Synthesis and *X*-Ray Crystal Structure of Chloro[2(1*H*)-pyridinethione-*S*]-bis(triphenylphosphine)copper(I)†

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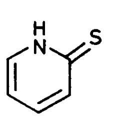
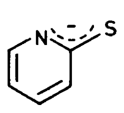
The preparation and single-crystal structure analysis of $[CuCl(C_5H_5NS)(PPh_3)_2]$ is reported. The geometry about the copper atom is distorted tetrahedral with one co-ordination site being occupied by the thione S atom of the neutral C_5H_5NS ligand; Cu–S 2.374(2) Å. The complex features a strong intramolecular hydrogen-bonding interaction between the nitrogen-bound hydrogen atom and the Cl atom; N–H $\cdots$ Cl of 2.219(8) Å. Crystals are monoclinic, space group $P2_1/c$ with unit-cell dimensions a = 14.456(4), b = 10.152(3), c = 24.517(5) Å, β = 93.40(2)°, and Z = 4. The structure was refined by a full-matrix least-squares procedure to R = 0.067 for 3 413 reflections for which $I \geqslant 2.5\sigma(I)$.

The ligand 2-mercaptopyridine (hereafter C_5H_5NS), which contains the –N(H)–C(=S)– chromophore, is a useful model compound for sulphur-containing analogues of purine and pyrimidine bases. Consequently, there has been considerable interest in the co-ordination properties of both the neutral thione, (**1**), and of the deprotonated thiolate, (**2**), ligands.[1,2] Crystallographic investigations have shown that the thione co-ordinates exclusively *via* the S atom.[3–8] In contrast, the thiolate, (**2**), can adopt a variety of co-ordination modes, namely: (*i*) S unidentate;[2] (*ii*) S, N chelating;[2,6,9–12] (*iii*) S, N, bridging;[6,13] and (*iv*) S unidentate (with a weak M $\cdots$ N interaction).[14,15]

Studies of the co-ordination of Cu^I by (**1**) or (**2**) have focused on the preparation and spectroscopic characterization of (*a*) insoluble species of general formula $[CuX(C_5H_5NS)_n]$ (X = Cl, Br, or I; n = 2 or 3),[16] and (*b*) $[Cu(C_5H_4NS)]$ and $[Cu(C_5H_4NS)(PPh_3)]$.[17] Crystallographic studies are available for $[Cu(C_5H_5NS)_3]^+$, which shows a distorted trigonal configuration about the copper centre defined by three S donor atoms,[3] $[Cu(C_5H_5NS)_4]^+$ in which the copper atom is tetrahedrally co-ordinated by four S donor atoms,[7] and $[Cu_2(C_5H_5NS)_6]Cl_2$ which exists as a dimer as a result of two bridging C_5H_5NS ligands (*via* the thione S atoms). The tetrahedral geometry about each copper atom is completed by two terminal C_5H_5NS ligands.[8] The preparation of the mixed-ligand complex $[CuCl(C_5H_5NS)(PPh_3)_2]$ and its crystal structure is reported herein.



(**1**)



(**2**)

Experimental

Preparation of $[CuCl(C_5H_5NS)(PPh_3)_2]$.—The starting material, $[CuCl(C_5H_5NS)]$, was prepared in the following manner: a solution of C_5H_5NS (Sigma) (4.5 mmol) in ethanol (15 cm^3) was added to a solution of $CuCl_2 \cdot 2H_2O$ (2.25 mmol) in ethanol (15 cm^3) which resulted in the formation of a yellow insoluble complex, formulated as $[CuCl(C_5H_5NS)]$.[16] The latter (0.95 mmol) was refluxed with PPh_3 (1.9 mmol) in chloroform (30 cm^3) for 2 h. The solvent was reduced to 1/3 of its original volume and the complex was precipitated by the addition of light petroleum (b.p. 60—80 °C) (2—3 cm^3). The yellow product was filtered off and dried *in vacuo* (Found: C, 67.1; H, 4.1; Cu, 8.4. Calc. for $C_{41}H_{35}ClCuNP_2S$: C, 67.0; H, 4.7; Cu 8.6%), m.p. 145—150 °C. Crystals suitable for *X*-ray studies were obtained from the slow evaporation of an $EtOH–CH_2Cl_2$ solution of the compound.

Crystallography.—Crystal data. $C_{41}H_{35}ClCuNP_2S$, M = 734.7, monoclinic, space group $P2_1/c$, a = 14.456(4), b = 10.152(3), c = 24.517(5) Å, β = 93.40(2)°, U = 3 591.7 Å^3, Z = 4, D_c = 1.359 g cm^{-3}, $F(000)$ = 1 520, Mo-K_α radiation, λ = 0.710 73 Å, μ = 8.18 cm^{-1}.

Intensity data for a crystal, 0.08 × 0.16 × 0.35 mm, were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-K_α radiation. The ω—2θ scan technique was employed to measure the intensities of 7 144 reflections ($\theta_{max.}$ 22.5°) which were corrected for Lorentz and polarization effects and absorption effects (maximum and minimum transmission factors 0.940 and 0.866).[18] A total of 6 317 reflections were unique (R_{merge} 0.039) and of these 3 413 satisfied $I \geqslant 2.5\sigma(I)$.

Solution and refinement of the structure. The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure in which the function $\Sigma w\Delta^2$ was minimized where $\Delta = ||F_o| - |F_c||$ and w was the weight applied to each reflection.[18] Non-phenyl, non-hydrogen atoms were refined anisotropically, phenyl rings were refined as hexagonal rigid groups, and hydrogen atoms (except for NH which was located from a difference map but not refined) were included in the model at their calculated positions. The refinement converged to R = 0.067, R' = 0.069 for $w = 1.58/[\sigma^2(F) + 0.002F^2]$. Fractional atomic co-ordinates and selected bond distances and angles are given Tables 1 and 2 respectively. The scattering factors for neutral Cu (corrected for anomalous dispersion) were from ref. 19 and those for the remaining atoms were incorporated in SHELX 76.[18]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates for $[CuCl(C_5H_5NS)(PPh_3)_2]$

Atom	*x*	*y*	*z*
Cu	0.239 02(9)	−0.192 92(9)	0.143 23(4)
Cl	0.267 2(1)	0.034 2(2)	0.156 6(1)
S	0.089 6(2)	−0.222 1(2)	0.099 3(1)
P(1)	0.242 4(1)	−0.260 7(2)	0.232 9(1)
P(2)	0.334 2(1)	−0.280 9(2)	0.081 5(1)
N(1)	0.066 0(5)	0.036 4(8)	0.107 7(3)
C(1)	0.032 0(6)	−0.078 4(9)	0.089 0(3)
C(2)	−0.055 4(7)	−0.070 0(12)	0.060 5(4)
C(3)	−0.099 8(8)	0.046 0(14)	0.053 0(5)
C(4)	−0.061 1(8)	0.162 2(13)	0.073 7(5)
C(5)	0.022 4(8)	0.154 9(11)	0.101 5(5)
C(6)	0.357 6(3)	−0.253 3(4)	0.267 5(2)
C(7)	0.397 9(3)	−0.130 0(4)	0.277 1(2)
C(8)	0.488 9(3)	−0.120 9(4)	0.299 1(2)
C(9)	0.539 6(3)	−0.235 0(4)	0.311 5(2)
C(10)	0.499 3(3)	−0.358 3(4)	0.301 9(2)
C(11)	0.408 3(3)	−0.367 5(4)	0.279 9(2)
C(12)	0.208 6(4)	−0.430 4(5)	0.245 3(2)
C(13)	0.217 5(4)	−0.519 0(5)	0.202 4(2)
C(14)	0.201 1(4)	−0.652 9(5)	0.210 3(2)
C(15)	0.175 7(4)	−0.698 1(5)	0.261 0(2)
C(16)	0.166 8(4)	−0.609 5(5)	0.303 9(2)
C(17)	0.183 2(4)	−0.475 6(5)	0.296 0(2)
C(18)	0.173 0(4)	−0.160 1(6)	0.277 2(2)
C(19)	0.089 4(4)	−0.110 6(6)	0.254 4(2)
C(20)	0.035 2(4)	−0.028 5(6)	0.285 2(2)
C(21)	0.064 7(4)	0.004 1(6)	0.338 7(2)
C(22)	0.148 3(4)	−0.045 4(6)	0.361 4(2)
C(23)	0.202 5(4)	−0.127 5(6)	0.330 7(2)
C(24)	0.295 8(3)	−0.445 7(5)	0.058 8(2)
C(25)	0.344 5(3)	−0.558 4(5)	0.075 9(2)
C(26)	0.307 6(3)	−0.682 8(5)	0.064 1(2)
C(27)	0.221 9(3)	−0.694 5(5)	0.035 2(2)
C(28)	0.173 2(3)	−0.581 8(5)	0.018 1(2)
C(29)	0.210 2(3)	−0.457 4(5)	0.029 9(2)
C(30)	0.457 8(3)	−0.302 7(6)	0.100 1(2)
C(31)	0.518 0(3)	−0.359 6(6)	0.064 5(2)
C(32)	0.612 1(3)	−0.371 2(6)	0.079 9(2)
C(33)	0.646 0(3)	−0.325 8(6)	0.131 0(2)
C(34)	0.585 8(3)	−0.268 8(6)	0.166 6(2)
C(35)	0.491 7(3)	−0.257 2(6)	0.151 2(2)
C(36)	0.341 9(4)	−0.189 2(4)	0.017 8(2)
C(37)	0.352 1(4)	−0.248 6(4)	−0.032 8(2)
C(38)	0.370 0(4)	−0.171 7(4)	−0.078 1(2)
C(39)	0.377 7(4)	−0.035 2(4)	−0.072 8(2)
C(40)	0.367 5(4)	0.024 3(4)	−0.022 3(2)
C(41)	0.349 6(4)	−0.052 7(4)	0.023 1(2)

Table 2. Selected interatomic bond distances (Å) and angles (°) for $[CuCl(C_5H_5NS)(PPh_3)_2]$

Cu–Cl	2.361(2)	Cu–S	2.374(2)
Cu–P(1)	2.301(2)	Cu–P(2)	2.286(2)
S–C(1)	1.692(9)	N(1)–C(1)	1.34(1)
N(1)–C(5)	1.36(1)	C(1)–C(2)	1.41(1)
C(2)–C(3)	1.35(2)	C(3)–C(4)	1.39(2)
C(4)–C(5)	1.35(1)		
Cl–Cu–S	109.2(1)	Cl–Cu–P(1)	99.6(1)
Cl–Cu–P(2)	111.6(1)	S–Cu–P(1)	111.3(1)
S–Cu–P(2)	102.6(1)	P(1)–Cu–P(2)	122.4(1)
Cu–S–C(1)	112.8(3)	S–C(1)–N(1)	122.2(6)
S–C(1)–C(2)	123.0(8)	N(1)–C(1)–C(2)	114.8(9)
C(1)–N(1)–C(5)	125.0(8)		

Results and Discussion

The crystals structure analysis, Figure, confirms the stoicheiometry of the compound as $[CuCl(C_5H_5NS)(PPh_3)_2]$. The Cu^I exists in a distorted tetrahedral environment with the largest deviation from the ideal geometry arising, in part, from the presence of the two PPh_3 ligands; P–Cu–P 122.4(1)°. The co-ordination about the Cu^I is unremarkable with similar geometries being found previously in $[CuCl(PPh_3)_2L]$ where L = 2-thiopyrrole-1,2-dicarboximide[20] or dithio-oxamide[21] (both ligands co-ordinating through a thione group). Of interest, however, is the mode of co-ordination of the C_5H_5NS ligand.

The C_5H_5NS ligand is co-ordinated through the S atom at a Cu–S distance of 2.374(2) Å. This distance is longer, as expected, than those of 2.213(5), 2.225(5), and 2.228(5) Å found[3] in the related compound $[Cu(C_5H_5NS)_3]^+$ in which the copper atom is in a distorted trigonal geometry, but lies in the range 2.273(3)—2.498(3) Å found for the tetrahedral copper atoms in $[Cu(C_5H_5NS)_4]^+$ [7] and $[Cu_2(C_5H_5NS)_6]^{2+}$.[8] It is noteworthy that the Cu–Cl, –P, and –S bond distances in $[CuCl(C_5H_5NS)(PPh_3)_2]$ are comparable to the equivalent distances found in the $[CuCl(PPh_3)_2L]$ complexes cited above.[20,21] The C_5H_5NS ligand is essentially planar [maximum deviation: 0.01(1) Å for C(5)] and the S atom lies 0.014(3) Å above this plane. The S–C(1) distance of 1.692(9) Å is equal to that found in the free ligand[22] [1.692(2) Å] and comparable to the C–S distances of 1.68(2)—1.70(2) Å found in $[Cu(C_5H_5NS)_3]^+$ [3] and 1.70(1)—1.71(1) Å in $[Cu(C_5H_5NS)_4]^+$.[7] However, in the other four structurally characterized complexes with the thione ligand, (**1**), the C–S bond is significantly lengthened: 1.730(9) Å in $[Sn(CH_3)_2Cl_2(C_5H_5NS)_2]$ (molecule has $\bar{1}$ symmetry);[4] 1.720(3) and 1.721(3) Å in $[CoCl_2(C_5H_5NS)_2]$;[5] 1.719(6) Å in $[Rh_2Cl_2(\mu\text{-}C_5H_4NS)_2(C_5H_5NS)_2(CO)_2]$ (molecule has two-fold symmetry);[6] and 1.719(8) and 1.725(9) Å for the terminal

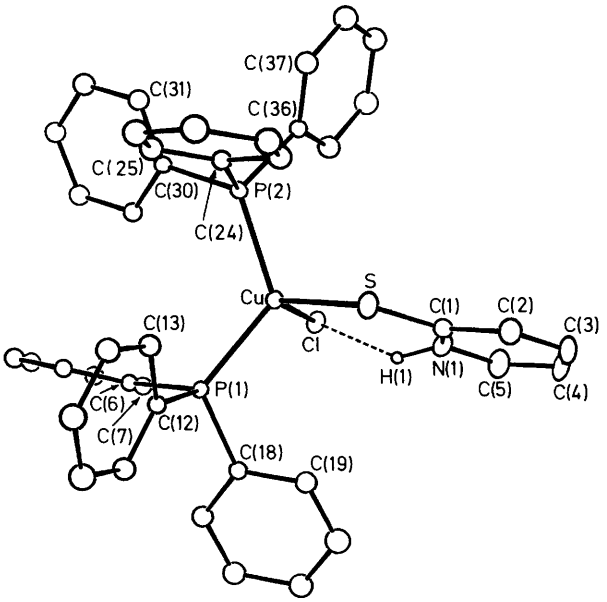
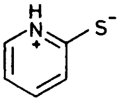


Figure. Crystallographic numbering scheme for $[CuCl(C_5H_5NS)(PPh_3)_2]$ drawn with ORTEP at 15% probability ellipsoids. All hydrogen atoms except for NH have been omitted for clarity



(3)

C_5H_5NS ligands in the $[Cu_2(C_5H_5NS)_6]^{2+}$ dimer.[8] The last four complexes appear to be examples where (**1**) co-ordinates more in the zwitterionic form, (**3**), than in the above copper examples where the thione form predominates. Interatomic parameters (Table 2) describing the C_5H_5NS ligand also suggest that this ligand functions as a thione in $[CuCl(C_5H_5NS)(PPh_3)_2]$.

As has been found previously in both the tin[4] and rhodium[6] complexes above, the nitrogen-bound hydrogen atom in $[CuCl(C_5H_5NS)(PPh_3)_2]$ participates in an intramolecular hydrogen-bonding contact with a metal-bound chloride atom; as illustrated for $[CuCl(C_5H_5NS)(PPh_3)_2]$ in the Figure, this results in the formation of a $\overline{\text{Cu–Cl–H–N–C–S}}$ six-membered ring. The hydrogen atom was located from the difference map and found to be 1.01 and 2.22 Å from the N and Cl atoms respectively [N···Cl 3.079(7) Å] and the N–H–Cl angle is 142°.

Acknowledgements

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