Cyano Bridge Copper (I) Complexes

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Summary: Cyano bridge copper (I) complexes such as $[CuCN(PPh_3)(py)]_2$ have been prepared through three different routes, from the known complexes $Cu(CN(py)_2$ and $CuCN(PPh_3)_2$, and were identified as Cis-symmetric, trans-symetric and unsymmetric cyano-bridged complexes on the basis of reaction with thiourea.

During the investigation of the structure of few isomeric cuprous halide complexes[1] of mixed ligands and thiocyanate copper (I) complexes[2], it was found necessary to study the behaviour of cyano group. Copper (I) cyanide complexes of formula $CuCN(py)_2$ and $CuCN(PPh_3)_2$ are known[3]. The complex $CuCN(PPh_3)_2$ has evidence of weak CN bridging in its infra-red spectrum, but to be monomeric in 2-aminoethanol (a coordinating solvent). The investigation of cyano cuprous complexes had led to the isolation of several compounds of new and interesting type. This paper describes the prepartion and properties of these complexes and discusses their infrared spectra. Copper (I) cyanide gives only one type of complexes with neutral ligand to metal ratio of 2:1 as against copper (I) halogeno complexes where examples of four different types of complexes with neutral ligand to metal ratio of 1:1, 2:1, 3:1, and 4:1 are known[4-6].

Complexes like $CuSCN(PPh_3)_2$ [2] and $CuI(PEt_3)_2$ [7] are non-electrolytes and not necessarily monomeric; rather, there are strong indications that these eomplexes have bridge structures. On the other hand complexes like $CuNO_3(PPh_3)_2$ [8] and $Cu(CH_3COO)(PPh_3)_2$ [9] have been shown to contain a four coordinated copper (I) with bidentate nitrate and acetate group respectively. In view of the uncertainity of having tricoordinated copper or bridging structure in the complexes $CuCN(PPh_3)_2$ pyridine was reacted with it to obtained mixed ligand complexes of the type $[CuCN(py)(PPh_3)]_2$. The complexes were obtained through three different routes and in each case these had the same stoichiometry $[CuCN(py)(PPh_3)]_2$. However, it was found that three complexes differ in their physical and chemical properties.

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 investigators[11] to differentiate between cis- and trans-isomers.

Experimental

Micro analyses were carried out by Berhardt(Elbach Uber Engelskirehen). Copper was determined by titration against standard disodium EDTA after degradation and oxidation of the complex by boiling H_2SO_4/HNO_3 mixtures. Molecular weight determinations were made on chloroform solutions at 37° using a Mechrolab osmometer. Conductivity measurements were carried out on nitrobenzene solutions thermostatted at 25°C using Mc 1 Mark V portable electrolytic conductivity set from Electronic Switchgear London Ltd. Infra-red spectra were recorded using a Unicam SP 200G spectrophotometer. Melting points were determined on an electrothermal Gallenkamp melting point apparatus and are uncorrected.

I. $[CuCN(py)_2]_2$
Tetra(pyridine)-μ-dicyanodicopper(I)

Cuprous cyanide (90 mg. 1m. mole) was dissolved in a saturated solution of sodium cyanide. To this a slight excess of pyridine was added and kept on reflux for four hours. White shining crystals obtained from the mother liquor on keeping it at room temperature over night. It was then filtered off and dried.

II. $[CuCN(PPh_3)_2]_2$
Tetra (triphenylphosphine)-μ-dicyanodicopper (I).

Cuprous cyanide (90 mg; 1 mmole) dissolved in a saturated solution of sodium cyanide was refluxed with triphenylphosphine (525 mg; 2 mmole) in methanol (20 ml) for four hours. White precipitate filtered off, washed with small portions of water, alcohol and acetone and dried.

III. *Trans-* $[CuCN(py)(PPh_3)]_2$
Trans-di (pyridine) bis (trphenylphosphine)-μ-dicyanodicopper (I).

Tetrakis (triphenylphosphine)-μ-dicyanodicopper (I) (1.228 gm, 1 mmole) was refluxed in methanol (20 ml) with a slight excess of pyridine (2 ml) for about six hours with constant stirring. White precipitate filtered off, washed and dried.

IV. *Cis-* $[CuCN(py)(PPh_3)]_2$
Cis-di (pyridine) bis (triphenylphosphine)-μ-dicyanodicopper (I)

Tetra (pyridine)-μ-dicyanodicopper (I) (495 mg, 1 mmole) and triphenylphosphine (132 mg; 0.5 mmole) dissolved in methanol (30 ml) was refluxed for four hours white powder obtained, was filtered washed and dried.

V. *Unsymm-* $[CuCN(py)(PPh_3)]_2$
Unsymm-di (pyridine) bis (trphenylphosphine)-μ-dicyanodicopper (I).

Tetra (pyridine)-μ-dicyanodicopper (I) (495 mg; 1 mmole) and tetrakis (triphenylphosphine)-μ-dicyanodicopper (I) (30 mg; 0.25 mmole) were refluxed together in methanol (25 ml) for four hours. White precipitate obtained was washed and dried.

VI. $Cu_2(CN)_2(Py)(PPh_3)_2\ Tu$
Pyridine bis (triphenylphosphine) thiourea-μ-dicyanodicopper (I).

Cis-di (pyridine) bis (triphenylphosphine)-μ-dicyanodicopper (I) (862 mg, 1 mmole) in methanol (15 ml) was mixed with a solution of thiourea (880 mg, 5 mmole) dissolved in methanol (15 ml). The solution was stirred under reflux for 2 hours. White crystals obtained by keeping the solution at room temperature for a day.

VII. $[CuCN(PPh_3)(Tu)]_2$
Bis (triphenylphosphine) di (thiourea)-μ-dicyanodicopper (I).

trans-dipyridinebis (triphenylphosphine)-μ-dicyanodicopper (I) (862 mg; 1 mmole) was mixed with a solution of thiourea (380 mg; 5 mmole) dissolved in methanol (30 ml). The solution was refluxed for two hours, white powder obtained from the solution filtered and dried.

Results & Discussion

The complex $CuCN(PPh_3)_2$ was prepared by the reaction of CuCN dissolved in potassium cyanide with triphenylphosphine dissolved in methanol. The product obtained is white, diamagnetic and non-ionic in nitrobenzene. Molecular weight found is slightly higher that the value required for a monomer. Infra-red spectra shows a strong peak at 2150 cm^{-1} for C-N stretching frequency. Molecular weight found shows a tetrahedral configuration for copper (I) in bridged dimerised structure than a tricordinated monomer.

The complex $CnCN(py)_2$ was also prepared by the action of pyridine on cuprous cyanide dissolved in potassium cyanide. The product obtained as white shining crystals, which are diamagnetic and non-ionic giving a non-conducting solution in nitrobenzene. Molecular weight determination gives value slightly higher than required for a monomer. The infra-red spectrum of cyanide complexes involve measurements of the intensity of absorption due to C-N stretching frequencies in the region between 2100-2200 cm^{-1} arising from the bonded cyanide[12]. The C-N vibration is not greatly affected in the inorganic ion, so that it is highly probable that other simple cyanides will also be identifiable by absorption within 2200-2000 cm^{-1} region. In the fused state[12] this moves to 2250 cm^{-1}. (Table 1).

Table 1.

Complex	Molecular Weight Required	Found	C-N Stretching frequencies	Main Infrared Bands in KBr. (in cm^{-1})
$[(CuCN(py)_2]_2$	495	a	2200(w) 2150(s)	1600(s), 1500(m), 1450(s), 1150 (m) 1065(m), 1040(m), 1010(m, 750(s) 690(s).
$[CuCN(PPh_3)_2]_2$	1228.16	820	2150(s) 2200(w)	1500(s), 1450(s), 1320(w), 1162(w) 1188(w), 1100(s), 1030(m), 1000(m) 750(s), 700(s).
Cis-$[CuCN(py)(PPh_3)]_2$	861.58	597	2150(s) 2100(m)	1600(s), 1475(m), 1450(s), 1155(m) 1100(s), 1090(m), 1040(m), 1010(w) 750(s), 690(s).
Trans$[CuCN(py)(PPh_3)]_2$	861.58	612	2100(s)	1600(m), 1475(m), 1450(s), 1175(w) 1160(w), 1100(s), 1030(w), 1000(w) 750(s), 690(s).
Unsym-$[CuCN(py)(PPh_3)]_2$	861.58	587	2200(s) 2100(m)	1600(m), 1475(m), 1450(s), 1100(m) 1025(w), 10009w), 750(s), 690(s)
$Cu_2(CN)_2(py)(PPh_3)_2$ (Tu)	858.71	576	2150(s)	1620(s), 1590(m), 1470(m), 1450(s) 1165(m), 1010(w), 750(s), 700(s) (nujol).
$Cu_2(CN)_2(PPh_3)_2(Tu)_2$	855.84	602	2100(s)	1625-1600(s), 1475(m), 1430(m), 1380-1365(s), 1160(w), 1100(s), 1030(w), 1000(w), 750(s), 690(s) (Nujol).

a=Insoluble

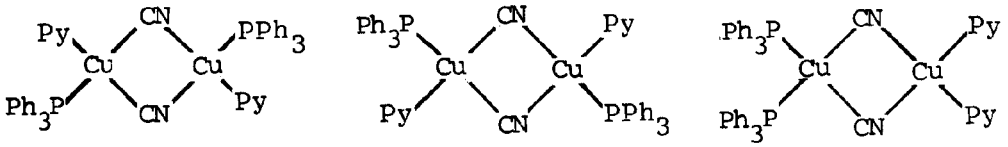
Table 2.

Solubility of $CuCN(py)(PPh_3)$ complexes (unit: gms/100 ml)

Complex	Water	Alcohol	Acetone	Ether	Benzene	Chloro form	Carbon tetra chloride
Cis $[CuCN(py)(PPh_3)]_2$	a	0.005	a	0.002	0.001	0.005	a
trans $[CuCN(py)(PPh_3)]_2$	a	0.001	0.1	0.001	a	0.001	a
Unsym $[CuCN(py)(PPh_3)]_2$	a	a	0.09	a	a	0.001	a

a=Insoluble

(Three isomeric forms)



Cis symmetric Trans symmetric Unsymmetric

The complex $CuCN(PPh_3)_2$ when reacted with pyridine gives $[CuCN(py)(PPh_3)]_2$ as product. It is white, diamagnetic and non-ionic in nitrobenzene. Molecular weight determination gives value higher than the monomeric formula weight. Infrared spectra shows a sharp band at 2100 cm^{-1} in KBr for C-N stretching frequency If the complex $CuCN(py)_2$ is reacted with triphenylphosphine the product obtained have the empirical formula as in the above case, i.e., CuCN(py) (PPh_3), but different physical and chemical characteristics. It is also white diamagnetic and nonionic in nitrobenzene. Molecular weight determination gives value higher than the monomeric formula weight, (Table 1). Infrared spectra shows two peaks at 2150 cm^{-1} and 2100 cm^{-1} for C-N stretching frequency.

Another complex having the same molecular formula $CuCN(py)(PPh_3)$ was obtained by the reaction of $CuCN(PPh_3)_2$ and $CuCN(py)_2$ in methanol. The product is white, diamagnetic and nonionic in nitrobenzene. Molecular weight found is higher than the calculated monomeric formula weight. Infrared spectra shows a strong band at 2200 cm^{-1} for C-N stretching frequency. Although the complex CuCN (py) PPh_3) was prepared by three different routes they acquire same molecular formula having molecular weight higher than required for a monomer. On the otherhand, they were found to have different physical and chemical characteristics, that is, their melting point differ from one another, their rate of solubility is different in different solvents (Table 2), their infrared spectra is not identical in all the three cases and also their behaviour towards thiourea is not the same. Considering all the properties of the complex $CuCN(py(PPh_3)$ obtained from three different routes, they were thought to have Cis-symmetric, trans-symmetric and unsymmetric structures. (Fig. 1).

To differentiate among the isomers, each of the three complexes was reacted with thiourea maintaining the same condition for each case. In this way the complex $CuCN(py)(PPh_3)$, obtained by the action of pyridine on $CuCN(PPh_3)_2$ when reacted with thiourea

gave a product $CuCN(PPh_3)(Tu)$. It is white, diamagnetic and nonionic in nitrobenzene. The I.R. spectra shows a strong peak at 2100 cm^{-1} for C-N stretching frequency and a strong and broad peak between 1625-1600 cm^{-1} shows the presence of thiourea. There is also strong peak at 1100 cm^{-1} for P-C stretching vibration. The over all reaction can be written as follows:

If the complex $CuCN(py)(PPh_3)$ obtained by the reaction of $CuCN(py)_2$ with triphenylphosphine is reacted with thiourea the product obtained is $CuCN(PPh_3)_2$ (Tu). It is white, diamagnetic and gives a non-conducting solution in nitrobenzene. The infraredspectra shows two bands for C-N stretching frequency, one at 2150 cm^{-1} and the other at 2100 cm^{-1}. The band at 1600 cm^{-1} and 1590 cm^{-1} indicating the presence of both pyridine and thiourea.

On the basis of their behaviour towards thiourea the first complex was named as trans isomer and the second as cis isomer. The third complex obtained by the reaction of $CuCN(PPh_3)_2$ and $CuCN(py)_2$ in methanol did not react with thiourea in the same conditions applied to the first two mentioned complexes. That is why it was considered to have an unsymmetric structure.

Table 3

Analysis

Complex	M.P.	Found (%)					Calculated (%)					
		C	H	N	Cu	P	C	H	N	Cu		P
$CuCN(PPh_3)_2$	226	72.19	5.03	2.28	10.09	9.85	72.39	4.88	2.28	10.35	10.06	
$CuCN(py)_2$	335	53.21	3.98	16.84	24.98	=	53.34	4.03	16.95	25.65	–	
trans$[CuCN(py)(PPh_3)]_2$	220	66.45	4.61	6.33	14.59	15.97	66.94	4.64	6.50	14.75	7.18	
Cis$[CuCN(py)(PPh_3)]_2$	225	66.56	4.59	6.28	14.26	7.01	66.94	4.64	6.50	14.75	7.18	
Unsymm$[CuCN(py)(PPh_3)]_2$	238	66.88	4.54	6.39	14.58	7.07	66,94	4.64	6.50	14.75	7.18	
$Cu_2CN_2py(PPh_3)_2$ Tu	235	60.97	4.39	7.95	14.01	7.11 S= 3.56	61.55	4.54	8.15	14.80	7.21	S= 3.73
$[CuCN(PPh_3)(Tu)]_2$	240	56.02	4.42	9.68	14.59	6.88 S= 7.02	56.15	4.44	9.81	14.85	7.25	S= 7.49

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