

CIS AND TRANS COMPLEXES OF COPPER(I)

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Abstract. Three different forms of bridged complex $[\text{CuI}(\text{Py})(\text{PPh}_3)]_2$ have been prepared for the first time through three different routes, and were identified as *cis*-symmetric, *trans*-symmetric, and unsymmetric bridged species on the basis of their reaction with thiourea. Also the preparation of the complexes $\text{CuIBrCu}(\text{Py})_2(\text{PPh}_3)_2$ and $\text{AgICuI}(\text{PPh}_3)_4$ suggest the presence of a double halogen-bridge in the complexes of copper(I) with ligand-metal ratio of 2:1.

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

Complexes like $\text{CuI}(\text{PMe}_2\text{Ph})_2$,¹ $\text{CuI}(\text{NMeC}_6\text{H}_4\text{-PMe}_2)_2$ and $\text{CuSCN}(\text{PPh}_3)_2$ ³ are nonelectrolytes and not necessarily monomeric; rather, there are strong indications that these complexes may have bridged structures. On the other hand complexes like $\text{CuNO}_3\text{-}(\text{PPh}_3)_2$ ⁴ and $\text{CuCH}_3\text{COO}(\text{PPh}_3)_2$ ⁵ have been shown to contain a four-coordinated copper(I) with bidentate nitrate and acetate groups, respectively. In view of the uncertainty of having tricoordinate copper or a bridging structure in the complex $\text{CuI}(\text{PPh}_3)_2$, pyridine was reacted with it to obtain mixed-ligand complexes of the type $[\text{CuX}(\text{Py})(\text{PPh}_3)]_2$. The complexes were obtained through three different routes and in each case these had the same stoichiometry, $[\text{CuI}(\text{Py})(\text{PPh}_3)]_2$. However, it was noticed that the three complexes differ in their physical and chemical properties.

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 nonpolar solvents. Therefore, they were distinguished by their behaviour towards thiourea, a well-known Kurnakov's test.⁶

Complexes having mixed anions like $\text{CuIBrCu}(\text{Py})_2\text{-}(\text{PPh}_3)_2$, and also mixed-metal complexes such as $\text{CuI}(\text{AgI}(\text{PPh}_3)_4)$, have also been prepared. The presence of such complexes strongly supports a bridged dimeric structure rather than a tricoordinated monomeric structure for the above-mentioned complexes.

Results and Discussions

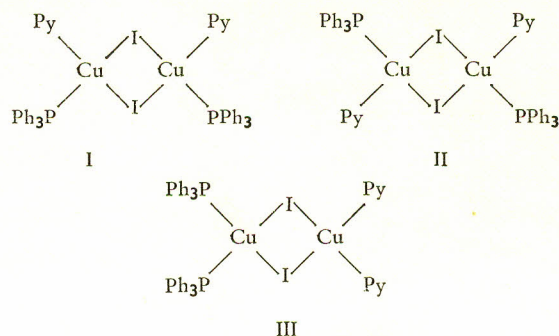
The complex $[\text{CuI}(\text{Py})(\text{PPh}_3)]_2$ was prepared through three different routes, i.e. by treating $[\text{CuI}(\text{Py})_2]_2$ with triphenylphosphine, or by treating $[\text{CuI}(\text{PPh}_3)_2]_2$ with pyridine and also by refluxing a mixture of $[\text{CuI}(\text{Py})_2]_2$ and $[\text{CuI}(\text{PPh}_3)_2]_2$. All the reactions were carried out in methanol. The complexes are white, diamagnetic and nonionic in nitrobenzene, and have the general formula $[\text{CuX}(\text{Py})(\text{PPh}_3)]_2$. There is a large difference in their m.p.s. suggesting that three isomeric forms must exist. The three complexes do not have identical IR spectra (Table 1). The complexes may be dimers with a

halogen-bridging structure as also indicated by their observed molecular weight which is higher than required for a monomer.

It seems likely that the more basic and weaker π -bonding monodentate ligands (e.g. pyridine) tend to lower the effective coordination number of copper(I), thus favouring a dimeric form required to satisfy the coordination number four and the effective atomic number⁷ for copper(I).

Chatt,⁸ Purdie⁹ and Cull¹⁰ suggest that *cis*- and *trans*-isomers have different physical and chemical characteristics, for example they melt at different temperature, and their rate of solubility is different in different solvents. Such behaviour was also noticed in the complexes prepared here (Table 2).

Three isomeric forms of the bridged complexes $[\text{CuI}(\text{Py})(\text{PPh}_3)]_2$ can theoretically exist.



Thus dipyridinebis(triphenylphosphine)diiodo-dicopper, $[(\text{Py})_2(\text{PPh}_3)_2(\text{CuI})_2]$, could have the *cis*-symmetric form I, the *trans*-symmetric form II, and the unsymmetric form III.

Due to the insolubility of the complexes in nonpolar solvents, the technique of dipole moment could not be applied to differentiate between *cis*- and *trans*-isomers. Therefore, each of the three isomeric forms of the complexes was reacted with thiourea. According to Mellor,¹⁰ this reaction has been used by various investigators¹² to differentiate between *cis*- and *trans*-isomers.

The reaction of these complexes with thiourea gives different products, again suggesting three possible isomeric forms. The work can be compared with the work of Chernyaev,⁹ who demonstrated the synthesis of three possible isomers of $[\text{Pt}(\text{NH}_3)(\text{Py})(\text{NH}_2\text{OH})(\text{NO}_2)]\text{Cl}$. However, the platinum(II) complexes are

TABLE 1. PHYSICAL PROPERTIES OF SOME HALOGENO COMPLEXES.

Compound	Formula weight		Main IR bands (cm ⁻¹) in KBr.
	Required for monomer	Found	
[CuI(Py) ₂] ₂	348.5	a	1600(s), 1480(m), 1437(s), 1270(m), 1150(w), 1070(m), 1035(m), 1010(w), 755(m), 750(m), 690(s).
[CuI(PPh ₃) ₂] ₂	715.08	1002.23	1625(w), 1488(s), 1430(s), 1330(w), 1320(w), 1165(w), 1100(s), 850(w), 745(s), 690(s).
<i>Cis</i> [CuI(Py)(PPh ₃) ₂] ₂	531.29	848.20	1590(s), 1470(s), 1435(m), 1430(m), 1210(m), 1180(w), 1090(s), 1062(m), 1035(w), 1025(w), 1005(w), 995(w), 945(w), 750(s), 700(s).
<i>Trans</i> [CuI(Py)(PPh ₃) ₂] ₂	531.29	914.61	1590(m), 1475(s), 1440(m), 1430(m), 1210(w), 1185(w), 1095(m), 1065(w), 1035(w), 750(s), 700(s).
Unsym[CuI(Py)(PPh ₃) ₂] ₂	531.29	736.31	1590(m), 1475(s), 1435(w), 1430(w), 1210(w), 1200-1180(m), 1120(m), 1090(m), 1060(m), 1035(w), 1025(w), 1005 995(w), 945(w), 725(m), 700(s).

a, Insoluble; s, strong; m, medium; w, weak.

TABLE 2. APPROXIMATE SOLUBILITY OF [CuI(Py)(PPh₃)₂] COMPLEXES (g/100 ml).

Compounds	Solvents						
	Water	Alcohol	Ether	Acetone	Benzene	Chloroform	Carbon tetrachloride
<i>Cis</i> [CuI(Py)(PPh ₃) ₂] ₂	a	0.002	a	0.1	0.001	a	a
<i>Trans</i> [CuI(Py)(PPh ₃) ₂] ₂	a	0.001	0.001	0.09	0.01	0.001	a
Unsym[CuI(Py)(PPh ₃) ₂] ₂	a	a	a	0.1	a	a	a

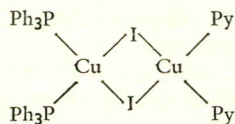
b, Insoluble.

planar and monomeric whereas the copper(I) complexes are tetrahedral and dimeric, sharing one edge of the tetrahedron.

The product obtained by the reaction of the complex [CuI(PPh₃)(Py)]₂, obtained from [CuI(PPh₃)₂] and pyridine had formula Cu₂I₂(Py)(PPh₃)₂Tu. This was confirmed by the IR spectrum and elemental analysis of nitrogen and phosphorus.

The reaction of the other isomer, obtained by the reaction of [CuI(Py)₂]₂ with triphenylphosphine gave with thiourea a different complex (CuI(PPh₃)₂Tu)₂. The two different products obtained show the presence of *cis*- and *trans*-isomers. In the second case pyridine is displaced by thiourea showing the *trans*-effect.¹³

The third isomer obtained by the reaction of CuI(PPh₃)₂ with CuI(Py)₂, fail to react even with a large quantity of thiourea, or refluxing it for a longer time, led to the idea of having an unsymmetrical structure.



The complex (Py)₂CuIBrCu(PPh₃)₂ was prepared

in order to obtain more support for the bridging structure suggested for copper(I) complex as with various ligands, having ligand-metal ratio 2:1. Thus another set of three isomers were obtained; these were established to be the *cis*-symmetric, *trans*-symmetric, and unsymmetric form respectively on the basis of their reaction with thiourea and of the study of the products formed.

In this respects a halogen bridged structure in the complexes of copper(I) with various ligands having ligand-metal ratio 2:1 and a general formula ML₂ seems reasonable to satisfy a coordination number of four for copper(I).

The reaction of a second metal as silver on the bridging complexes of the type CuI(PPh₃)₂ was also tried and was found to be applicable to achieve mixed-metal-halogeno-bridged complexes such as CuIAGl(PPh₃)₄.

The effect of coordination on the IR spectrum of triphenylphosphine have been discussed by Deacon and Green.¹⁴ According to these authors, the sensitive modes are P—C stretching vibrations at 1089 and 698 cm⁻¹. The former increases in both frequency and intensity, while the latter moves also to higher frequencies. This shift in P—C stretching vibrations to 1100 cm⁻¹ has been observed in all triphenylphosphine complexes prepared here (Table 3).

TABLE 3. PHYSICAL PROPERTIES OF HALOGENO COPPER(I) COMPLEXES.

Compound	Formula weight		Main IR bands (cm ⁻¹) in KBr.
	Required	Found	
Cu ₂ I ₂ (PPh ₃) ₂ (Tu) ₂	1057.84	698.93	1610-1590(s), 1472(s), 1440(m), 1430(m), 1390-1375(s), 1095(m), 745(m), 715(m).
Cu ₂ I ₂ (PPh ₃) ₂ (Tu)(Py)	1060.71	801.23	1620(s), 1600(s), 1472(s), 1440(m), 1430(s), 1405-1390(s), 1325(w), 1305(w), 1180(w), 1155(m), 1090(s), 1065(w), 1025(m), 995(w), 850(w), 745(s), 720(m) 695(s).
(Py) ₂ CuI ₂ BrCu(Py) ₂	648	a	1590(s), 1480(s), 1460(m), 1445(s), 1380(s), 1360(w), 1235(w), 1215(s), 1155(m), 1070(s), 1040(s), 1010(m), 750(s), 700(s).
(PPh ₃) ₂ CuI ₂ BrCu(PPh ₃) ₂	1381.16	1120	1465(w), 13430(m), 1375(s), 1180(w), 1160(w), 1150(s), 1070(w), 1030(m), 1010(w), 860(w), 750(s), 725(w), 700(s).
<i>Cis</i> (PPh ₃) ₂ Cu ₂ I ₂ Br(Py) ₂	1014.58	817.70	1590(s), 1460(w), 1440(w), 1370(s), 1210(m), 1145(w), 1100(m), 1060(m), 1030(m), 1005(w), 750(s), 645(s).
<i>Trans</i> (PPh ₃) ₂ Cu ₂ I ₂ Br(Py) ₂	1014.58	845.9	1590(s), 1460(w), 1440(m), 1430(m), 1370(s), 1305(vw), 1205(m), 1180(w), 1150(w), 1090(s), 1060(m), 1030(w), 1020(w), 990(w), 940(w), 850(w), 750(s), 710(m), 700(m).
Unsym(PPh ₃) ₂ Cu ₂ I ₂ Br(Py) ₂	1014.58	743.3	1590(m), 1460(w), 1440(w), 1370(s), 1205(w), 1115(w), 1090(m), 1060(w), 1030(w), 750(s), 720(m) 700(s).
Cu ₂ I ₂ Br(PPh ₃) ₂ (Tu)(Py)	1013.71	817.8	1620(s), 1600(s), 1580(w), 1480(w), 1465(w), 1445(w), 1430(w), 1375(m), 1330(w), 1310(m), 1190(w), 1160(m), 1090(s), 1070(w), 1030(s), 1000(m), 970(w), 855(m), 755(w), 750(s), 735(s), 700(s).
Cu ₂ I ₂ Br(PPh ₃) ₂ (Tu) ₂	1010.84	827	1615-1595(s), 1465(w), 1440(w), 1400-1380(s), 1095(m), 750(s), 715(s), 710(s).
CuI ₂ AgI(PPh ₃) ₄	1474.16	975	1520(s), 1450(s), 1190(w), 1165(w), 1100(s), 1035(m), 1010(m), 745(s), 695(s).

s, strong; m, medium; w, weak

Experimental

[CuI(PPh₃)₂]₂. Di- μ -iodotetrakis(triphenylphosphine)dicopper(I) was prepared by refluxing copper(I) dissolved in KI and triphenylphosphine in methanol in the ratio of 1:2 respectively. White shining crystals obtained (Table 4).

[CuI(Py)₂]₂. Di- μ -iodotetrakis(pyridine)dicopper(I) was prepared by refluxing copper iodide dissolved in KI and pyridine in methanol taken as 1:2 molar respectively. Dirty white powder obtained after 4 hr.

Cis[CuI(Py)(PPh₃)]₂. *Cis*-di- μ -bis[(pyridine)(triphenylphosphine)]dicopper(I) was obtained by the reaction of pyridine (in slight excess) with di- μ -iodotetrakis(triphenylphosphine) (1 mole) in presence of methanol. White powder obtained washed and dried.

Trans[CuI(Py)(PPh₃)]₂. Di- μ -iodobis[(pyridine)(triphenylphosphine)]dicopper(I) was obtained by refluxing di- μ -iodotetrakis(pyridine)dicopper(I) with triphenylphosphine in methanol taken in the ratio of 1:0.5 molar for 4 hr.

Unsymmetrical[CuI(Py)(PPh₃)]₂. Unsymmetrical di- μ -iodobis-[(pyridine)(triphenylphosphine)]dicopper(I)

prepared by refluxing di- μ -tetrakis(pyridine)dicopper(I) and di- μ -tetrakis(triphenylphosphine)dicopper(I) taken in the ratio of 1:0.25 in methanol for about 4 hr.

[Cu₂I₂(PPh₃)₂(Tu)₂]. Di- μ -iodobis[(triphenylphosphine)(thiourea)]dicopper(I) was obtained by refluxing *trans*-di- μ -iodobis[(pyridine)(triphenylphosphine)]dicopper(I) (1 mole) with thiourea (5 mole) dissolved in methanol for 3 hr. Shining crystals obtained at room temperature.

Cu₂I₂(Py)(PPh₃)₂(Tu). Di- μ -diiodo(pyridine)bis(triphenylphosphine)thiourea dicopper(I) was obtained by treating *cis*-di- μ -iodobis[(pyridine)(triphenylphosphine)]dicopper(I) (1 mole) with thiourea (5 mole) dissolved in methanol for 3 hr. White shining crystal obtained at room temperature.

(Py)₂CuI₂BrCu(Py)₂. Iodo-bromotetrakis(pyridine)dicopper(I) was obtained by the reaction of KBr (0.25 mole) with di- μ -tetrakis(pyridine)dicopper (I) (1 mole) in methanol.

(PPh₃)₂CuI₂BrCu(PPh₃)₂. Bromo-iodotetrakis(triphenylphosphine)dicopper(I) was prepared by the reaction of potassium iodide (0.25 mole) on di- μ -bromotetrakis(triphenylphosphine)dicopper(I) in methanol.

TABLE 4. ANALYSIS.

Complex	M.ps.°C	Calculated(%)					Found (%)				
		C	H	N	Cu	Halogen	C	H	N	Cu	Halogen
[Cu(Py) ₂] ₂	200			8.03	18.22	36.16			7.79	18.10	36.0
[Cu(PPh ₃) ₂] ₂	220				8.88	17.76				8.86	17.72
<i>Cis</i> [Cu(Py)(PPh ₃) ₂] ₂	230	51.9	3.72	2.63	11.94	23.97	51.98	3.70	2.52	11.9	23.95
<i>Trans</i> [Cu(Py)(PPh ₃) ₂] ₂	198-200	51.9	3.72	2.63	11.94	23.97	51.76	3.60	2.55	11.9	23.98
Unsym[Cu(Py)(PPh ₃) ₂] ₂	304-305	51.9	3.72	2.63	11.94	23.97	51.89	3.65	2.60	11.91	23.96
Cu ₂ I ₂ (PPh ₃) ₂ (Py)(Tu)	250			3.96	11.98	26.96			3.90	11.89	26.82
[Cu(PPh ₃)(Tu)] ₂	190			5.35	12.19	24.20			5.26	12.06	24.16
Cu ₂ I ₂ Br(Py) ₄	196(d)			10.56	23.96	23.96			10.39	23.66	23.52
						I					Br
Cu ₂ I ₂ Br(PPh ₃) ₄	256-258				9.19	9.19	5.78		9.00	8.98	5.52
<i>Cis</i> [Cu ₂ I ₂ Br(Py) ₂ (PPh ₃) ₂]	232			2.75	12.49	12.49	7.87		2.52	12.26	12.21
<i>Trans</i> [Cu ₂ I ₂ Br(Py) ₂ (PPh ₃) ₂]	200(d)			2.75	12.49	12.49	7.87		2.62	12.32	12.31
Unsym[Cu ₂ I ₂ Br(Py) ₂ (PPh ₃) ₂]	300(d)			2.75	12.49	12.49	7.87		2.67	12.38	12.41
Cu ₂ I ₂ Br(PPh ₃) ₂ (Py)(Tu)	278			4.14	12.52	12.52	7.74		4.00	12.43	12.43
Cu ₂ I ₂ Br(PPh ₃) ₂ (Tu) ₂	245			5.54	12.56	12.56	7.91		5.32	12.30	12.42
						Cu-Ag			Cu-Ag		17.11
CuAgI(PPh ₃) ₄	218-220					17.22	—				—
				4.30-7.32					4.19	7.02	

Cis(Py)₂CuI₂BrCu(PPh₃)₂. *Cis*-bromo-iodobis[(pyridine)(triphenylphosphine)]dicopper(I) was obtained by refluxing bromo-iodotetrakis(triphenylphosphine)dicopper(I) (1 mole) with pyridine (a slight excess) for 4 hr.

Trans(Py)₂CuI₂BrCu(PPh₃)₂. *Trans*-bromo-iodobis[(pyridine)(triphenylphosphine)]dicopper(I) was prepared by the reaction of bromo-iodotetrakis(pyridine)dicopper(I) (1 mole) with triphenylphosphine (0.25 mole) in methanol.

Unsym(Py)₂CuI₂BrCu(PPh₃)₂. Unsymmetrical bromo-iodobis[(pyridine)(triphenylphosphine)]dicopper(I) obtained by the reaction of bromo-iodotetrakis(pyridine)dicopper(I) (1 mole) with bromo-iodotetrakis(triphenylphosphine)dicopper(I) (0.25 mole) in methanol.

Cu₂I₂Br(Py)(PPh₃)₂Tu. Bromo-iodo(pyridine)bis(triphenylphosphine)thiourea dicopper(I) prepared by refluxing (5 moles) thiourea dissolved in methanol with (1 mole) of *cis*-bromo-iodobis[(pyridine)(triphenylphosphine)]dicopper(I) for about 3 hr. White crystals obtained at room temperature.

Cu₂I₂Br(PPh₃)₂(Tu)₂. Bromo-iodobis[(triphenylphosphine)(thiourea)]dicopper(I) was obtained by refluxing (1 mole) of *trans*-bromo-iodobis[(pyridine)(triphenylphosphine)]dicopper(I) with 5 moles thiourea dissolved in methanol for 3 hr. White shining crystals obtained.

CuAgI(PPh₃)₄. Diodotetrakis(triphenylphosphine)copper(I) silver(I) was obtained by treating equimolar quantities of di- μ -iodotetrakis(triphenylphosphine)dicopper(I) and di- μ -iodotetrakis(tri-

phenylphosphine)disilver(I) (previously prepared) in chloroform and refluxing for 4 hr.

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