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# The chemistry of pyridinethiols and related ligands—VII. Preparation and spectroscopy of mixed-ligand copper(I) complexes: the crystal structure of first mixed-ligand dinuclear [iodo(pyridine-2-thione)(tri-*p*-tolylphosphine)copper(I)]$_2$ complex

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**Abstract**—Direct reaction of copper(I) iodide with pyridine-2-thione ($C_5H_5NS$) and tri-*p*-tolyl phosphine (*p*-$Tol_3P$) in 1 : 1 : 2 ratio in refluxing chloroform formed a product of stoichiometry, [CuI($C_5H_5NS$)(*p*-$Tol_3P$)]$_2$ (**5**), whose X-ray crystal structure has been determined. It crystallises from a dichloromethane-ethanol mixture and exists as a centrosymmetric sulfur bridged dimer with distorted tetrahedral geometry about each Cu atom; the other two positions of each Cu atom being occupied by a P atom from *p*-$Tol_3P$ and a iodine atom and the central core $Cu_2S_2$ of the dimer is planar. The interatomic important parameters are: Cu—P = 2.243(3), Cu—S, 2.393(4), 2.425(4), Cu—I, 2.603(2), C—S, 1.690(12) Å, Cu—S—Cu, S—Cu—S, and Cu—S—C bond angles are 85.25(13), 94.75(13) and 107.0(4) respectively. The dimer structure is stabilised by strong intramolecular N—H· · ·I hydrogen bonds. The solution phase behaviour of **5** and other related mixed-ligand copper(I) complexes, [CuX($C_5H_5NS$)L]$_2$ [X = Cl, L = *p*-$Tol_3P$ (**1**), X = Br, L = *m*-$Tol_3P$ (**2**), *p*-$Tol_3P$ (**3**), X = I, L = *m*-$Tol_3P$ (**4**)] is also studied using electronic absorption and multinuclear ($^1H$, $^{13}C$ and $^{31}P$) NMR spectroscopy. © 1997 Elsevier Science Ltd

*Keywords*: tri-*p*-tolylphosphine; pyridine-2-thione; sulphur-bridged dimer; copper(I) complex; multinuclear NMR solution phase studies.

The coordination chemistry of copper is interesting due to its presence in copper proteins and thus a pursuit for modelling its coordination sites [1]. Heterocyclic thiones are one class of biochemically significant compounds used for studying their binding properties with soft Lewis acid like $Cu^I$ and this interaction is highly flexible, thus forming a variety of stereochemistries [1–5].

Neutral pyridine-2-thione (hereafter $C_5H_5NS$) and its substituted analogues with $Cu^I$ form several complexes, notably: [Cu($\eta^1$-S-$C_5H_5NS$)$_3$]($NO_3$) [6] and [Cu($\eta^1$-S-$C_5H_5NS$)$_4$]($ClO_4$) [7]. [$Cu_2$($\eta^1$-S-$C_5H_5NS$)$_2$($\eta^2$-$\mu$-S-$C_5H_5NS$)$_2$$I_2$] [8,9], [$Cu_2$($\eta^1$-S-$C_5H_5NS$)$_4$($\eta^2$-$\mu$-S-$C_5H_5NS$)$_2$]$X_2$ (X = Cl, Br) [9–11], [$Cu_2L_4L'_2$]($PF_6$)$_2$ and [$Cu_2L_6$]($PF_6$)$_2$ [L = 4-Me-$C_5H_4NS$, 4-Et-$C_5H_4NS$, L′ = $C_2H_5OH$, $C_5H_5NS$) [12]]. Similarly, deprotonated $C_5H_4NS^-$ or its substituted analogues, form hexanuclear [$Cu^I_6L_6$] complexes [12,13] containing bridging L (N,S-*cum*-S-bridging, $\eta^3$-mode). A few other deprotonated, but structurally uncharacterised $Cu^I$ complexes, $(CuL)_n$ [L = $C_5H_4NS^-$ or $\{C_5H_3NS\text{-}3\text{-}SiMe_3\}^-$] [11,14] as well as $Cu^{II}$ complexes, [$CuL_2$] {$L^-$ = $\eta^2$-N,S-$C_5HNS$-3-CN-4-$R^1$-6-$R^2$; $R^1$, $R^2$: *p*-$CH_3OC_6H_4$, Ph (or $CH_3$); Ph, Ph (or $CH_3$); *p*-$ClC_6H_4$, Ph (or $CH_3$)] [15], analogous to 1-oxopyridine-2-thione complexes [16,17] have also been reported.

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The mixed-ligand complexes of $Cu^I$ investigated with tertiary phosphines and neutral pyridine-2-thione are: (i) monomeric $[CuX(HL)L'_n]$ $\{HL = \eta^1$-S-$C_5H_5NS$, X = Cl, Br, $n = 2$ for $L' = PPh_3$, and 1 for $Ph_2P$-$(CH_2)_m$-$PPh_2$, $m = 1$–$4\}$ [18–21], $[Cu(PPh_3)_2(HL)_2]$ $(NO_3)$ [22] $\{HL = \eta^1$-S-$C_5H_5NS\}$ and (ii) dimeric $[Cu(HL)XL']_2$ $\{HL = \eta^2$-$\mu$-S-$C_5H_5NS$, X = Cl, Br, I; $L' = PPh_3$, *p*-$Tol_3P$; X = Br, L = *m*-$Tol_3P$—*Tol is a tolyl group*} [18,23,24] as well as a deprotonated substituted pyridine-2-thione complex, *viz.* $[Cu_2(\eta^1$-S-$C_5H_3NS$-3-$SiMe_3)_2L_3]$ containing chelating and bridging L $\{L = Ph_2P$-$(CH_2)_2$-$PPh_2\}$ [25].

The crystal structures of the dimeric complexes, $[CuBr(C_5H_5NS)L]_2$ ($L = PPh_3$, *m*-$Tol_3P$) have shown thione bridging in complexes and formation of a planar $Cu_2S_2$ central core in which weak Cu· · ·Cu or S· · ·S interactions are indicated [18,24]. The role of iodo- anion on such interactions as well as on bonding properties of pyridine-2-thione in analogous mixed-ligand complexes is not explored. This paper describes the crystal and molecular structure of first iodo-copper(I) mixed ligand complex with a substituted phosphine and compare the structure with other dimeric complexes as well as study the solution phase behaviour of this and related mixed-ligand copper(I) complexes.

## EXPERIMENTAL

### *General materials*

2-Hydroxypyridine was procured from M/s Sisco Laboratories, Bombay, while *meta*- and *para*-tolyl phosphines (*m*-$Tol_3P$, *p*-$Tol_3P$) were procured from Pressure Chemicals Co. Ltd. Pittsburg, U.S.A. Copper(II) chloride dihydrate was procured from M/s Sarabhai Chemicals and its bromide prepared by treating with conc. HBr acid. Copper(I) iodide was prepared from aqueous solution of copper(II) sulphate-pentahydrate by reducing it with $SO_2$ gas in the presence of excess sodium iodide. Pyridine-2-thione ($C_5H_5NS$) was prepared by a literature method [21] by treating 2-hydroxypyridine with solid $P_2S_5$. Other starting materials, $CuCl(C_5H_5NS)$ and $CuBr_2(C_5H_5NS)_2$ were prepared by the reported methods [21].

### *Preparation of complexes*

The complexes were prepared by one of the following methods.

*Method* 1. $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$ (**5**). To CuI (0.100 g, 0.52 mmol) suspended in $CHCl_3$ (20 $cm^3$) was added solid $C_5H_5NS$ (0.058 g, 0.52 mmol) and excess of *p*-$Tol_3P$ (0.318 g, 1.04 mmol) followed by refluxing for 2 h when a clear yellow solution was formed. It was concentrated to 1/3 of its initial volume and addition of 10 $cm^3$ of petroleum-ether (60–80°C) formed a bright yellow solid which was filtered, washed with diethyl ether and dried *in vacuo*. Yield, 75%, m.p., 200–205°C, analytical data (%), found, C, 50.4, H, 3.90, N, 2.46, required for $C_{26}H_{26}NSPICu$, C, 51.5, H, 4.29, N, 2.31. UV data ($\lambda_{max}$, nm), 356vwb(CS), 287m(py), 248s(Ph). IR data ($cm^{-1}$), 3105w($\nu$N—H), 1599m, 1569s, 1124s($\nu$C=S), 1096($\nu$P—C), 806vs($\rho$C—$CH_3$), 744m, 724w, 710w, 515s, 484w, 208sb($\nu$Cu—S), 132sb($\nu$Cu—I). NMR ($^{31}P$, $\delta$, ppm), $\delta$P, −7.96sb (s-singlet, b-broad), $\Delta\delta$P ($\delta_{complex} - \delta_{ligand}$), 1.24.

$[CuI(C_5H_5NS)(m\text{-}Tol_3P)]_2$ (**4**) was also prepared by Method 1 whose analytical data and other details are as follows: Analytical data (%), found, C, 51.1, H, 4.30, N, 2.22, required for $C_{26}H_{26}NSPICu$, C, 51.5, H, 4.29, N, 2.31, m.p. (°C), 128–30, yield 75%. UV data ($\lambda_{max}$, nm) 356vwb(CS), 289sh(py), 249s(Ph). IR data ($cm^{-1}$), 3105w($\nu$N—H), 1591s, 1573s, 1126s($\nu$C=S), 1107s($\nu$P—C), 780s ($\rho$C—$CH_3$), 724m, 695vs, 551s, 454s, 218sb($\nu$Cu—S), 124sb($\nu$Cu—I). NMR ($^{31}P$, $\delta$, ppm), $\delta$P, −5.66sb, $\Delta\delta$P, 0.94.

*Method* 2. $[CuCl(C_5H_5NS)(p\text{-}Tol_3P)]_2$ (**1**). To $CuCl(C_5H_5NS)$ {0.100 g, 0.48 mmol) suspended in $CHCl_3$ (15 $cm^3$) was added a solution of excess *p*-$Tol_3P$ (0.280 g, 0.96 mmol) in $CHCl_3$ (15 $cm^3$) and contents refluxed for 2 h. The clear solution formed was filtered, concentrated when a yellow solid started forming on cooling to room temperature, which was filtered, washed with ethanol and dried *in vacuo*. Yield 70%, m.p. 190–192°C; analytical data (%), found, C, 60.8, H, 4.86, N, 2.34; required for $C_{26}H_{26}NSPClCu$, C, 60.7, H, 5.06, N, 2.72. UV data ($\lambda_{max}$, nm) 366mb(CS), 288s(py), 252s(Ph). IR data ($cm^{-1}$), 3165w ($\nu$N—H), 1608m, 1597m, 1576s, 1127vs($\nu$C=S), 1098s($\nu$P—C), 808s($\rho$C—$CH_3$), 747s, 725m, 517s, 511s, 484m, 327sb($\nu$Cu—Cl), 230sb($\nu$Cu—S). NMR ($^{31}P$, $\delta$, ppm), $\delta$P, −7.64sb, $\Delta\delta$P, 1.56.

### *Other complexes prepared by Method* 2

$[CuBr(C_5H_5NS)(m\text{-}Tol_3P)]_2$ (**2**). Yield, 70%, m.p. 122–125°C; analytical data (%), found, C, 54.5, H, 4.52, N, 2.45; required for $C_{26}H_{26}NSPBrCu$, C, 55.9, H, 4.65, N, 2.51. UV data ($\lambda_{max}$, nm), 370mb(CS), 289.5s(py), 250.5s(Ph). IR data ($cm^{-1}$), 3162w($\nu$N—H), 1605m, 1573vs, 1124s($\nu$C=S), 1103m ($\nu$P—C), 782s($\rho$C—$CH_3$), 753s, 723m, 693s, 547m, 486m, 310s($\nu$Cu—Br), 224sb($\nu$Cu—S). NMR ($^{31}P$, $\delta$, ppm), $\delta$P, −5.24sb, $\Delta\delta$P, 1.36.

$[CuBr(C_5H_5NS)(p\text{-}Tol_3P)]_2$ (**3**). Yield, 70%, m.p. 208–210°C; analytical data (%), found, C, 55.3, H, 4.22, N, 2.50; required for $C_{26}H_{26}NSPBrCu$, C, 55.9, H, 4.65, N, 2.50. UV data ($\lambda_{max}$, nm), 367mb(CS), 288s(py), 251s(Ph). IR data ($cm^{-1}$), 3162w($\nu$N—H), 1603m, 1573s, 1127s($\nu$C=S), 1098s($\nu$P—C), 809s($\rho$C—$CH_3$), 746m, 722w, 710w, 514s, 485w, 315s($\nu$Cu—Br), 219sb($\nu$Cu—S). NMR ($^{31}P$, $\delta$, ppm), $\delta$P, −6.85sb, $\Delta\delta$P, 2.35.

### *Physical measurements*

The elemental analysis for C, H and N were obtained with a Carlo–Erba 1108 microanalyser. The melting points were determined with a Gallenkamp electrically heated apparatus. The infrared spectra were recorded in KBr pellets (4000–400 cm$^{-1}$) or nujol mull in polyethene sheets (500–100 cm$^{-1}$) on a Bruker IFS 66V spectrometer. The NMR spectra were recorded in $CDCl_3$ using (i) Bruker AMX 300 spectrometer at 300.14, and 75.48 MHz probe frequencies ($^1$H and $^{13}$C, respectively) with TMS as the internal reference and (ii) Bruker AMX 500 spectrometer at 202.45 MHz probe frequency $\{^{31}P(^1H)\}$ with 85% $H_3PO_4$ as the external reference ($\delta$P, 27.5 ppm). The electronic absorption spectra were recorded on a Shimadzu Graphicord 240 UV–vis spectrophotometer.

### *X-ray data collection and reduction*

A yellow prismatic crystal of $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$ was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least squares refinement of the diffraction data from 25 reflections in the range of $8.73 < \Theta < 12.31°$ in an Enraf–Nonius MACH3 automatic diffractometer [26]. Data were collected at 293 K using $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å) and the $\omega$ scan technique and corrected for Lorentz and polarization effects [27]. An empirical absorption correction was made [28]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

### *Structure solution and refinement*

The structure was solved by direct methods [29] which revealed the position of all non-hydrogen atoms, and refined on $F^2$ by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [30]. The hydrogen atoms were located in their calculated positions (C—H = 0.93–0.96 Å) and were refined using a riding model. After all shift/e.s.d. ratios were less than 0.001, the refinement converged to the agreement factors listed in Table 1. Atomic scattering factors taken from *International Tables for X-ray Crystallography* [31], while molecular graphics from *ZORTEP* [32].

## RESULTS AND DISCUSSION

### *Solid state studies*

Direct reaction of CuI with $C_5H_5NS$ and *m*-$Tol_3P$ or *p*-$Tol_3P$ in 1 : 1 :1 (or 1 : 1 : 2) mole ratio (Method 1) formed the products of same stoichiometry, *viz.* $CuI(C_5H_5NS)L$ {L = *m*-$Tol_3P$ (**4**) or *p*-$Tol_3P$ (**5**)}. Complexes **1**–**3** were prepared by the reaction of $CuCl(C_5H_5NS)$ or $CuBr_2(C_5H_5NS)_2$ with excess tertiary phosphines (1 : 2 mole ratio, Method 2), but the stoichiometry was the same as for **4** and **5** above, unlike $CuX(C_5H_5NS)(PPh_3)_2$ (X = Cl, Br) or bisphosphine analogues reported by the same Method 2 earlier [20,21]. Method 1 gave more random stoichiometries for **1**–**3**, unlike for **4** and **5**, and thus Method 2 was used. All the complexes are stable to air and moisture and are soluble in solvents like $CHCl_3$, $CH_2Cl_2$ etc., but have low solubility in alcohols. It may be worthy of mention here that no complex with tri-*o*-tolyl phosphine could be prepared by either of the methods and appears to be due to steric effect of methyl group in the ortho position.

The IR spectra of the complexes show peaks due to $C_5H_5NS$ and substituted tertiary phosphines at altered positions and some characteristic peaks are listed in experimental section. The presence of $\nu$N—H peak in the region 3105–3165 cm$^{-1}$ as a weak to medium peak in the complexes show that $C_5H_5NS$ is not deprotonated in the complexes and strong $\nu$C=S peak at 1139 cm$^{-1}$ in free thione ligand shifts to low-energy in the region, 1124–1127 cm$^{-1}$ again as a strong peak in the complexes. This shows that $C_5H_5NS$ coordinates to Cu$^I$ center *via* its thione sulfur and magnitude of coordination shift is somewhat lower than that observed in the analogous Cu$^I$-pyridine-2-thione complexes with $PPh_3$ and bisphosphines [21]. The presence of $CH_3$ substituent in the phenyl ring increases their Lewis basicity, but lowers their $\pi$-accepting property and higher basicity appears to decrease the coordination shift of $\nu$C=S.

### *Description of crystal structure of dinuclear* $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$

The selected bond lengths and angles are given in Table 2, while the molecular structure with numbering scheme and packing arrangement of the complex in the unit cell are depicted in Figs 1 and 2, respectively. The basic structural unit is a centrosymmetric dimer, $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$, and the S atoms of the pyridine-2-thione molecules bridge two Cu atoms forming a strictly planar $Cu_2S_2$ core. Each Cu atom is further bonded to a P atom of *p*-$Tol_3P$ and one iodine atom and thus Cu acquires a distorted tetrahedral geometry. Two tetrahedra share S—S edge and the *trans* iodine atoms stabilise the complex with two strong intramolecular hydrogen bonds [N···I = 3.616(11), H···I = 2.795(11) Å (sum of the van der Waals radii, 3.15 Å) [8b] and N—H—I bond angle = 160.14(19)°], similar to those observed in literature [8]. The pyridyl ring of the thione ligand is planar and makes an angle of 66.29° with the plane of the $Cu_2S_2$ core (Table 3). The Cu—I bond distance, 2.603 Å is shorter (sum of ionic radii, 2.97 Å) [8b] than that (2.674 Å) in $[Cu_2(\eta^1\text{-S-}C_5H_5NS)_2(\eta^2\text{-}\mu\text{-S-}C_5H_5NS)_2I_2]$ [8,9]. The two short and two longer Cu—S bonds, 2.393 and 2.425 Å form a parallelogram

Table 1. Crystal data and structure refinement for $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$

| | |
|---|---|
| Empirical formula | $C_{52}H_{52}Cu_2I_2N_2P_2S_2$ |
| Formula weight | 1211.90 |
| Crystal system/Space group | Triclinic/P-1 |
| Unit cell dimensions | $a = 9.796(8)$ Å $\alpha = 83.81(5)^\circ$ |
| | $b = 10.351(9)$ Å $\beta = 73.62(6)^\circ$ |
| | $c = 14.754(9)$ Å $\gamma = 63.12(6)^\circ$ |
| Volume | 1280(2) Å$^3$ |
| $Z$ | 1 |
| Density (calculated) | 1.572 Mg/m$^3$ |
| Absorption coefficient | 2.217 mm$^{-1}$ |
| F(000) | 604 |
| Crystal description | yellow prism |
| Crystal size | 0.35 × 0.10 × 0.05 mm |
| $\theta$ range for data collection | 2.53 to 24.64° |
| Index ranges | $0 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 12$, $-16 \leqslant l \leqslant 17$ |
| Reflections collected | 4614 |
| Independent reflections | 4336 [$R_{int} = 0.0677$] |
| Reflections observed | 1780 |
| Criterion for observation | $> 2\sigma(I)$ |
| Max. and min. transmission | 1.000 and 0.294 |
| Measurement method | $\omega$ |
| No. of standard reflections | 3 |
| Interval time | 7200 |
| Decay | 0% |
| Structure solution | SHELXS-86 (Sheldrick, 1990) |
| Structure refinement | SHELXL-93 (Sheldrick, 1993) |
| Molecular graphics | ZORTEP (Zsolnai, 1994) |
| Publication material | SHELXL-93 (Sheldrick, 1993) |
| Weighting scheme | $w = 1/[s^2(Fo^2)+(0.0487P)^2+0.0000P]$ where $P = (Fo^2+2Fc^2)/3$ |
| Data/parameters | 4336/283 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0553$, $wR_2 = 0.1040$ |
| Goodness-of-fit on $F^2$ | 0.991 |
| Largest diff. peak and hole | 0.707 and $-0.902$ e·Å$^{-3}$ |

of the $Cu_2S_2$ core, similar to other dimeric Cu$^I$ complexes listed in Table 4 and bond lengths are similar in values. The asymmetry in Cu—S distances is close to that of complex **7**, while **6** and **8** exhibit largest asymmetry.

The Cu—P bond distance of 2.243 Å is only slightly shorter than in **6**, but longer than in **7** or **8**. These Cu—P distances are slightly shorter than those in monomeric tetrahedral complexes [20,24]. The C—S bond distance of 1.690 Å in **5** is shortest among all the dimeric complexes listed in Table 4 [**6**, 1.721, **7**, 1.716, **8**, 1.703 Å] and close to the value, 1.692 Å, shown by monomeric tetrahedral complex, $CuCl(C_5H_5NS)(PPh_3)_2$ [20]. The Cu—S—C angle (107.0°) is similar to those shown by **7** (108.1°) and **8** (107.1°), but shorter than that in **6** (111.4°) or monomeric tetrahedral complexes [20,24].

It will be interesting to compare the Cu···Cu and S···S separations as well as Cu—S—Cu and S—Cu—S bond angles of the central planar $Cu_2S_2$ cores of the dimers (Table 4). It can be seen that the decrease of Cu···Cu separation is accompanied by the corresponding increase of S···S separation and **5** shows the next shortest Cu···Cu separation after **6**, though this separation is more close to that in **7** or **8**. The Cu···Cu separation in **6** is less than the sum of van der Waals radii of Cu atoms (2.80 Å) and S···S separation is more than the sum of van der Waals radii of S atoms (3.60 Å) [8b]. It is apparent that whereas in **6**, Cu···Cu interaction is indicated, in all other cases weak S···S interaction appears possible. Further, significantly, Cu—S—Cu and S—Cu—S bond angles in the two $p$-Tol$_3$P complexes (**5** and **8**) are similar [as were their C—S distances of Cu—S—C bond angles as discussed earlier] despite their dissimilar heterocyclic thione ligands and agree with the predicted geometry for $Y_2MX_2MY_2$ dimers according to a theoretically proposed criteria [33].

Finally, the interbond angles around Cu atoms in **5** show distortions from the idealized tetrahedral geometry. The geometry within tri-p-tolyl phosphine and the pyridine-2-thione molecules in **5** are consistent with those commonly found in other complexes [18,23,24].

### *Solution phase studies*

*UV spectral studies.* The C=S chromophore of free $C_5H_5NS$ absorbs at $\lambda_{max}$, 370 nm as a strong peak and

Table 2. Selected bond lengths (Å) angles (°) for $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$ (**5**)

| | |
|---|---|
| Cu—P | 2.243(3) |
| Cu—S$^a$ | 2.393(4) |
| Cu—S | 2.425(4) |
| Cu—I | 2.603(2) |
| Cu—Cu$^a$ | 3.263(4) |
| P—C(21) | 1.805(11) |
| P—C(11) | 1.810(10) |
| P—C(31) | 1.819(11) |
| S—S$^a$ | 3.545(7) |
| S—C(2) | 1.690(12) |
| P—Cu—S$^a$ | 106.77(13) |
| P—Cu—S | 119.71(14) |
| S—Cu—S$^a$ | 94.75(13) |
| P—Cu—I | 111.54(11) |
| S—Cu—I$^a$ | 116.19(11) |
| S—Cu—I | 107.26(11) |
| C(21)—P—C(11) | 103.4(5) |
| C(21)—P—C(31) | 102.3(5) |
| C(11)—P—C(31) | 102.7(5) |
| C(21)—P—Cu | 118.7(4) |
| C(11)—P—Cu | 116.7(3) |
| C(31)—P—Cu | 110.9(4) |
| C(2)—S—Cu$^a$ | 116.5(5) |
| C(2)—S—Cu | 107.0(4) |
| Cu—S—Cu$^a$ | 85.25(13) |

[a] Symmetry operations used to generate equivalent atoms: $-x+1,\ -y+2,\ -z+1$.

it shows considerable intensity changes [21] and it appears as a very weak to medium intensity broad peak in its complexes in the region 355–370 nm (cf Experimental). The iodide complexes showed the largest shifts in the $\lambda$C=S peak positions to the high energy region as anticipated in view of the enhanced Cu—S interaction due to increased softness of Cu$^I$ bonded to polarizable iodide group and the peaks almost disappear. The second peak due to the pyridyl ring at 290 nm of free pyridine-2-thione ligand also shows significant intensity changes for **4** and **5** and less for **1**–**3**. The peaks due to *m*-$Tol_3P$ and *p*-$Tol_3P$ ($\pi$–$\pi^*$) located in the region 248–251 nm as strong peaks are not significantly changed in the complexes and is in agreement with the general behaviour of aryl phosphines [23,24]—the n(P) to $\pi^*$ (tolyl group) transition is obscured by the pyridyl group, however.

*NMR spectral studies.* The complexes show broad $^{31}$P NMR signals at low field position supporting coordination of tertiary phosphines to Cu$^I$ center. The coordination shifts [$\Delta\delta = \delta_{complex} - \delta_{ligand}$] are not large as compared to those shown by other metals [34], however, these values do not support weak Cu—P interaction, as the solid state structure of complex (**5**) has established a normal Cu—P bond (*vide supra*); rather may be attributed to the lability of Cu—P bond and tendency to dissociate L, for example, according to eq. (1):

$$Cu_2X_2(C_5H_5NS)_2L_2 \leftrightarrow Cu_2X_2(C_5H_5NS)_2L + L$$
$$(X = Cl, Br, I;\ L = m\text{-}Tol_3P, p\text{-}Tol_3P) \quad (1)$$

Thus the broadness of all $^{31}$P signals shows that free and coordinated L are fast exchanging on NMR time scale giving rise to the exchange-averaged broad signals.

Table 5 lists the $^1$H and $^{13}$C NMR data of the com-

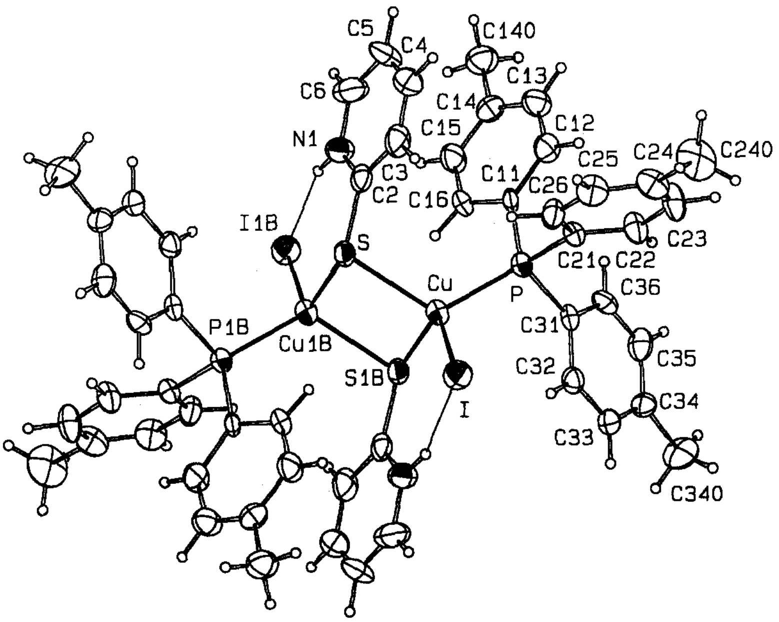


Fig. 1. Perspective view of $[CuI(C_5H_5NS)(p\text{-}Tol_3P)]_2$ (**5**) molecule with the numbering scheme. The thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are drawn with an arbitrary radius of 0.1 Å and are represented by open circles.

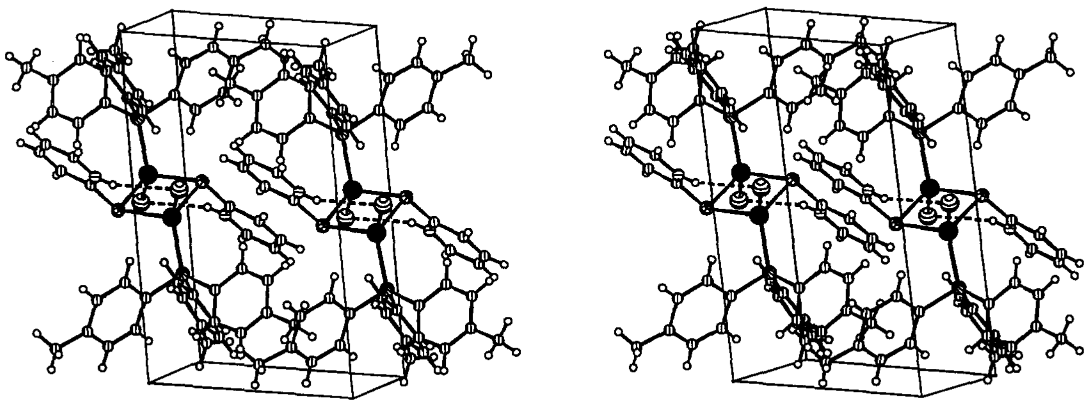


Fig. 2. Molecular packing in the crystal. Hydrogen bonds are denoted by dashed lines.

Table 3. The angles between various planes of complex **5**

| Plane | Rms[a] | Atoms defining a plane | Angles between planes |
|---|---|---|---|
| I | 0.004 | $N^1, C^2, C^3, C^4, C^5, C^6$, S | — |
| II | 0.000 | Cu, S, Cu*, S* | 66.29° (I & II) |
| III | 0.020 | $C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}$, P, $C^{140}$ | 75.39° (II & III) |
| IV | 0.012 | $C^{21}, C^{22}, C^{23}, C^{24}, C^{25}, C^{26}$, P, $C^{240}$ | 71.63° (III & IV) |
| V | 0.002 | $C^{31}, C^{32}, C^{33}, C^{34}, C^{35}, C^{36}$, P, $C^{340}$ | 81.85° (IV & V) |

[a] Rms deviations of fitted atoms.

Table 4. Selected bond lengths (Å) and bond angles (°) in related $Cu^I$ complexes

| Complex | Cu—P | Cu—S | Cu···Cu | S···S | Cu—S—Cu | S—Cu—S |
|---|---|---|---|---|---|---|
| **(5)** | 2.243 | 2.393<br>2.425 | 3.263 | 3.545 | 85.3 | 94.8 |
| **(6)** | 2.253 | 2.335<br>2.488 | 2.691 | 4.005 | 67.7 | 112.3 |
| **(7)** | 2.229 | 2.383<br>2.392 | 3.420 | 3.332 | 91.5 | 88.5 |
| **(8)** | 2.227 | 2.356<br>2.470 | 3.316 | 3.508 | 86.7 | 93.2 |

**(6)** $[CuBr(C_5H_5NS)(m\text{-}Tol_3P)]_2$ (Ref. 24).
**(7)** $[CuBr(C_5H_5NS)(PPh_3)]_2$, (Ref. 18).
**(8)** $[CuCl(pymtH)(p\text{-}Tol_3P)]_2$ (Ref. 23), pymtH = pyrimidine-2-thione.

plexes and the ligands. The presence of broad NH proton signal at low field in the range $\delta$ 13.90–14.95 ppm (free ligand, $\delta_{NH}$ 13.40 ppm) shows that pyridine-2-thione is coordinating to $Cu^I$ centre in the neutral form in the complexes. H(6), H(5) and H(4) protons of $C_5H_5NS$ all show low field shifts, while H(3) protons are nearly unaffected. Significant changes occur in $^3J_{H\text{-}H}$ coupling constants; for example, for H(6) protons $J_5$ values decrease; $J_4$, $J_3$ disappear, while coupling from NH protons appears in **2** and **5**. For H(4) protons, $J_3$ and $J_5$ become equal while $J_6$ marginally decreases in the complexes. Finally for H(3), $J_4$ and for H(5), $J_4$ and $J_6$ decrease marginally and in the latter case remain equal in the complexes as well.

The chemical shift($\delta$) values for the phosphine proton signals are marginally affected in the complexes (Table 5). As before, $J_{H\text{-}H}$ and $J_{H\text{-}P}$ coupling constants are more sensitive to coordination changes; for example, $^3J_{H\text{-}H}$ of *m*-H and *p*-H of *m*-$Tol_3P$ decrease significantly in the complexes. Similarly, $^3J_{H\text{-}P}$ coupling constants involving *o*-$C_1H$ and *o*-$C_2H$ protons of *m*-$Tol_3P$ as well as $^3J_{H\text{-}H}$ and $^3J_{H\text{-}P}$ coupling constants

Table 5. The $^{1}H$ NMR data (δ, ppm, J, Hz) of the copper(I) compounds[a–d]

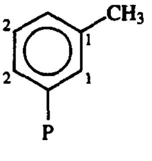
| | $CH_3$ | o-H<br>($^{3}J_{H-H}/^{3}J_{H-P}$) | m-H<br>($^{3}J_{H-H}$) | p-H<br>($^{3}J_{H-H}$) |
|---|---|---|---|---|
| m-$Tol_3P$ | 2.32s | 7.18d(3H, o-$C_1H$)<br>(3.8, $^{3}J_{H-P}$)<br>7.26d(3H, o-$C_2H$)<br>(6.6, $^{3}J_{H-P}$) | 7.10t<br>(3H, m-$C_2H$)<br>(7.3) | 7.16d<br>(7.6) |
| p-$Tol_3P$ | 2.36s | 7.23t(6H)<br>(7.8, $^{3}J_{H-H}$, $^{3}J_{H-P}$) | 7.15d(6H)<br>(7.3) | — |
| 1 | 2.30s | 7.35dd(6H)<br>(8.2, $^{3}J_{H-H}$, 10.0, $^{3}J_{H-P}$) | 7.05d(6H)<br>(7.7) | — |
| 2 | 2.23s | 7.19d(3H, o-$C_1H$)<br>(6.4, $^{3}J_{H-P}$)<br>7.29d(3H, o-$C_2H$)<br>(11.5, $^{3}J_{H-P}$) | 7.14t<br>(3H, m-$C_2H$)<br>(4.5) | 7.17d<br>(3.8) |
| 3 | 2.27s | 7.30dd(6H)<br>(8.1, $^{3}J_{H-H}$, 10.3, $^{3}J_{H-P}$) | 7.07d(6H)<br>(7.4) | — |
| 4 | 2.22s | 7.18d(3H, o-$C_1H$)<br>(7.2, $^{3}J_{H-P}$)<br>7.30d(3H, o-$C_2H$)<br>(13.5, $^{3}J_{H-P}$) | 7.13t<br>(3H, m-$C_2H$)<br>(4.3) | 7.16d<br>(3.5) |
| 5 | 2.33s | 7.39dd(6H)<br>(8.1, $^{3}J_{H-H}$, 9.9, $^{3}J_{H-P}$) | 7.12d(6H)<br>(7.0) | — |
| | H(6) | H(4) | H(3) | H(5) |
| 1 | 7.72d<br>(5.5, $J_5$) | 7.42td<br>(8.7, $J_3$, $J_5$, 1.5, $J_6$) | 7.46d<br>(8.0, $J_4$) | 6.82td<br>(6.4, $J_4$, $J_6$, 1.6, $J_3$) |
| 2 | 7.72t<br>(5.9, $J_5$, $J_{N-H}$) | 7.44td<br>(8.6, $J_3$, $J_5$, 1.6, $J_6$) | 7.48d<br>(7.6, $J_4$) | 6.86td<br>6.3, $J_4$, $J_6$, 1.4 $J_3$) |
| 3 | 7.71d<br>(4.1, $J_5$) | 7.43td<br>(8.9, $J_3$, $J_5$, 1.6, $J_6$) | 7.46d<br>(7.3, $J_4$) | 6.84td<br>(6.2, $J_4$, $J_6$, 2.0 $J_3$) |
| 4 | 7.67d<br>(6.2, $J_5$) | 7.44td<br>(8.8, $J_3$, $J_5$, 1.5, $J_6$) | 7.47d<br>(7.7, $J_4$) | 6.87td<br>6.2, $J_4$, $J_6$, 2.0, $J_3$) |
| 5 | 7.67t<br>(4.8, $J_5$, $J_{N-H}$) | 7.46td<br>(8.9, $J_3$, $J_5$, 1.6, $J_6$) | 7.50d<br>(8.3, $J_4$) | 6.90td<br>(6.2, $J_4$, $J_6$, 2.0, $J_3$) |
| $C_5H_5NS$ | 7.56ddd<br>(6.3, $J_5$, 1.6, $J_4$, 0.8, $J_3$) | 7.34ddd<br>(8.7, $J_3$, 7.0, $J_5$, 1.8, $J_6$) | 7.49dt<br>(8.7, $J_4$, 0.8, $J_5$, $J_6$) | 6.73td<br>(6.7, $J_4$, $J_6$, 1.2, $J_3$) |

[a] See figure below for numbering scheme.

[b] n.o.—not observed.

[c] d-doublet, t-triplet, dd-doublet of doublets, td-triplet of doublets, dt-doublet of triplets.

[d] $\delta_{NH}$ for 1–5 and ligand are 14.95, 14.44, 14.43, 13.93, 13.90 and 13.40 ppm, respectively.



of o-H protons of p-$Tol_3P$ are all increased in the complexes (see Table 5 for numbering scheme for m-$Tol_3P$).

The C(2) carbon signal of free $C_5H_5NS$ shows up-field shift in its complexes; C(6) signals are marginally downfield, but C(4) signals are nearly unaffected (Table 6). Further, while the C(3) signal shows down-field shift, more divergent trends are visible in C(5) signals, notably up-field and different magnitude of chemical shifts for m-$Tol_3P$ and p-$Tol_3P$ complexes. The shift to high-field is more for p-$Tol_3P$ than for m-$Tol_3P$ complexes and coupled with $^{31}P$ NMR shifts, it can be suggested that p-$Tol_3P$ is somewhat a better Lewis base as compared to m-$Tol_3P$. The up-field shift of C(2) carbon signal suggests that coordination of $C_5H_5NS$ to the $Cu^{I}$ center increases the aromatic character of pyridyl ring. It is worth mentioning here that anionic $C_5H_4NS^-$ shows up-field shifts, if it binds to a metal center *via* sulfur only and it is attributed to aromatisation of pyridyl ring [35]. The $^{13}C$ NMR signals of tertiary phosphines in the complexes are more complex; however, the information obtained is

Table 6. The $^{13}$C NMR data ($\delta$ ppm, J, Hz) of the copper(I) compounds

|  | CH3 | *i*-C<br>($^1J_{C-P}$) | *o*-C<br>($^2J_{C-P}$) | *m*-C<br>($^3J_{C-P}$) | *p*-C |
|---|---|---|---|---|---|
| *m*-Tol$_3$P | 20.45 | 135.8 | 129.7(*o*-C$_1$) | 137.0(*m*-C$_1$) | 128.7 |
|  |  | (8.8) | (16.6) | (8.0) |  |
|  |  |  | 133.5(*o*-C$_2$) | 127.3(*m*-C$_2$) |  |
|  |  |  | (22.0) | (6.6) |  |
| *p*-Tol$_3$P | 20.30 | 133.0 | 132.6 | 128.3 | 137.6 |
|  |  | (8.8) | (19.5) | (7.2) |  |
| **1** | 20.38 | 130.9 | 132.8 | 128.3 | 138.8 |
|  |  |  | (15.0) | (9.5) |  |
| **2** | 20.45 | 131.7 | 129.9(*o*-C$_1$) | 137.2(*m*-C$_1$) | 129.7 |
|  |  |  | (13.7) | (9.9) |  |
|  |  |  | 132.5(*o*-C$_2$) | 127.4(*m*-C$_2$) |  |
|  |  |  | (16.4) | (9.6) |  |
| **3** | 20.38 | 131.0 | 132.8 | 128.4 | 138.9 |
|  |  |  | (15.1) | (9.9) |  |
| **4** | 20.43 | 131.5 | 130.0(*o*-C$_1$) | 137.2(*m*-C$_1$) | 129.7 |
|  |  |  | (13.3) | (10.1) |  |
|  |  |  | 133.6(*o*-C$_2$) | 127.4(*m*-C$_2$) |  |
|  |  |  | (16.2) | (9.5) |  |
| **5** | 20.37 | 131.3 | 132.9 | 128.3 | 138.7 |
|  |  |  | (14.6) | (10.0) |  |
|  | C(2) | C(6) | C(4) | C(5) | C(3) |
| **1** | 172.1 | 137.6 | 136.2 | 128.8 | 114.4 |
| **2** | 171.6 | 137.7 | 136.0 | 131.1 | 114.5 |
| **3** | 171.5 | 137.8 | 136.0 | 128.7 | 114.6 |
| **4** | — | 137.7 | 136.0 | 131.3 | 114.1 |
| **5** | 170.8 | 137.5 | 135.9 | 128.9 | 114.3 |
| $C_5H_5NS$ | 175.6 | 137.0 | 135.9 | 132.8 | 113.4 |

summarised as follows: (i) $CH_3$ group shows little or no variation in $\delta$ value, (ii) *p*-C of *m*-Tol$_3$P and *p*-Tol$_3$P show low-field shifts, (iii) *o*-C and *m*-C of both ligands remain nearly unaffected and finally (iv) i-C of both ligands show up-field shifts.

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