

Chemistry of mercaptopyridines and related ligands: Part 1—Synthesis & spectroscopic studies of complexes of copper(I) with 2(1H)-pyridinethione-S and tertiaryphosphines

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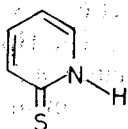
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Reaction of 2(1H)-pyridinethione-S(HpyS) with copper(II) chloride gives a copper(I) complex of stoichiometry, $\text{CuCl}(\text{HpyS})$ which on further reaction with triphenylphosphine (Ph_3P) and bis(diphenylphosphino) alkanes, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) gives mixed ligand complexes, $\text{CuCl}(\text{HpyS})\text{L}_n$ ($n=2$ for Ph_3P and 1 for other ligands). On the other hand, the reaction of copper(II) bromide with HpyS gives a copper(II) complex, $\text{CuBr}_2(\text{HpyS})_2$ which on similar reactions with phosphine ligands gives the analogous copper(I) complexes, $\text{CuBr}(\text{HpyS})\text{L}_n$. The X-ray crystal structure for $\text{CuCl}(\text{HpyS})(\text{Ph}_3\text{P})_2$ supports the formulated geometries for other complexes.

The coordination chemistry of 2(1H)-pyridinethione-S (hereafter HpyS) (structure I) has received a considerable attention in the recent past on account of the biochemical activity of compounds of HpyS and its derivatives with different metal ions^{1,2}. Evans and Wilkinson³ reported the reactions of copper(II) halides with HpyS which gave $\text{CuCl}(\text{HpyS})$ and $\text{CuBr}_2(\text{HpyS})_2$. There is no simple explanation for lack of expected reduction of $\text{Cu(II)} \rightarrow \text{Cu(I)}$ in the latter case. Moreover, these compounds have extremely poor solubility in various organic solvents. This note reports the reactions of $\text{CuCl}(\text{HpyS})$ and $\text{CuBr}_2(\text{HpyS})_2$ with a series of tertiaryphosphine ligands which include Ph_3P and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1$, mdp; $n=2$, edp; $n=3$, pdp; and $n=4$, bdp).

Experimental

2-Hydroxypyridine and Ph_3P were procured from M/s. Sisco Laboratories, Bombay, while



(Structure I)

$\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1, 3$) were procured from M/s Pressure Chemicals, Pittsburg. $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=2,4$) and 2(1H)-pyridinethione-S were prepared by the literature methods^{4,5(a)}. Copper(II) halides were of reagent grade and used as such.

Preparation of the complexes

Preparation of $\text{CuCl}(\text{HpyS})(\text{PPh}_3)_2$ —The starting material, $\text{CuCl}(\text{HpyS})$ was prepared in the following manner: a solution of HpyS (4.5 mmol) in ethanol (15 ml) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.25 mmol) in ethanol (15 ml) which resulted in the formation of a yellow complex, formulated as $\text{CuCl}(\text{HpyS})^3$. The latter (0.95 mmol) was refluxed with PPh_3 (1.9 ml) in chloroform (30 ml) for 2 h. The solvent was reduced to 1/3rd of its original volume and the complex was precipitated by the addition of petroleum-ether (b.p. 60-80°C). The yellow product so obtained was filtered off and dried *in vacuo*.

The procedure for the remaining $\text{CuCl}(\text{HpyS})\text{L}_n$ ($n=1$) as well as $\text{CuBr}_2(\text{HpyS})_2$ and $\text{CuBr}(\text{HpyS})\text{L}_n$ ($n=1$) complexes was similar. Table 1 contains the analytical data and various other physical properties of the complexes.

Infrared spectra were recorded using KBr pellets on a PYE UNICAM SP3-300 IR spectrophotometer (range 4000-200 cm^{-1}). Solution phase UV spectra were recorded in ethanol/ CHCl_3 on a Shimadzu UV-visible recording spectrophotometer UV-240. Conductance measurements were made in nitrobenzene on a Toshniwal conductivity bridge type CLOI/02A. The X-band (9.442 GHz) ESR spectrum of the powdered sample of complex (7, see Table 1 for numbering of complexes) was recorded on a JEOL JES-FE3XG ESR spectrometer (field range: 3000 ± 2500 gauss). The C, H analyses were obtained from RSIC, Panjab University, Chandigarh. Copper was estimated by EDTA method^{5(b)}.

Results and discussion

The reactions of sparingly soluble compounds, $\text{CuCl}(\text{HpyS})$ and $\text{CuBr}_2(\text{HpyS})_2$ with Ph_3P and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) in chloroform gave copper(I) complexes in both the cases having stoichiometry, $\text{CuX}(\text{HpyS})\text{L}_n$ ($\text{X}=\text{Cl}, \text{Br}$, $n=2$ for Ph_3P and $n=1$ for bidentate ligands). These mixed ligand complexes are soluble in various organic

Table 1 – Analytical data and physical properties of copper complexes

Sl No.	Compound (m.p., °C)	Found (Calc.), %			Color	$\nu(\text{C}=\text{S})^e$, cm^{-1}	$\nu(\text{Cu}-\text{X})$, cm^{-1} (X = Cl, Br)
		C	H	Cu			
1	CuCl(HpyS) (80-85d)	28.59 (28.57)	2.00 (2.38)	31.11 (30.23)	Orange	1120m	300w
2	CuCl(HpyS)(Ph ₃ P) ₂ (145-50d)	67.10 (67.02)	4.10 (4.70)	9.14 (8.65)	Yellow	1120m	305w
3	CuCl(HpyS)(mdp) ^a (95-100d)	56.53 (56.00)	4.39 (4.20)	10.41 (9.71)	Yellow	1120m	—
4	CuCl(HpyS)(edp) (70-80d)	62.50 (61.18)	4.97 (4.76)	9.01 (10.44)	Yellow	1120m	300w
5	CuCl(HpyS)(pdp) ^b (70-80d)	59.40 (59.40)	4.80 (4.79)	9.52 (9.74)	Yellow	1120m	300w
6	CuCl(HpyS)(bdp) ^c (205-10d)	55.94 (55.84)	4.76 (4.65)	8.00 (8.75)	Light yellow	1120m	295w
7	CuBr ₂ (HpyS) ₂ ^{a,d} (160-70d)	25.70 (26.93)	1.63 (2.20)	14.92 (14.20)	Orange	1120m	265w
8	CuBr(HpyS)(Ph ₃ P) ₂ ^a (110-20d)	59.50 (59.42)	4.40 (4.23)	8.57 (7.57)	Yellow	1130m	260w
9	CuBr(HpyS)(mdp) ^a (95-100d)	52.90 (52.43)	4.40 (3.93)	10.79 (9.09)	Yellow	1120m	260w
10	CuBr(HpyS)(edp) ^a (95-100d)	51.80 (51.35)	4.20 (4.00)	9.20 (8.55)	Yellow	1120m	260w
11	CuBr(HpyS)(bdp) (170-80d)	56.00 (56.15)	5.57 (4.67)	9.52 (8.93)	Light orange	1125m	260w

^a0.5 CHCl₃; ^b0.25 CHCl₃; ^c0.75 CHCl₃; ^dcopper(II); ^efree HpyS 1138 cm⁻¹ (m)

solvents such as CHCl₃, CH₂Cl₂ and partly soluble in benzene and alcohols.

Significantly, when CuCl(HpyS) and CuBr₂(HpyS)₂ were reacted with Ph₃P in 1:2 or Ph₂P(CH₂)_nPPh₂ in 1:1 molar ratio, no insoluble material was left. Further, the analogous phosphine/arsine ligands such as Ph₃PO, Ph₃PS, Ph₃PSe and Ph₃As did not react with the CuCl(HpyS) or CuBr₂(HpyS)₂ even after refluxing the contents for a prolonged period. This difference is attributed to the better Lewis basicity of Ph₃P and Ph₂P(CH₂)_nPPh₂ ligands possibly on account of the better σ -donor and π -accepting property of the tertiaryphosphines containing trivalent phosphorus.

The complexes do not melt but undergo decomposition (Table 1). The percentage yield expectedly was more than 80%. All the complexes were confirmed to be nonconducting in nitrobenzene. The complexes were found to be stable in the presence of moisture and air, but reacted with the coordinating solvents like CH₃CN forming green colored solutions.

The IR spectra of the complexes showed that HpyS coordinates to Cu(I) via its thione sulphur (Table 1). The fall in $\nu(\text{C}=\text{S})$ is small in magni-

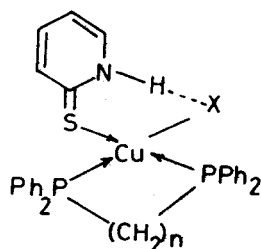
tude though consistent in variation and the behaviour is similar to that reported in literature^{6,7}. Similarly tentative assignments of $\nu(\text{Cu}-\text{X})$ peaks have been made (Table 1).

The solution phase UV spectra of the free HpyS, Ph₃P and Ph₂P(CH₂)_nPPh₂ showed bands at 290s, 370s; 240m, 260m; and 250s nm respectively⁹. In the complex (2), the peak at 260nm ($n-\pi^*$) underwent considerable high energy shift and merged with the peak at 240nm which was raised in intensity. The behaviour of ligands in other complexes was similar. These shifts reveal coordination by the tertiaryphosphine ligands.

The X-ray crystal structure of a representative complex, CuCl(HpyS)(Ph₃P)₂ showed that the geometry about Cu(I) was distorted tetrahedral¹⁰ with the largest deviation from the ideal geometry arising in part from the presence of two bulky Ph₃P ligands, P-Cu-P, 122.4°. Other angles are: Cl-Cu-S, 109.2; Cl-Cu-P(1), 99.6, Cl-Cu-P(2), 111.6 S-Cu-P(2), 102.6 S-Cu-P(1), 111.3°. The HpyS binds to Cu via S atom at a Cu-S distance of 2.374 Å. The hydrogen bonded to nitrogen atom in the complex participates in intramolecular hydrogen bonding with a chlorine atom bonded to Cu. This results in the

formation of a $\text{Cu}-\text{Cl}\cdots\text{H}-\text{N}-\text{C}-\text{S}$ six-membered ring similar to those reported for tin(IV) and Rh(II) complexes^{11,12}.

For other complexes, similar structures are suggested with bidentate ligands acting as chelating ones (structure II, $n=1$). The ESR spectrum of $\text{CuBr}_2(\text{HpyS})_2$ gave a single broad peak at a g -value of 2.15 suggesting a tetrahedral structure.



(Structure II, $n=1$)

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