

COPPER(I) COMPLEXES OF TRIPHENYLPHOSPHINE AND 2-METHYLPYRIDINE

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Copper (I) complexes with triphenylphosphine and α -picoline have been prepared. The variation in stoichiometry and the probable structures of these complexes have been discussed on the basis of their chemical and spectral data; these complexes have been suggested to have dimeric structure and the experimental data are in support of the bridging of halides, nitrate or thiocyanate groups between the two copper atoms.

Key words: Copper Complexes, Triphenylphosphine, Methylpyridine.

Introduction

Copper(I) forms different types of complexes with metal ligand ratio of 1:1, 1:2, 1:3 and 1:4 having a tetrahedral configuration with a coordination number of four.

Complexes like $\text{CuI}(\text{PMe}_2\text{Ph})_2$ [1], $[\text{CuI}(\text{NMeC}_6\text{H}_4\text{PMe}_2)_2]$ [2] and $\text{CuSCN}(\text{PPh}_3)_2$ [3] are non-electrolytes and not necessarily monomeric; rather there are strong indications that these complexes may have bridged structures.

The mixed ligand complexes of the type $[\text{CuNO}_3(\text{PPh}_3)(\text{biL})]$ [4], $[\text{CuI}(\text{PPh}_3)(\text{Py})]$ [5], $[\text{CuX}(\text{PPh}_3)(\text{HOx})_2]$ [6] and $[\text{AgX}(\text{PPh}_3)_y(\text{HOx})_z]_n$ [7] $[\text{AgX}(\text{PPh}_3)(\text{An})_2]$ [8] $[\text{CuX}(\text{PPh}_3)(\text{Quin})_n]$ [9] {where X = Cl⁻, Br⁻, I⁻, NO₃⁻ and SCN⁻; PPh₃ = triphenylphosphine, biL = 1, 10 phenanthroline or 2, 2-biquinoyl; Py = pyridine; HOx = 8-hydroxyquinoline; An = aniline and Quin = quinoline} have been reported.

The complexes of copper(I) containing mixed ligands are reported here. The ligands introduced are triphenylphosphine and 2-methylpyridine (C₆H₇N). 2-Methylpyridine forms different compounds with copper triphenylphosphine with the ratio 1:1, 2:1 and also in little excess. The infrared spectral studies in the region 4000-700 cm⁻¹ suggest that copper(I) has the coordination number 4, 5 and 6 in these complexes. They are sparingly soluble in most of the organic solvents consistent with a polymeric character.

Experimental

A. $[\text{Cu}_2\text{X}_2(\text{PPh}_3)_2(\text{Mepy})]$: (X = Cl⁻, Br⁻ or I⁻) was prepared by stirring under reflux equimolar quantities of tetrakis[halo(triphenylphosphine) copper(I)] [5] and 2-methylpyridine in benzene for 4-5 hrs. The mother liquor after several crystallization gave the crystalline product of the above formula; melting points were determined.

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B. $[\text{CuX}(\text{PPh}_3)_2(\text{Mepy})]$: (X = Cl⁻, Br⁻ or I⁻) was obtained in crystalline state from the mother liquor, on addition of methylpyridine to di- μ -[halobis(triphenylphosphine) copper(I)] [5] in equimolar ratio in benzene and refluxing the resultant solution for 3-4 h. Crystals were washed with benzene followed by diethylether and dried.

C. $[\text{CuZ}(\text{PPh}_3)_2(\text{Mepy})]$: (Z = NO₃⁻ or SCN⁻) was obtained by refluxing excess (4 moles) of methylpyridine with one mole of di- μ -[nitratobis(triphenylphosphine)copper (I)] [4] in ethanol for 4-5 hrs. and crystallizing at room temperature; m.p. 222°C.

For the thiocyanato complex, chloroform was used in place of ethanol; m.p. 274°C.

The IR spectra were recorded in KBr discs using a Perkin Elmer Spectrophotometer. Carbon, hydrogen and nitrogen were estimated by micro analytical method on C, H and N analyzer. Copper was estimated spectrophotometrically using atomic absorption spectrophotometer at the absorption line of 324.8 nm (Table 1). Phosphorous estimation was carried out spectrophotometrically by the Heteropoly Blue Method [10] using a Shimadzu SP 160 Spectrophotometer. 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.

Results and Discussion

The complexes are light coloured, diamagnetic and non-ionic in nitrobenzene. It was not possible to differentiate between cis and trans isomers using the technique of dipole moment due to the insolubility of the complexes in non polar solvents. Some of these complexes may have anionic bridging structure as the more basic and weaker π bonding monodentate 2-methylpyridine may tend to lower the effective coordination number of copper(I), thus favouring a

TABLE I. ANALYTICAL DATA OF COPPER PHOSPHINE METHYLPYRIDINE COMPLEXES

No	Compound	M.Pt.°C (Colour)	Found (Calc.), %					
			C	H	N	X	Cu	P
1	[Cu ₂ Cl ₂ (PPh ₃) ₂ (C ₆ H ₇ N)]	224 light green	61.5 (61.8)	4.2 (4.5)	1.5 (1.7)	8.1 (8.5)	15.0 (15.5)	7.5 (7.6)
2	[Cu ₂ Br ₂ (PPh ₃) ₂ (C ₆ H ₇ N)]	232 light green	56 (55.8)	4.3 (4.1)	2.1 (1.5)	17.6 (17.5)	14.4 (14)	6.9 (6.8)
3	[Cu ₂ I ₂ (PPh ₃) ₂ (C ₆ H ₇ N)]	190 white	62.5 (62.3)	4.2 (4.5)	1.8 (1.73)	16.1 (16.3)	8 (7.8)	8 (7.6)
4	[CuCl(PPh ₃) ₂ (C ₆ H ₇ N)]	156 yellow	68.7 (68.7)	4.9 (5.1)	1.8 (1.95)	5.0 (4.95)	9 (8.8)	7.4 (7.3)
5	[CuBr(PPh ₃) ₂ (C ₆ H ₇ N)]	228 light green	66.0 (66.3)	4.5 (4.8)	7.5 (1.8)	10 (10.3)	8.1 (8.3)	7.9 (8.1)
6	[CuI(PPh ₃) ₂ (C ₆ H ₇ N)]	184 white	62.6 (62.3)	4.2 (4.5)	1.7 (1.73)	16.7 (16.5)	7.6 (7.8)	7.5 (7.6)
7	[Cu ₄ (SCN) ₂ (PPh ₃) ₂ (C ₆ H ₇ N)]	270 white	53.2 (53.4)	3.5 (3.7)	4.7 (4.2)	- -	25.2 (25.7)	6.1 (6.2)
8	[Cu ₄ (NO ₃) ₂ (PPh ₃) ₂ (C ₆ H ₇ N)]	222 white	49.9 (50.4)	3.3 (3.7)	4.0 (4.2)	- (-)	24.9 (25.4)	5.9 (6.2)

dimeric form required to satisfy the coordination number four and the effective atomic number for copper(I) [11].

The complex [CuCl(PPh₃)₂]₂ when treated with 2-methylpyridine in equimolar ratio gave [Cu₂Cl₂(PPh₃)₂(Mepy)] m.p. 224°C and with excess of the ligand (1:5, M:L), the compound [CuCl(PPh₃)₂] crystallized out, whereas the bromo compound gave [Cu₂Br₂(PPh₃)₂(Mepy)], m.p. 212°C.

When methyl pyridine was added to CuI(PPh₃)₂, it gave the compound [Cu₂I₂(PPh₃)₂(Mepy)]; m.p. 180°C.

On addition of methylpyridine to di-μ-[halobis(triphenylphosphine)copper(I)] [CuX(PPh₃)₂]₂ in equimolar ratio the compounds so formed were [CuX(PPh₃)₂(Mepy)] and when excess of methylpyridine was used then the compounds of the same formula alongwith traces of methylpyridine were obtained.

The addition of excess of methylpyridine in [CuNO₃(PPh₃)₂]₂ in ethanol gave [Cu₄(NO₃)₂(PPh₃)₂(Mepy)], whereas the thiocyanato compound in chloroform resulted in [Cu₄(SCN)₂(PPh₃)₂(Mepy)].

The effect of coordination on the IR spectrum of triphenylphosphine has been discussed by Deacons and Green [12]. According to them the sensitive modes are P-C stretching vibrations at 1089 and 698 cm⁻¹, the phenyl ring directly attached to the phosphorous atom displaying an unusually sharp and relatively strong aromatic band at 1430 cm⁻¹.

A weak but sharp band at 2780 cm⁻¹ is also apparent due to the shift of the carbon hydrogen assymmetric bending vibration. In the synthesized complexes, a sharp band at 690 cm⁻¹ is assigned to C-H out of plane bending vibration of the aro-

matic ring. The bands at 1430-1110 and 1000 cm⁻¹ in case of halo compounds and 1430, 1095-1120 and 1010-1000 cm⁻¹ in nitrate and thiocyanato compounds respectively are assigned to phosphine absorption. The shift of the absorption may be attributed to the coordination of phosphine as a monodentate or a bridging ligand.

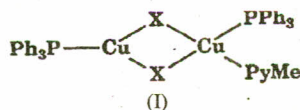
In the infrared region, pyridine and picoline all show C-H absorptions in the range 3070-3020 cm⁻¹ which appear as a series of multiple absorptions under high resolution [13]. The C-H out of plane bending vibrations in 781-740, 752-746 cm⁻¹ is assigned for 2-substituted pyridine. The main absorption bands of α-picoline appearing in 1600-1590 cm⁻¹ and 1500 cm⁻¹ are due to C=C and C=N interactions; 1240 cm⁻¹ and 1043 cm⁻¹ are due to ring vibration or hydrogen deformation and the N-H and C-H stretching vibrations in 4000-3000 cm⁻¹ region (Table 2).

In the synthesized complexes, the halo compounds show sharp absorption in 3040-3020 cm⁻¹ region, whereas the bands at 1580 and 1480 cm⁻¹ are due to the C=C and C=N absorptions. All the absorption bands below 1000 cm⁻¹ are assigned to C-H deformation of both the ligands. The sharp peaks in 550 - 400 cm⁻¹ region show the M-X linkage whereas X behaves as a bridging ligand. On the basis of spectral studies and elemental analysis the proposed structure for the halo compounds [Cu₂X₂(PPh₃)₂(C₆H₇N)] (Structure I) is a halo bridged dimer. This structure is proposed on the basis of the reported Cu₂Cl₂(PPh₃)₃ [14,15]; while the other compound [CuX(PPh₃)₂(C₆H₇N)]₂ may be considered as a simple square planar structure with dsp² hybridization or a square pyramid with anion bridging.

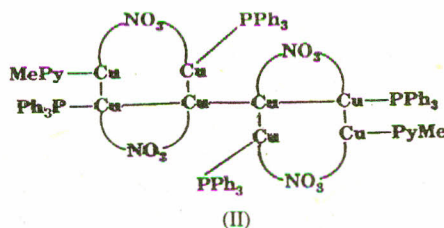
TABLE 2. INFRARED SPECTRA OF COPPER TRIPHENYLPHOSPHINE METHYLPYRIDINE COMPLEXES

S No	Compounds	Bands
1.	$[\text{Cu}_2\text{Cl}_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3060 (s) 1960 (s.br) 1880 (s) 1820 (s) 1580 (s) 1480 (s) 1438 (s) 1310 (s) 1180 (s) 1120 (s) 1098 (s) 1028 (s) 1000(s) 760 740 (db) 690 (s) 520-490 (db.s)
2.	$[\text{Cu}_2\text{Br}_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3040 (s) 1580 (m) 1478 (s) 1430 (s) 1180 (s) 1095 (s) 1020 (s) 998 (s) 740 (s) 690 (s) 580 (s) 490 (s.db)
3.	$[\text{Cu}_2\text{I}_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3050 (s) 1590 (s) 1480 (s) 1430 (s) 1196 (s) 158 (s) 1090 (s) 1082 (s) 1000 (db.s) 742 (s.db) 690 (s.db) 570 (s) 440 (s)
4.	$[\text{CuCl}(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3060 (s.sm) 1960 (s) 1880 (s) 1820 (s) 1580 (s) 1480 (s) 1438 (s) 1310 (s) 1180 (s) 1120 (s) 1098 (s) 1028 (s) 1000 (s) 760 (s) 740 (s.db) 690 (s) 510 (s) 430 (s)
5.	$[\text{CuBr}(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3040 (s) 1580 (m) 1478 (s) 1430 (s) 1180 (s) 1095 (s) 1020 (s) 998 (s) 740 (s) 690 (s) 570 (s) 480 (s)
6.	$[\text{CuI}(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3020 (m) 1580 (m) 1480 (s) 1430 (s) 1300 (s.sm) 1180 (s) 1150 (m.s) 1090 (s) 1020 (m) 990 (m) 740 (s) 680 (s) 580 (s) 480 (s) 430 (s)
7.	$[\text{Cu}_4(\text{SCN})_2(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{N})]$	3040 (m) 2100 (s) 1580 (s) 1480 (s) 1430 (s) 1418 (s) 1180 (qd.s) 1120 (qd.s) 1098 (qd.s) 1020 (s) 998 (s) 738 (db.s) 690 (s)
8.	$[\text{Cu}_4(\text{NO}_3)_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]$	3050 (m) 1590 (s) 1570 (s) 1478 (s) 1460 (db.s) 1438 (s) 1380 (s) 1290 (db.s) 1100 (s) 1070 (m.s) 1020 (s) 1000 (s) 970 (m.s) 805 (s) 738-742 (db.s) 690-710 (db.s)
9.	2-methylpyridine	4000-3000 (s) 1600-1590 (s) 1500-1400 (2db) 1380-1300 (s.b) 1200-1000 (4 s.qd) 850-700 (2 s.db)

s = sharp; br = broad; sm = small; db = doublet; qd = quadruplet

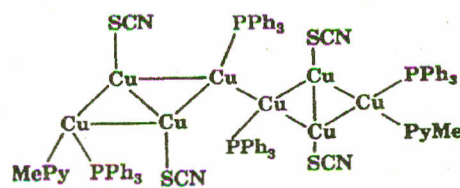


In the nitrate compound $[\text{Cu}_4(\text{NO}_3)_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]_2$, there is a sharp doublet at 720 cm^{-1} for NO_2 bending vibration while the N-O stretching vibrations are observed in $1390\text{--}1370\text{ cm}^{-1}$ region and two sharp peaks at 1550 cm^{-1} for N=O stretching band. It has been noted that the absorption at 1360 cm^{-1} and 810 cm^{-1} is an indication of the presence of a bidentate group [16] which appeared at $1390\text{--}1370\text{ cm}^{-1}$ and 850 cm^{-1} in our compounds showing that NO_3 acts as a bridging group using its nitrogen and oxygen terminal. The proposed structure for this compound is shown in Structure II.



The thiocyanate compound $[\text{Cu}_4(\text{SCN})_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]_2$ also shows similar absorption as that of halo compounds along with the characteristic peak at 2100 cm^{-1} . Chatt and coworkers [17] and later Vallarino [18] have shown that C-N stretching frequency is at $2182\text{--}2150\text{ cm}^{-1}$ when thiocyanato group is bridging and in the range $2150\text{--}2100\text{ cm}^{-1}$ when it acts as a

monodentate ligand. The other question is that of coordination via N or S of the thiocyanate ion. Such situation is faced and studied during the synthesis of Pt(II) and Pd(II) cyanate compounds [19]; this study reveals that if the bonding is of the type M-SCN, the absorption would be in $720\text{--}690\text{ cm}^{-1}$ region, while if it is of the type M-NCS, then the absorption appeared at $860\text{--}780\text{ cm}^{-1}$ region. In our compounds, the absorption falls in $720\text{--}690\text{ cm}^{-1}$ region showing M-S linkage, which is further confirmed on the basis of Lewis acid base concept. Since copper(I) is a soft acid, it has a greater affinity towards the soft base 'S' as compared to hard base 'N'. After conformation that SCN is acting as a monodentate group, we propose the structure for $[\text{Cu}_4(\text{SCN})_2(\text{PPh}_3)_2(\text{C}_6\text{H}_7\text{N})]_2$ as shown in structure III.



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