Chemistry of Mercaptopyridines and Related Ligands. Part 3.[1] Novel Examples of Copper(II)–Tertiary Phosphine Complexes stabilized by 1-Hydroxypyridine-2-thione

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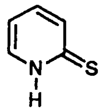
Reaction of 1-hydroxypyridine-2-thione (C_5H_5NOS) with copper(II) chloride dihydrate gave an insoluble dirty yellow compound of stoichiometry, [$CuCl(C_5H_4NOS)$] **1** which is ESR active. Similar reaction with copper(II) bromide gave the ESR-active green compound [$CuBr(C_5H_4NOS)(C_5H_5NOS)_2$] **7**. Reactions of **1** and **7** with tertiary phosphines gave mixed-ligand complexes of stoichiometry $CuX(C_5H_4NOS)L_n$ [n = 2 for PPh_3 and 1 for $Ph_2P(CH_2)_mPPh_2$, m = 1–4; X = Cl or Br], all of which are ESR active. The latter complexes represent the first novel examples of air- and moisture-stable copper(II)–tertiary phosphine complexes in which Cu^{II} is bonded to one halogen, one oxygen, one sulfur and two phosphorus atoms.

A number of copper(I)–tertiary phosphine complexes have been reported[2] but there are few reports on the formation of corresponding copper(II) complexes.[3–6] One study[3–5] describes the reactions of bis(tri- or hexa-fluoroacetylacetonato)copper(II) with phosphines forming air-sensitive copper(II) complexes which are stable only under a nitrogen atmosphere. In another study,[6] 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid (HY) was used to obtain a phosphine adduct of Cu^{II}, namely [$\{CuY(PPh_3)\}_2$] which has a dimeric structure with a weak Cu • • • Cu interaction. In these examples the chromophore CuO_4 appears responsible for the existence of the copper(II)–tertiary phosphine bonds. However, the reactions of copper(II) halides with tertiary phosphines failed to give copper(II) halide–tertiary phosphine complexes.[7]

Recently, we reported complexes of 2(1*H*)-pyridinethione (C_5H_5NS, structure **A**) with iron(III) and copper(I).[1,8,9] It was found that the reactions of this ligand with copper(II) halides and subsequently with tertiary phosphines gave stable copper(I) complexes[8,9] [$CuX(C_5H_5NS)L_n$] [n = 2 for L = PPh_3 and n = 1 for L = $Ph_2P(CH_2)_mPPh_2$, m = 1–4; X = Cl or Br].[1,8]

It was therefore intended to compare the donor properties of 1-hydroxypyridine-2-thione (C_5H_5NOS, structure **B**)[10,11] towards copper(II) halides followed by reactions with tertiary phosphines eventually so as to stabilize copper(II)–tertiary phosphine bonds. This ligand is reported to form only one copper(II) complex, [$Cu(C_5H_4NOS)_2$],[12,13] although complexes with other metals such as V,[14] Cr,[12] Mo,[15] W,[15,16] Fe[12] and Ni[12,17a] are also known. The anion C_5H_4NOS is believed to act as a chelating agent.[11,17b]

This paper reports a series of new copper(II)–tertiary phosphine complexes stabilized by 1-hydroxypyridine-2-thione.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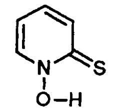
B

Experimental

2-Chloropyridine and PPh_3 were procured from M/s Sisco Laboratories, Bombay, bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_mPPh_2$ (m = 1 or 3) from Pressure Chemicals, Pittsburg. For m = 2 or 4 the ligands were prepared by the literature method.[18] Copper(II) halides and other reagents were of analytical reagent grade and used as such.

Synthesis, Physical and Spectral Properties of 1-*Hydroxypyridine*-2-*thione*.—2-Chloropyridine *N*-oxide[19] was prepared by heating a mixture of 2-chloropyridine (4.800 g), hydrogen peroxide (16 cm^3, 30%), glacial acetic acid (50 cm^3) and five to six drops of concentrated sulfuric acid at 70 °C for 3 h. The volume of the solution was reduced to 15–20 cm^3 under reduced pressure. Distilled water (15 cm^3) was added and the volume again reduced to 10–15 cm^3. The solution was made alkaline using sodium hydrogencarbonate and the 2-chloropyridine *N*-oxide formed was extracted (once) using chloroform (25–30 cm^3). The chloroform layer was washed with water, dried over anhydrous sodium sulfate and finally distilled to get 2-chloropyridine *N*-oxide, yield *ca.* 70%.

Sodium hydrogensulfide[20] was prepared by bubbling H_2S gas through a solution of sodium ethoxide (2.00 g of sodium metal dissolved in 40 cm^3 of dry ethanol) in dry ethanol. The crude NaHS was filtered off and the filtrate on treatment with an excess of anhydrous diethyl ether gave pure NaHS which was filtered off and dried under vacuum.

For the preparation of C_5H_5NOS,[21] a mixture of sodium hydrogensulfide (0.948 g, 16.928 mmol) and sodium sulfide (0.720 g, 9.230 mmol) in water (12 cm^3) was slowly added to a solution of 2-chloropyridine *N*-oxide (2.00 g, 15.444 mmol) in water (9 cm^3) during 10 min at 95 °C. The heating was continued for 0.5 h, followed by cooling to room temperature and treatment with concentrated hydrochloric acid (5–6 cm^3). On addition of a few pieces of ice, a brown precipitate was formed and then dissolved in chloroform. The chloroform layer was washed with cold water, dried over anhydrous sodium sulfate and finally chloroform was distilled off to obtain the solid material. It was recrystallized from ethanol as off-white crystals. Yield 40%, m.p. 65–68 °C (uncorrected) (Found: C, 47.30; H, 3.85. C_5H_5NOS requires C, 47.20; H, 3.90%). IR:[12] ν(N–O) 1090s, δ(N–O) 835s and ν(C=S) 1175s cm^{-1}. UV/VIS ($CHCl_3$): 285s and 350m nm, attributed to a transition from a molecular orbital centred on nitrogen to an empty orbital on the pyridine ring and probably to the C=S chromophore, respectively. NMR ($CDCl_3$, reference $SiMe_4$): ^1H, δ 6.83 (br s, 1 H, C^4H), 7.31 (t, 1 H, C^5H), 7.65 (d, 1 H, C^3H), 8.13 (br, 1 H, C^6H) and 11.53 (br, D_2O-exchangeable OH); ^{13}C, δ 166.36 (s, C^2), 132.37 (s, C^6), 131.59 (s, C^3), 131.09 (s, C^5) and 113.89 (s, C^4).

Preparation of Complexes.—[$CuCl(C_5H_4NOS)(PPh_3)_2$]. To

Table 1 Analytical data and some physical properties of copper(II)–phosphine complexes[a]

Complex	Analysis[b] (%) C	H	Cu	Melting point (°C)[c]	Colour
1 [$CuCl(C_5H_4NOS)$]	26.00 (26.65)	1.60 (1.75)	21.20 (22.70)	250–255 (decomp.)	Dirty yellow
2 [$CuCl(C_5H_4NOS)(PPh_3)_2$][d]	59.50 (59.75)	3.90 (4.15)	7.60 (7.55)	130–135 (decomp.)	Green
3 [$CuCl(C_5H_4NOS)$(dppm)]	58.75 (59.10)	4.60 (4.25)	11.10 (10.40)	110–115 (decomp.)	Green
4 [$CuCl(C_5H_4NOS)$(dppe)][d]	54.90 (54.10)	4.30 (4.20)	—	95–100 (decomp.)	Green
5 [$CuCl(C_5H_4NOS)$(dppp)]	59.80 (59.70)	4.60 (4.50)	9.50 (10.20)	120–125 (decomp.)	Green
6 [$CuCl(C_5H_4NOS)$(dppb)]	61.70 (60.80)	5.00 (4.90)	9.50 (9.75)	120–125	Green
7 [$CuBr(C_5H_4NOS)(C_5H_5NOS)_2$]	34.55 (34.40)	2.25 (2.65)	7.95 (8.05)	200	Green
8 [$CuBr(C_5H_4NOS)(PPh_3)_2$][e]	52.05 (52.45)	3.80 (3.65)	6.60 (6.55)	100–105 (decomp.)	Dull brown
9 [$CuBr(C_5H_4NOS)$(dppm)]	56.70 (55.10)	3.50 (3.95)	10.45 (9.70)	120–125 (decomp.)	Green
10 [$CuBr(C_5H_4NOS)$(dppe)][f]	53.55 (53.80)	3.50 (4.05)	10.15 (9.10)	200	Green
11 [$CuBr(C_5H_4NOS)$(dppb)][f]	55.35 (55.00)	4.55 (4.45)	9.50 (8.75)	175–180 (decomp.)	Dirty green

[a] Ligand abbreviations: $Ph_2P(CH_2)_mPPh_2$, $m = 1$, dppm; $m = 2$, dppe; $m = 3$, dppp; and $m = 4$, dppb. [b] Calculated values in parentheses. [c] Uncorrected. [d] 0.75 $CHCl_3$. [e] 1.5 $CHCl_3$. [f] 0.25 $CHCl_3$.

a solution of $CuCl_2 \cdot 2H_2O$ (0.100 g, 0.58 mmol) in ethanol (15 cm^3) was added a solution of C_5H_5NOS (0.074 g, 0.58 mmol) in ethanol (15 cm^3). A dirty yellow product of stoichiometry $CuCl(C_5H_4NOS)$ was formed. A portion of this complex (0.100 g, 0.44 mmol) was suspended in chloroform (10 cm^3) and to it was added a solution of PPh_3 (0.230 g, 0.88 mmol) in $CHCl_3$ (10 cm^3). During refluxing, the insoluble solid started to react with PPh_3 and a clear solution was formed over 1.5–2.0 h. The volume of the solution was reduced to a few cm^3 and the addition of light petroleum (b.p. 60–80 °C, *ca.* 10 cm^3) gave a green product; yield 90%. The solid was recrystallized from chloroform and dried *in vacuo*. Other complexes were prepared similarly.

[$CuBr(C_5H_4NOS)(PPh_3)_2$]. To a solution of $CuBr_2 \cdot 2H_2O$ (0.200 g, 0.76 mmol) in ethanol (15 cm^3) was added a solution of C_5H_5NOS (0.100 g, 0.77 mmol) in ethanol (15 cm^3). A green insoluble product of stoichiometry $CuBr(C_5H_4NOS)(C_5H_5NOS)_2$ was formed. A portion of this complex (0.100 g, 0.19 mmol) was suspended in chloroform (10 cm^3) and to it was added a solution of PPh_3 (0.100 g, 0.38 mmol) in chloroform (10 cm^3). After refluxing for 2 h a clear solution was formed. On concentration and addition of light petroleum (b.p. 60–80 °C) a yellow product was obtained; yield 90%. The solid was recrystallized from chloroform and dried *in vacuo*. Other complexes were prepared similarly.

The analytical data and physical properties for the complexes are given in Table 1.

Techniques.—The IR spectra were recorded using KBr pellets on a Philips Analytical SP 3-300 spectrometer (4000–200 cm^{-1}), UV/VIS spectra of 10^{-2} mol dm^{-3} solutions of the complexes in chloroform on a Shimadzu UV-240 recording spectrophotometer. The conductance measurements were made in nitrobenzene on a Toshniwal type CLOI/02A conductivity bridge. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer, and the X-band (9.44 GHz) ESR spectra of powdered samples on a JEOL JES-FE 3XG spectrometer [field set, 3000 G; scan range ±2500 G (0.25 T)]. The magnetic susceptibility measurements of the complexes were carried out using a Guoy balance with $HgCo(NCS)_4$ as the calibrant at the University of Surrey, Guildford. The elemental analyses for C and H were obtained from RSIC, Panjab University, Chandigarh. Copper was estimated by the ethylenediaminetetraacetate method.[22]

Results and Discussion

The analytical data reveal that the reactions of copper(II) halides with C_5H_5NOS in ethanol gave insoluble materials of composition $CuCl(C_5H_4NOS)$ and $CuBr(C_5H_4NOS) \cdot 2C_5H_5NOS$ which on further reactions with a series of tertiary phosphines gave the mixed-ligand copper(II) complexes of stoichiometry $CuX(C_5H_4NOS)L_n$ [X = Cl or Br, $n = 2$ for L = PPh_3; $n = 1$ for L = $Ph_2P(CH_2)_mPPh_2$, $m = 1$–4]. In contrast, reactions of the ligand 2(1-*H*)-pyridinethione (C_5H_5NS) with copper(II) halides gave copper(I) complexes, $CuX(C_5H_5NS)L_n$ (X,L same as above).[8,9] The copper(II) complexes are soluble in chloroform and dichloromethane, partly soluble in benzene and alcohols. All these mixed-ligand complexes were found to be non-electrolytes in nitrobenzene and are stable to air and moisture. During determination of the melting points the complexes generally decomposed near the melting point of the respective ligand.

Table 2 contains some of the major IR spectral peaks observed for the complexes. The most significant peak assignment pertains to the copper(II)–oxygen (from C_5H_4NOS) stretching modes which appeared as single (medium to strong) peaks in the range 370–390 cm^{-1}.[23] The ν(N–O), δ(N–O) and ν(C=S) peaks for the free ligand C_5H_5NOS appeared at 1090s, 835s and 1175s cm^{-1} respectively. Whereas δ(N–O) invariably showed shifts to lower energy on co-ordination, the same was not true of ν(N–O) and ν(C=S) which is anticipated in view of coupling of ligand normal modes.[12,24] It may be mentioned here that ν(C=S) of C_5H_5NS showed low-energy shifts in the IR spectra of analogous copper(I) complexes, $CuX(C_5H_5NS)L_n$ as mentioned above.[8,9] Tentative assignments to ν(Cu–Cl) and ν(Cu–Br) are made in the ranges 280–312 and 250–256 cm^{-1},[23] respectively.

In respect of the electronic spectra of the complexes, only the solution-phase absorptions merit discussion here. The UV spectrum of free ligand in chloroform shows two peaks at λ_{max} 350 and 285 nm and that of PPh_3 in chloroform shows two

Table 2 Infrared spectral data (cm^{-1}) and magnetic moment data for copper(II)–tertiary phosphine complexes[a]

Complex	ν(N–O)	δ(N–O)	ν(C=S)	ν(Cu–O)	μ
1	1090m	820s	1140s	380s	1.32
2	1085m	825m	1140m	380s	2.35[b] (2.34)[c]
3	1085m	825m	1140w	380m	2.30
4	1090m	830m	1145w	380m	1.34[b] (1.28)[c]
5	1090w	830m	1150w	380m	1.38
6	1080w	820w	1140w	375m	1.30
7	1090m	830s	1140s	380s	2.20
8	1090m	830m	1150m	380m	2.24
9	1090m	830m	1140m	380m	2.28
10	1090m	830m	1150m	390m	2.36
11	1090 (sh)	830m	1150m	390m	2.34

[a] C_5H_5NOS: ν(N–O) 1090s, δ(N–O) 835s, ν(C=S) 1175s cm^{-1}. [b] Room-temperature values (293 K). [c] At 93 K.

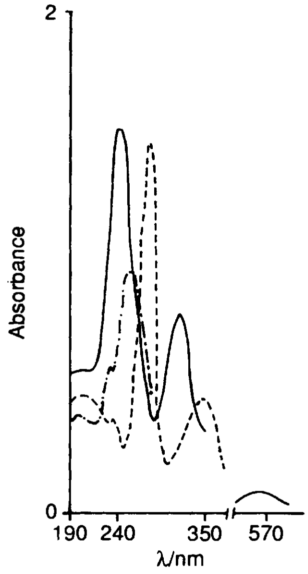

Fig. 1 The UV/VIS spectra of $[CuCl(C_5H_4NOS)(PPh_3)_2]$ (——), C_5H_5NOS (– – – –) and PPh_3 (– · – · –)

peaks at λ_{max} 260 and 240 nm. The complex $[CuCl(C_5H_4NOS)(PPh_3)_2]$ **2** (**1** and **7** are insoluble in chloroform) shows the spectrum in Fig. 1. The peak at 350 nm shifts to 320 nm and that at 285 nm appears as a shoulder at 270 nm to the main peak at 248 nm, which results upon shifting the peak of PPh_3 at 260 nm and overlapping with the second peak of free PPh_3 at 240 nm. These data reveal participation of the ligand as the chelating anion $C_5H_4NOS^-$ *via* O and S donor sites. The spectral behaviour of the other mixed-ligand complexes was similar (Fig. 2). Further, the spectra were virtually independent of complex concentration. Thus any aggregation of the complexes appears to be taking place *via* halogen atoms while the ligand $C_5H_4NOS^-$ remains attached to a copper centre. The complexes showed medium and broad peaks due to d–d transitions at 570 nm, observed for analogous complexes with square-pyramidal or octahedral geometries.[23,25–28]

All the complexes are ESR active. Compound **1** showed a single broad ESR line at g = 2.11 [Fig. 3(*a*)]. The spectra of **2** and **8** [Fig. 3(*b*)] and also of **7**, **10** and **11** [Fig. 3(*d*)] are similar with $g_{\parallel} \approx 2.16$ and $g_{\perp} \approx 2.06$. The spectra of the other complexes are complicated [**3** and **9**, Fig. 3(*c*); **4**–**6**, Fig. 3(*e*)] and involve hyperfine coupling, the origin of which is not yet clear.

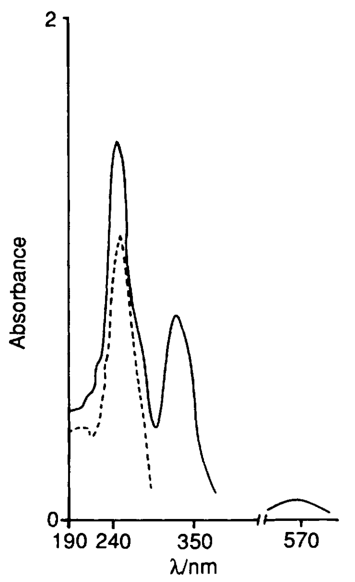

Fig. 2 The UV/VIS spectra of $[CuCl(C_5H_4NOS)(dppe)]$ (——) and dppe (– – – –)

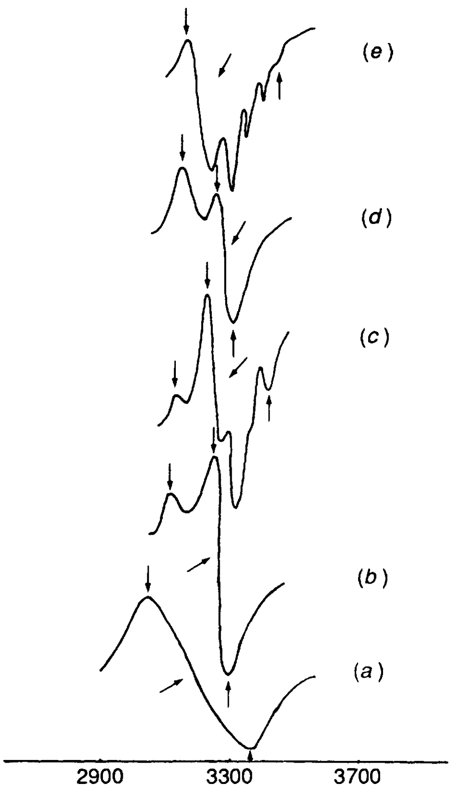

Fig. 3 The ESR spectra of (*a*) $[CuCl(C_5H_4NOS)]$, (*b*) $[CuCl(C_5H_4NOS)(PPh_3)_2]$, (*c*) $[CuCl(C_5H_4NOS)(dppm)]$, (*d*) $[CuBr(C_5H_4NOS)(dppe)]$ and (*e*) $[CuCl(C_5H_4NOS)(dppb)]$

Based on the ESR data, square-pyramidal (complexes **2** and **8**) or elongated octahedral structures (complexes **3**–**6**, **9**–**11**) are suggested.[27,29] The magnetic moment data suggest the possibility of antiferromagnetic exchange interaction between the copper centres. For instance, a μ value of 1.34 for complex **4** at 293 K was obtained which shifted to 1.28 at 93 K. Unfortunately, the crystals grown for representative complexes turned out to be poor diffractors of X-rays (checked at three different crystallographic centres) and thus a single-crystal X-ray study could not be carried out for any complex.

Finally, it is worth mentioning that compounds **1** and **7** reacted only with tertiary phosphines and totally failed to react with the analogous phosphine oxides/chalcogenides and arsines such as PPh_3O, PPh_3S, PPh_3Se and $AsPh_3$. This difference in reactivity may be attributed to the higher Lewis basicity of PPh_3 and $Ph_2P(CH_2)_mPPh_2$ ($m = 1$–4) on account of their better σ-donor and π-acceptor properties. It may be emphasized that the stabilization of copper(II)–tertiary phosphine bonding may be attributed to the combined effect of the electronegative oxygen, one halogen and the π-accepting property of tertiary phosphines.

Acknowledgements

Financial assistance of University Grants Commission [Scheme No. F.12-76/84 (SR-III)] Delhi, research facilities (to P. K. B.) from the Guru Nanak Dev University and magnetic susceptibility measurements by Dr. L. F. Larkworthy, University of Surrey, Guildford, are gratefully acknowledged.

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Received 14*th October* 1991; *Paper* 1/05195D