $[\text{CuZ}(\text{PPh}_3)_2]$  [where  $\text{X} =$  halide and  $\text{Z} = \text{NO}_3^-$  or  $\text{SCN}^-$ ]. Structurally they are considered bridged tetramers, tetrahedrals and bridged dimers respectively.

In previous papers [6-11] we have reported mixed ligand complexes of copper (I) and silver (I) of the type  $[\text{CuX}(\text{PPh}_3)(\text{HOx})_2]$  [6],  $[\text{AgX}(\text{PPh}_3)_y(\text{HOx})_z]$  [7],  $[\text{Cu}_2\text{X}_2(\text{PPh}_3)_2\text{Pz}]$  and  $[\text{Cu}_4\text{Z}_4(\text{PPh}_3)_6\text{Pz}]$  [8],  $[\text{AgX}(\text{PPh}_3)\text{An}]_2$  [9],  $[\text{CuX}(\text{PPh}_3)_n(\text{Quin})_n]$  [10] and  $[\text{Cu}_2\text{X}_2(\text{PPh}_3)_2(\text{Mepy})]$ ,  $[\text{CuX}(\text{PPh}_3)_2(\text{Mepy})]$  [11] [Where  $\text{HOx} = 8$ - hydroxy-quinoline,  $\text{Pz} =$  pyrazine,  $\text{An} =$  aniline,  $\text{Quin} =$  quinoline and  $\text{Mepy} = 2$ - Methylpyridine].

In this paper preparation and characterization of copper (I) complexes of triphenylphosphine and 2-aminophenol (1:1-n metal-ligand ratio) are reported.

### Experimental

$[\text{CuX}(\text{PPh}_3)(\text{Amph})]$ . was prepared by refluxing equimolar quantities of tetrakis [halo (triphenylphosphine) copper (I)] [12] and 2-aminophenol in benzene for 4 hr. The mother liquor after repeated crystallizations gave the products of the above formula. m.pt.  $[\text{CuCl}(\text{PPh}_3)(\text{Amph})] = 224^\circ\text{C}$ ;  $[\text{CuBr}(\text{PPh}_3)(\text{Amph})] = 212^\circ\text{C}$ ;  $[\text{CuI}(\text{PPh}_3)(\text{Amph})] = 208^\circ\text{C}$ .

$[\text{Cu}_2\text{X}_2(\text{PPh}_3)_3(\text{Amph})]$ . Was prepared by refluxing di-halobis(triphenylphosphine) dicopper (I)  $[\text{CuX}(\text{PPh}_3)_2]$  and aminophenol in equimolar ratio in benzene for 4-5 hr. The resulting solution gave colored crystals on cooling at room

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temperature which were washed with benzene followed by diethyl ether and dried. m. pt. ;  $[\text{Cu}_2\text{Cl}_2(\text{PPh}_3)_3(\text{Amph})] = 156^\circ\text{C}$ ;  $[\text{Cu}_2\text{Br}_2(\text{PPh}_3)_3(\text{Amph})] = 192^\circ\text{C}$ ;  $[\text{Cu}_2\text{I}_2(\text{PPh}_3)_3(\text{Amph})] = 200^\circ\text{C}$ .

When the concentration of the ligand was doubled in the above reaction,  $[\text{CuCl}(\text{PPh}_3)_2]$  gave crystals of aminophenol, the bromide compound gave the product  $[\text{CuBr}(\text{PPh}_3)(\text{Amph})]$  m.pt =  $212^\circ\text{C}$ ; whereas in case of the iodo compound, the parent compound  $[\text{CuI}(\text{PPh}_3)_2]$  itself crystallized out.

$[\text{Cu}_5(\text{NO}_3)_3(\text{PPh}_3)_2(\text{Amph})]$ . Was synthesized by refluxing one mole of di-u-[nitratobis(triphenylphosphine) dicopper (I)] and excess (4 mols) of 2-aminophenol in ethanol for 2-3 hr. The solution was then left overnight for crystallization at room temperature. Crystals so obtained were washed and dried, m.p.t. =  $200^\circ\text{C}$ .

$[\text{Cu}_4(\text{SCN})_4(\text{PPh}_3)_2(\text{Amph})]$ : The procedure adopted was same as mentioned above except that chloroform was used instead of ethanol. m.p.  $260^\circ\text{C}$ .

**Spectral and analytical measurements.** IR spectra of the complexes were recorded in CsI pellets by the courtesy of Material Science Corporation, Chicago.

Carbon, hydrogen and nitrogen were estimated by micro analytical method on C, H and N analyzed by the courtesy of Prof. S.F.A. Kettle, University of East Anglia, Sheffield, England. Copper was estimated spectrophotometrically using atomic absorption spectrophotometer at the absorption line of 324.8 nm. Halides were estimated volumetrically by Volhard's method [13]. Phosphorous was estimated spectrophotometrically by the Hetero Poly Blue Method [14]. Conductance measurements were carried out on a conductometric bridge using nitrobenzene as solvent. Magnetic susceptibility measurements were carried out on a Guoy Balance and all the complexes were found to be diamagnetic.



Table 1. Characterization Data of the Complexes.

No.	Compound	M.P.(C°)	Colour	Elements →	C	H	N	X	Cu	P
1	[CuCl(PPh <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> NO)]	224	brown	Calculated	61.2	4.6	2.9	7.5	13.5	11.8
				Found	61.1	4.8	3.0	7.8	14.0	11.6
2	[CuBr(PPh <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> NO)]	212	d.brown	Calculated	56.1	4.28	2.72	15.3	12.3	6.0
				Found	55.8	4.16	2.53	15.0	12.01	6.0
3	[CuI(PPh <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> NO)]	208	d.brown	Calculated	51.3	3.92	2.49	22.6	11.22	5.5
				Found	51.01	3.89	2.16	23.2	10.9	5.6
4	[Cu <sub>2</sub> Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> (C <sub>6</sub> H <sub>7</sub> NO)]	156	b.black	Calculated	68.8	5.0	1.9	4.84	8.67	3.0
				Found	68.1	5.01	1.7	4.71	8.80	3.2
5	[Cu <sub>2</sub> Br <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> (C <sub>6</sub> H <sub>7</sub> NO)]	192	d.brown	Calculated	61.0	4.4	1.81	13.3	10.76	7.8
				Found	59.81	4.21	1.07	14	10.5	7.9
6	[Cu <sub>2</sub> I <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> (C <sub>6</sub> H <sub>7</sub> NO)]	214	l.brown	Calculated	56.4	4.0	1.0	19.9	9.96	7.2
				Found	56.8	3.99	0.9	20.2	10.1	7.1
7	[Cu <sub>4</sub> (SCN) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>7</sub> NO)]	260	l.brown	Calculated	54	3.9	2.9	-	26.8	6.5
				Found	54.8	3.7	3	-	26.4	6.5
8	[Cu <sub>5</sub> (NO <sub>3</sub> ) <sub>5</sub> (PPh <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>7</sub> NO)]	210	black	Calculated	39.79	2.9	6.6	-	25	4.88
				Found	39.8	2.6	6.9	-	25	4.9

### Results and Discussion

All the complexes are air stable at room temperature and can be kept for months in well stoppered vials. They are soluble in common solvents such as ethanol, methanol, butanol and acetone and sparingly soluble in carbon tetrachloride, chloroform, benzene, cyclohexane, dimethylsulfoxide and nitrobenzene to the extent that solution spectra and conductance data could be obtained. This property suggests that ionic species are unlikely.

Various workers have studied the absorption spectra of aminophenol complexes. It is evident from the spectral data that copper is coordinated tetrahedrally. The IR spectral data in Table 2 represents the main features of the complexes.

On the basis of elemental analysis these complexes may be classified into three types. (1) [CuX(PPh<sub>3</sub>)(Amph)], (2) [Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>(Amph)] and (3) [Cu<sub>4</sub>(SCN)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>(Amph)] and [Cu<sub>5</sub>(NO<sub>3</sub>)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(Amph)].

The very low solubility of these complexes in common organic solvents precluded molecular weight determination. These complexes are usually dark brown or black in color, probably due to charge transfer since the complexes themselves are diamagnetic. Anion bridged dimers may be assumed to show distorted tetrahedral and pentagonal structures. Conductance measurements showed them to be non-ionic in nature.

In halo-tetrakis (triphenylphosphine) and halo bis (triphenyl phosphine) copper (I), there are three coordination groups in the monomeric formula which do not complete square coordination of copper and hence the bridged structure has to be assumed for them [15].

The reaction of tetrakis[halo(triphenylphosphine) copper (I)] [CuX(PPh<sub>3</sub>)<sub>4</sub>] with 2-aminophenol in equimolar quan-

ties gave compounds of the type [CuX(PPh<sub>3</sub>)(Amph)]; when the concentration of the ligand was doubled or increased to four fold in the above reaction still the same product was obtained as that from equimolar ratio.

The di-u-[halobis (triphenylphosphine) dicopper(I)] complexes when treated with aminophenol in equimolar ratio in benzene gave [Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>(Amph)]; on increasing the concentration of the ligand aminophenol itself separated out in case of chloro compound; whereas in bromo complex we get [CuBr(pph<sub>3</sub>)(Amph)]. The [CuI(PPh<sub>3</sub>)<sub>2</sub>] compound gave parent compound [CuI(PPh<sub>3</sub>)<sub>2</sub>] with some impurities of aminophenol crystallized out.

The absorption in the region 690-710 cm<sup>-1</sup> [16] attributed to out of plane ring deformations is observed in the region 690-700 cm<sup>-1</sup> in our complex. Shifts in the position of this peak coupled with an increase in intensity relative to the peak observed for the free ligand are a diagnostic of the coordination of triphenylphosphine [17].

According to Sheldon and Tyree [15] a band is observed near 720 cm<sup>-1</sup> whenever phosphine acts as a donor or it is in the four coordinated state. This band in our complexes occurs in association with the band of 698 cm<sup>-1</sup> in the form of a doublet at 740-750 cm<sup>-1</sup>.

Absorption in the region 1090 - 1105 cm<sup>-1</sup> of the complexes prepared indicate that phosphorus atom is coordinated to copper as discussed Deacons and Green [16] and the shifts to higher energies with the increased intensity supports the assumption that the phosphine groups are coordinated.

The absorption range for the O-H valence stretching vibration of an unbonded hydroxyl group is shown at 3700-3500cm<sup>-1</sup>[18]. Related work in this field suggests that stretching frequencies for free OH groups are within much narrower



limits and that the overall range may not be greater than 3650-3590 [19], 3636-3618 [20] and 3644-3605  $\text{cm}^{-1}$  [21].

The influence of aromatic ring also lowers the free OH frequency and the band occurs at 3616-3588  $\text{cm}^{-1}$ . The intermolecular hydrogen bond vibration in single bridge compounds appear around 3500  $\text{cm}^{-1}$  (v) sharp, while the polymeric association appears as a broad band at 3400-3200  $\text{cm}^{-1}$  [22].

An OH frequency of 2600  $\text{cm}^{-1}$  has also been found in compounds involving a chelated hydroxyl group and a heterocyclic nitrogen atom [23]. In many cases of this type the absence of any OH absorption in the fundamental region has been reported, presumably owing to its being a weak band which has been superimposed upon the strong CH stretching absorption near 3000  $\text{cm}^{-1}$ .

The OH deformation and C-O stretching absorptions of phenols are found at 1200  $\text{cm}^{-1}$  and 1410-1310  $\text{cm}^{-1}$ . In phenols, despite studies in a series of different states [24,25], there is still doubt as to whether the OH deformation mode may occur near 1200  $\text{cm}^{-1}$  or near 1350  $\text{cm}^{-1}$  as both these absorptions are sensitive to changes in the hydrogen bonding pattern. The 1075-1000  $\text{cm}^{-1}$  region is considered to C-O stretching mode [26,27] but others relate it to OH deforma-

tion [28]. in phenols the C-O stretching mode absorbs at higher frequencies under the influence of aromatic ring, therefore possibilities are for coupling between O-H and C-O frequencies or between C-O and aromatic ring vibration. In case of phenol, the 1180  $\text{cm}^{-1}$  band is regarded as the strongest O-H character possessing band [29]. The main coupling pattern in this case is probably the aromatic ring vibration at 1310  $\text{cm}^{-1}$ , although other aromatic absorption could also be involved.

2-aminophenol itself absorbs in 3400-2510  $\text{cm}^{-1}$  region giving two broad and one sharp doublet. The other main i.r bands are given in Table 2.

In the prepared complexes, the medium broad peak at 3420  $\text{cm}^{-1}$  is assigned for the O-H absorption and the C-H stretching vibrations [22]. The absorption bands found in the window region 2700-1850  $\text{cm}^{-1}$  are assigned to C=C vibrations. The 1410 and 1320  $\text{cm}^{-1}$  peaks are due to C-O stretching vibrations and the 1260  $\text{cm}^{-1}$  absorption is assigned to OH in plane deformation. As common 1460-1430, 745-740 and 690  $\text{cm}^{-1}$  peaks are due to triphenyl phosphine coordination.

The characteristic absorption at 1180  $\text{cm}^{-1}$  which has strongest OH character [30] is found in between 1180-1170

TABLE 2. COMPOUNDS AND THEIR IR ABSORPTION BANDS

S.No	Compounds	Bands
1.	$(\text{C}_6\text{H}_5)_3\text{P}$	3100 (s.qd) 1500-1400 (s. trip) 1080 (s) 1025 (s) 745 (s.db) 690-700 (s.db)
2.	$\text{NH}_2\text{C}_6\text{H}_4\text{OH}$	3400-2510 (br& 1db) 1600 (s) 1480 (s) 1430(s) 1380 (sh) 1300-1200 (2bd.s) 1150-1140 (db.s) 1080-1060 (db.s) 1030 (s) 920 (sm) 900, 850 (br.sh) 800,760,740 (db.s) 730(s)
3.	$[\text{CuCl}(\text{PPh}_3)(\text{Amph})_2]$	3420 (m.br) 3020 (trip.s) 1960 (db.s) 1900-1880 (db) 1586 (m) 1470(s) 1420(s) 1300 (s) 1180(s) 1150 (s) ?090 (s) 1060 (s) 1020 (s) 990(s) 910(s) 840 (s) 740 (s) 690 (db.s) 610 (m) 500 (db.br)420 (trip.)
4.	$[\text{CuBr}(\text{PPh}_3)(\text{Amph})]$	3380(s) 3280(s) 3020 (db) 2160-1580 (db) 1490 (s) 1460 (s) 1410 (s) 1390 (m) 1320 (m) 1300 (m)1270(sm)1260(s)1226(db.sm)1020(sh) 990(s)896(m)840(m)740(s)690(db.s)510(s)490(db) 430 (m)
5.	$[\text{CuI}(\text{PPh}_3)(\text{Amph})_2]$	3450 (s) 3290 (s) 3000 (s) 2580 (s) 1575 (s) 1480 (s) 1440 (s) 1400 (s) 1380 (s) 1260-1240 (db.s) 1200-1190 (db.s) 1120 (s) 1050-1040 (s) 1010 (s) 990 (s) 870 (s) 820 (s) 740 (s) 710 (s) 660 (s) 490
6.	$[\text{CuCl}_2(\text{PPh}_3)(\text{Amph})_2]$	3040 (s.trip) 1985 (m) 1880 (sm) 1650 (m) 1580 (s) 1560 (s) 1480 (s) 1560 (s) 1480 (s) 1425 (s) 1380 (s) 1270 (db.) 1180 (s) 1090 (s) 1060 (s) 1020 (s) 990 (s) 850 (s) 745 (s) 690-670 (db.s) 610 (s) 500-480 (trip) 460 (db)
7.	$[\text{Cu}_2\text{Br}_2(\text{PPh}_3)(\text{Amph})_2]$	3020 (s.trip) 1950 (sm) 1880 (br) 1800(br) 1650 (db) 1580 (sm) 1560 (sm) 1470 (s) 1420 (s) 1380 (sm) 1270 (sm) 1250 (s) 1180 (m) 1150 (s) 1090 (s) 1060 (s) 1020 (s) 990 (s) 960 (sm) 920 (sm) 850 (sm) 745 (sm) 670-690 (db.s) 610 (m) 480-500 (trip.s) 460 (db).
8.	$[\text{Cu}_2\text{I}_2(\text{PPh}_3)(\text{Amph})_2]$	3040 (s) 1950 (s) 1580 (s) 1477 (s) 1430 (s) 1380 (s) 1270-1250 (db.s) 1180 (db.s) 1090 (s) 1060 (s)1036(s) 1010(s) 990 (s) 870 (s) 745 (s) 690 (s) 610 (s) 490-470 (db.s)
9.	$[\text{Cu}_4\text{SCN}(\text{PPh}_3)_2(\text{Amph})]$	3280 (s) 3040 (s) 3100 (s) 1596 (s) 1480 (s) 1435 (s) 1180 (s) 1130 (s) 1098 (s) 1030 (s) 1000 (s) 742 (db.s) 690 (s)
10.	$[\text{Cu}_3(\text{NO}_3)_5(\text{PPh}_3)_2(\text{Amph})]$	3420 (s) 3020 (s) 2720 (s) 2320(s) 2070 (s) 1590 (s) 1485 (s) 1435 (s) 1380 (s) 1240 (s) 1160 (s) 1090 (s) 1050 (s) 1030 (s) 990 (s) 840 (s) 810 (s) 745 (s) 690 (s) 520 (s) 460



$\text{cm}^{-1}$ , this shift, of  $\pm 10 \text{ cm}^{-1}$  is due to coordination.

A sharp peak in the region  $840\text{-}830 \text{ cm}^{-1}$  in our complexes has been shown by other workers in the metal chelates ranging from  $870\text{-}850 \text{ cm}^{-1}$ , is assigned to a diatomic vibration possibly due to the carbon oxygen bond or a metal oxygen stretching frequency. Secondly due to the presence of amino group, the bonding may be through the nitrogen of amino group, showing absorption in  $800 \text{ cm}^{-1}$  region, thus we can say that aminophenol may act as a bidentate ligand, bonded, through oxygen of the OH and nitrogen of the  $\text{NH}_2$  group.

Although in all the compounds there is a strong absorption in  $830 - 800 \text{ cm}^{-1}$  region, but it has been found in the literature that if there is a strong band in  $2600 \text{ cm}^{-1}$  region, for OH frequency then there is a chelated hydroxyl group [31], as no such band is observed in our complexes except nitrate complex, so we can say that aminophenol is acting as a monodentate ligand and the band at  $840 - 800 \text{ cm}^{-1}$  is due to M-O bonding. The proposed structure for the halo compounds could be an anionic bridged dimer or polymer.

For  $[\text{CuCl}(\text{PPh}_3)_2(\text{Amph})]$ , the compound have square planar structure, with  $D_{2h}$  symmetry and  $\text{dsp}^2$  hybridization.

The reaction of aminophenol with di-u-[thiocyanatobis (triphenylphosphine) dicopper (I)] in excess (4 mole) gave the compound  $[\text{Cu}_4(\text{SCN})_4(\text{PPh}_3)_2(\text{Amph})]$ . The i.r. spectrum of the compound shows strong absorption in the thiocyanate C-N region at  $2108 \text{ cm}^{-1}$  and no absorption in  $800 \text{ cm}^{-1}$  region proposed it a S bonded ligand. Similarly no absorption at  $2600 \text{ cm}^{-1}$  characterized that aminophenol is acting as a non-chelated ligand. Band at this energy suggests that sulphur bonded groups are determined by Mitchell and Williams [32]. It is expected that N-bonding of Cu(I) may facilitate the  $\pi$ -acceptor behavior of triphenylphosphine and may favor S-coordination.

The spectrum of the complex presents a strong band at lower frequency than the value required for a bridging thiocyanato group as stated in case of  $(\text{NH}_4)[\text{Cd}(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$  [33] it may be due to the presence of 2 ligands having a large difference in basicity and in a bonding ability towards the copper (II) atoms. Similar results were obtained by Toeindiskoetter and Solomon [34] when examining several complexes of N-heterocyclic amines with Cu(I) and Cu(II) thiocyanates.

In case of nitrate complex  $[\text{Cu}_5(\text{NO}_3)_5(\text{PPh}_3)_2(\text{Amph})]$  there may be two possible structures to be considered; tricoordinate monomer and a nitrate bridged dimer.  $[\text{CuNO}_3(\text{PPh}_3)_2]$  on the basis of X-ray analysis has shown to contain tetrahedrally coordinated copper (I) and a bidentate nitrate group [35]. In the present nitrate complexes bands at  $1284 \text{ cm}^{-1}$  supported the bidentate nature of  $\text{NO}_3$  [36]. Simi-

larly the absorption at  $2720 \text{ cm}^{-1}$  and  $2070 \text{ cm}^{-1}$  is found only in this compound confirming the chelating nature of aminophenol along with the absorption at  $810\text{-}800 \text{ cm}^{-1}$  confirming the bidentate nature of  $\text{NO}_3$  ion. On the basis of this IR knowledge we may suggest the structure of  $(\text{Cu}_5(\text{NO}_3)_5(\text{PPh}_3)_2(\text{Amph}))$  with a distorted pentacoordinated shape. In conclusion we can say, in aminophenol complexes, only in nitrate compound, this ligand act as a bidentate, otherwise it appeared as a monodentate ligand in halo and thiocyanato compounds.

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