



Metal–heterocyclic thione interactions.

13. Pyridine-2-thione derivatives of copper(I): crystal structure of dinuclear [bromo(pyridine-2-thione)(tri-*p*-tolylphosphine)copper(I)]₂ complexTarlok S. Lobana^{a,*}, Alfonso Castineiras^b^a Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, Punjab, India^b Departamento de Química Inorgánica, Universidade de Santiago, 15706 Santiago, Galicia, Spain

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Abstract

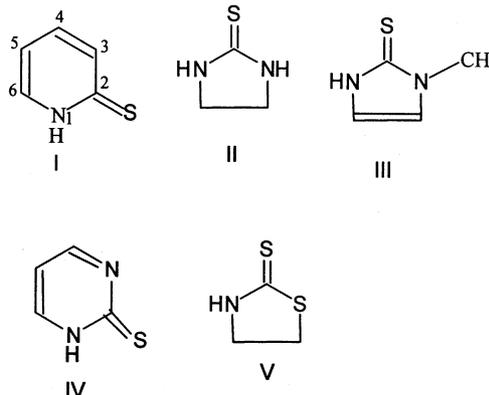
The sulfur-bridged dinuclear copper (I) complex, [CuBr(η²-S-μ-C₅H₅NS)(*p*-Tol₃P)]₂ (**1**) was prepared by the reaction of insoluble CuBr₂(C₅H₅NS)₂ {from copper(II) bromide and pyridine-2-thione(C₅H₅NS) in ethanol} with excess tri-*p*-tolylphosphine (*p*-Tol₃P) in chloroform (1:2 mole ratio). Similarly, other copper(I) complexes of stoichiometry [CuX(C₅H₅NS)(Ph₃P)]₂ {X = Cl, **2** and I, **3**} were prepared. Compound **1** crystallised from a dichloromethane–chloroform–methanol 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*-Tol₃P and a bromine atom. The central core Cu₂S₂ of the dimer is a parallelogram with the important interatomic parameters as follows: Cu–P, 2.2376(13), Cu–S, 2.3895(19), 2.415(2), Cu–Br, 2.4455(11), S–C(2), 1.717(4), Cu–Cu*, 3.250(2), S–S*, 3.539(3) Å; Cu–S–Cu*, 85.14(6), S–Cu–S*, 94.86(6), Cu–S–C(2), 108.41(14), 113.12(16)°. The dimer structure is stabilised by strong intramolecular N–H···Br hydrogen bonds [3.319(5) Å]. The X-ray study of **2** showed that it has transformed into monomer [CuCl(η¹-S-μ-C₅H₅NS)(Ph₃P)]₂ (**4**) during crystal growth. The strong intramolecular N–H···Cl hydrogen bonding appears to stabilise the monomer. All the compounds were characterised using analytical data, IR and far-IR (4000–100 cm⁻¹), UV–Vis spectra, NMR (¹H, ¹³C) and for **1** and **4** using X-ray crystallography. The factors controlling Cu···Cu interaction in the sulfur-bridged dinuclear copper(I)-heterocyclic thione complexes are described. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Pyridine-2-thione; Tri-*p*-tolylphosphine; Triphenylphosphine; Sulfur-bridged dimer; Copper(I) complexes

1. Introduction

The interaction of transition and main-group metals with heterocyclic thioamides have been the focus of several investigations because these compounds contain chemically active –N(H)–C(=S)– ⇌ –N=C(–SH)– groups and bind to metals both as neutral and deprotonated species via a variety of modes forming monomers, dimers and oligomers [1–4]. The simplest prototype of heterocyclic-2-thiones, i.e. pyridine-2-thione (hereafter C₅H₅NS, see I), has been intensively

studied and it has shown several modes of bonding [5].



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The coordination chemistry of copper is important for a variety of reasons such as modelling its sites present in biological systems, display of stereochemical diversity on interaction with organic substrates, formation of oligomers and polymers, interesting magnetic properties etc. [1–23]. In view of our interest in the study of metal–sulfur bonds, structural and spectroscopic properties of interaction of heterocyclic thiones, thiosemicarbazones and phosphine sulfides/selenides with several transition and non-transition metals have been reported [9–42].

In the literature, neutral heterocyclic thiones form sulfur-bridged dinuclear copper(I) complexes, namely $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_4\text{I}_2]$ (**5**) [24], $[\text{Cu}_2(\text{imdtH}_2)_4\text{Cl}_2]$ (**6**) {imdtH₂ = 1,3-imidazolidine-2-thione, II} [25], $[\text{Cu}_2(\text{meimtH})_4\text{Cl}_2]$ (**7**) [26], $[\text{Cu}_2(\text{meimtH})_4(\text{SCN})_2]$ (**8**) [27], $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_6]\text{X}_2$ {X = Cl, **9**, Br, **10**} [28,29], $[\text{Cu}_2(\text{meimtH})_6](\text{BF}_4)_2$ (**11**) {meimtH = 1-methylimidazole-2-thione, III} [30], $[\text{Cu}_2(\text{imdtH}_2)_6](\text{ClO}_4)_2$ (**12**) [31], $[\text{Cu}_2(\text{pymtH})_2\text{Cl}_2(p\text{-Tol}_3\text{P})_2]$ (**13**) {pymtH = pyrimidine-2-thione, IV} [32], $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{Br}_2(m\text{-Tol}_3\text{P})_2]$ (**14**) [33], $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{Br}_2(\text{PPh}_3)_2]$ (**15**) [34], $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{I}_2(p\text{-Tol}_3\text{P})_2]$ (**16**) [6], $[\text{Cu}_2(\text{tzdtH})_2\text{Cl}_2(p\text{-Tol}_3\text{P})_2]$ (**17**) (tzdtH = 1,3-thiazolidine-2-thione, V} [35] and $[\text{Cu}_2(\text{meimtH})_5](\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (**18**) [36].

In this paper, copper(I) complexes with C₅H₅NS containing tertiary phosphines as co-ligands are reported with the objectives of: (i) understanding the effect of substituents on Ph groups attached to P atoms and anion on the Lewis acidity of the Cu(I) centre; (ii) studying the Cu(I)··Cu(I) interaction; and (iii) analysing factors controlling the formation of sulfur-bridged dinuclear copper(I) complexes with various heterocyclic thioamides. It may be mentioned that preparations and other details of the complexes have appeared elsewhere [12,32,34].

2. Experimental

2.1. Preparation of complexes

2.1.1. $[\text{CuBr}(\eta^2\text{-S}-\mu\text{-C}_5\text{H}_5\text{NS})(p\text{-Tol}_3\text{P})_2]$ (**1**)

NMR spectroscopy and also preparation details of compound **1** are described earlier [6]. To $\text{CuBr}_2(\text{C}_5\text{H}_5\text{NS})_2$ {0.100 g, 0.22 mmol} suspended in CHCl_3 (15 cm³) was added a solution of excess *p*-Tol₃P (0.136 g, 0.44 mmol) in CHCl_3 (15 cm³) and the mixture was refluxed for 2 h. The clear solution formed was filtered and concentrated. A yellow solid started forming on cooling to room temperature (r.t.), which was filtered, washed with EtOH and dried in vacuo. Yield: 70%, m.p. 208–210 °C. Anal. Found: C, 55.3; H, 4.22; N, 2.50. Calc. for C₅₂H₅₂Br₂Cu₂N₂P₂S₂: C, 55.9; H, 4.65; N, 2.50%. UV data (λ_{max}, nm): 367mb (CS), 288s (py), 251s (Ph). IR data (cm⁻¹): 3162w (νN–H), 1127s

(νC=S), 1098s (νP–C), 809s (ρC–CH₃), 219sb (νCu–Br) [7,8]. The crystals were grown from CH₂Cl₂–CHCl₃–MeOH mixture.

2.1.2. $[\text{CuCl}(\text{C}_5\text{H}_5\text{NS})(\text{Ph}_3\text{P})_2]$ (**2**)

To $\text{CuCl}(\text{C}_5\text{H}_5\text{NS})$ {0.100 g, 0.48 mmol} suspended in CHCl_3 (15 cm³) was added a solution of Ph₃P (0.125 g, 0.48 mmol) in CHCl_3 (15 cm³) and the mixture was refluxed for 2 h. The clear solution formed was filtered and concentrated. A yellow solid started forming on cooling to r.t., which was filtered, washed with EtOH and dried in vacuo. Yield: 65%, m.p. 190–192 °C. Anal. Found: C, 57.6; H, 4.40; N, 2.94. Calc. for C₄₆H₄₀Cl₂Cu₂N₂P₂S₂: C, 58.5; H, 4.23; N, 2.97%. UV data (λ_{max}, nm): 367mb (CS), 285s (py), 250s (Ph). IR data (cm⁻¹): 1126s (νC=S), 1097s (νP–C), 327sb (νCu–Cl).

2.1.3. $[\text{CuI}(\text{C}_5\text{H}_5\text{NS})(\text{Ph}_3\text{P})_2]$ (**3**)

To CuI {0.100 g, 0.52 mmol} suspended in CHCl_3 (20 cm³) was added solid C₅H₅NS (0.058 g, 0.52 mmol) and a solution of Ph₃P (0.138 g, 0.52 mmol) in CHCl_3 (15 cm³) and the mixture was refluxed for 2 h. The clear solution formed was filtered, concentrated to 1/3 of its initial volume and addition of 10 cm³ of petroleum-ether (60–80 °C) formed a bright yellow solid which was filtered, washed with Et₂O and dried in vacuo. Yield: 70%, m.p. 218–220 °C. Anal. Found: C, 49.2; H, 3.69; N, 2.56. Calc. for C₄₆H₄₀Cu₂I₂N₂P₂S₂: C, 49.0; H, 3.55; N, 2.49%. UV data (λ_{max}, nm): 355wb (CS), 285s (py), 247 (Ph). IR data (cm⁻¹): 3105w (νN–H), 1124s (νC=S), 1096s (νP–C), 136sb (νCu–I).

2.1.4. $[\text{CuCl}(\eta^1\text{-S}-\mu\text{-C}_5\text{H}_5\text{NS})(\text{Ph}_3\text{P})_2]$ (**4**)

The crystallisation of **2** from CH₂Cl₂–EtOH mixture resulted in the formation of the monomer **4** as revealed by its X-ray crystal determination.

2.2. Elemental analyses and spectroscopic techniques.

The C, H and N elemental analyses were obtained with a Carlo-Erba 1108 microanalyser. The m.p. was determined with a Gallenkamp electrically heated apparatus. The electronic absorption spectra were recorded on a Shimadzu Graphicord 240 UV–Vis spectrophotometer. The IR spectra were recorded in KBr pellets (4000–400 cm⁻¹) or Nujol mull in polythene sheets (500–100 cm⁻¹) on a Bruker IFS 66V spectrometer. The NMR spectra were recorded in CDCl₃ using a Bruker AMX 300 spectrometer at 300.14, and 75.48 MHz probe frequencies (¹H and ¹³C, respectively) with TMS as the internal reference.

2.3. Crystal structure determinations

A yellow crystal of **1** (or yellow plate crystals of **4**) was mounted on a glass fibre and used for data collection. Cell constants and orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $14.077^\circ < \theta < 42.253^\circ$ for **1** and $16.036^\circ < \theta < 19.597^\circ$ for **4** on an Enraf–Nonius CAD 4 automatic diffractometer [43]. Data were collected at 293 K using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) and the ω -scan technique and corrected for Lp effects [44]. A semi-empirical absorption correction (ψ -scan) was made [45].

The structure was solved by direct method [46] and subsequent difference Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [47]. For **1** all hydrogen atoms were located from difference Fourier maps while for **4** all hydrogens were located in their calculated positions (C–H 0.93 \AA) except the one bonded to N1, which was located from the Fourier map. The located hydrogens were refined isotropically whereas calculated ones were refined using a riding model. Atomic scattering factors were taken from International Tables for X-ray crystallography [48] and molecular graphics from ZORTEP [49]. A summary of the crystal data, experimental details and refinement results are listed in Table 1. Tables 2 and 3 contain bond lengths and angles while NMR data are given in Tables 4 and 5.

3. Results and discussion

3.1. Synthesis, IR and NMR spectral studies

Reaction of $\text{CuBr}_2(\text{C}_5\text{H}_5\text{NS})_2$ with *p*-Tol₃P in CHCl_3 in a 1:2 mole ratio formed dinuclear compound **1** which yielded crystals in the CH_2Cl_2 – CHCl_3 – CH_3OH solvent mixture. Similarly $\text{CuCl}(\text{C}_5\text{H}_5\text{NS})$ reacted with Ph_3P in CHCl_3 (1:1 mole ratio) to form **2**; while compound **3** was formed by reacting CuI with $\text{C}_5\text{H}_5\text{NS}$ and Ph_3P in a 1:1:1 mole ratio. The melting points of complexes **2** and **3** are different, though close, to the reported values {lit. value [34], **2**, 196–199 $^\circ\text{C}$; **3**, 210–212 $^\circ\text{C}$ } and the difference may be attributed to the different packing densities. The crystallisation of **2** from a CH_2Cl_2 – $\text{C}_2\text{H}_5\text{OH}$ mixture resulted in the formation of **4** as revealed by X-ray crystallography. It is significant to note that reaction of $\text{CuCl}(\text{C}_5\text{H}_5\text{NS})$ with Ph_3P in a 1:2 mole ratio formed the monomer **4** [12]. Compound **3** did not yield good quality crystals.

The IR spectra of the complexes showed characteristic peaks due to $\text{C}_5\text{H}_5\text{NS}$ and tertiary phosphines at altered positions and some important ones are listed in Section 2. The presence of a $\nu(\text{N–H})$ peak in the region 3105–3164 cm^{-1} as a weak peak in the complexes shows that

Table 1
Summary of crystal data for compounds **1** and **4**

	1	4
Empirical formula	$\text{C}_{52}\text{H}_{52}\text{Br}_2\text{Cu}_2\text{N}_2\text{P}_2\text{S}_2$	$\text{C}_{41}\text{H}_{35}\text{ClCuNP}_2\text{S}$
Formula weight (MW)	1117.92	734.69
<i>T</i> (K)	293(2)	293(2)
λ (\AA)	1.54184	1.54184
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (\AA)	9.790(5)	14.4776(13)
<i>b</i> (\AA)	10.391(7)	10.1609(19)
<i>c</i> (\AA)	14.600(5)	24.5402(9)
α ($^\circ$)	83.64(4)	
β ($^\circ$)	73.82(3)	93.367(14)
γ ($^\circ$)	62.16(4)	
<i>V</i> (\AA^3)	1261.0(11)	3603.8(6)
<i>Z</i>	1	4
<i>D</i> _{calc} (g cm^{-3})	1.472	1.354
$\mu(\text{Cu K}\alpha)$ (mm^{-1})	4.543	3.144
<i>F</i> (000)	568	1520
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Crystal size (mm)	$0.30 \times 0.10 \times 0.05$	$0.20 \times 0.20 \times 0.10$
2θ Range ($^\circ$)	3.15–74.33	3.06–64.92
Index ranges	$-12 \leq h \leq 0,$ $-12 \leq k \leq 11,$ $18 \leq l \leq 17$	$-17 \leq h \leq 0,$ $0 \leq k \leq 11,$ $-28 \leq l \leq 28$
Reflections collected	5438	6380
Unique reflections, <i>R</i> _{int}	5122, 0.0227	6117, 0.0672
Max./min. transmission	0.978 and 0.907	0.910 and 0.803
Reflections with [<i>I</i> > 2 σ (<i>I</i>)], parameters	5122, 384	6117, 429
Final <i>R</i> indices	$R_1 = 0.0414,$ $wR_2 = 0.1011$	$R_1 = 0.0705,$ $wR_2 = 0.1433$
<i>R</i> indices (all data)	$R_1 = 0.0867,$ $wR_2 = 0.1195$	$R_1 = 0.2669,$ $wR_2 = 0.2092$
<i>S</i> on F^2	1.010	1.067
Peak and hole (e \AA^{-3})	0.324 and -0.711	0.466 and -0.410

$\text{C}_5\text{H}_5\text{NS}$ is not deprotonated in the complexes and a strong $\nu(\text{C=S})$ peak at 1139 cm^{-1} in the free ligand shifts to the low energy region, 1124–1127 cm^{-1} , again as a strong peak in the complexes. This shows that $\text{C}_5\text{H}_5\text{NS}$ coordinates to the Cu(I) centre via its thione sulfur and the magnitude of the coordination shift is similar to that reported in the literature [6]. Tentative assignments to $\nu(\text{Cu–X})$ X = halogen bands are also made (cf. Section 2) [6–8].

The presence of a broad signal due to NH protons in the range δ 13.93–14.92 ppm at a lowfield shows that pyridine-2-thione is coordinating to the Cu(I) centre as a neutral ligand (free ligand, $\delta_{\text{NH}} = 13.40$ ppm) (Table 4). There is a lowfield shift in H(6), H(5) and H(4) protons of $\text{C}_5\text{H}_5\text{NS}$, while H(3) protons remain nearly unaffected. The 3J coupling constants show variable trends for different ring protons; for example, the J_5 value for H(6) proton decreases, for H(4) proton J_3 and J_5 become equal, for H(3) J_4 and for H(5) J_4 and J_6

Table 2
Bond lengths (Å) and angles (°) for compounds **1** and **4**

Parameters	1	Parameters	4
<i>Bond lengths</i>			
Cu–P	2.2376(13)	Cu–P1	2.300(2)
		Cu–P2	2.288(2)
Cu–S	2.3895(19)	Cu–S1	2.381(2)
Cu–S*	2.415(2)	Cu–Cl	2.367(2)
Cu–Br	2.4455(11)	S(1)–C(2)	1.688(9)
Cu–Cu*	3.250(2)	N(1)–H(1)	1.14(12)
S–S*	3.539(3)	H(1)···Cl	1.94(12)
S(1)–C(2)	1.717(4)		
N(1)–H(1)	0.93(5)		
H(1)···Br	2.41(5)		
<i>Bond angles</i>			
S–Cu–S*	94.86(6)	P(2)–Cu–P(1)	122.31(9)
Cu–S–Cu*	85.14(6)	P(2)–Cu–Cl	111.84(9)
Cu–S–C(2)	108.41(14)	P(1)–Cu–Cl	99.46(8)
Cu*–S–C(2)	113.12(16)	P(2)–Cu–S(1)	102.83(9)
		P(1)–Cu–S(1)	111.10(9)
		Cl–Cu–S(1)	109.08(9)
		Cu–S(1)–C(2)	113.3(4)

Symmetry transformations used to generate equivalent atoms:
 $-x+2, -y+1, -z+1$.

decrease marginally. As regards phosphines, *o*-, *m*- and *p*-protons show lowfield shifts but are unresolved for Ph₃P (Table 4).

The C(2) signal of coordinated C₅H₅NS shows a significant upfield shift relative to the free ligand; C(6) and C(3) signals show small lowfield shifts; C(4) signals are nearly unaffected and finally C(5) signals also show upfield shift (Table 5). The upfield shift of C(2) signals shows that coordination of Cu(I) to the S atom of C₅H₅NS increases the aromatic character of the pyridyl ring. The anionic C₅H₄NS⁻ shows upfield shifts if it binds to a metal centre via S only and it is attributed to

increased aromatic character of the pyridyl ring [6]. As regards ¹³C NMR signals for the phosphines, the behaviour is summarised as follows: (i) *ipso*-carbons for both ligands show upfield shifts; (ii) *ortho*-carbons for Ph₃P also show the same behaviour, but for *p*-Tol₃P they are nearly unaffected; (iii) the *para*-carbon for Ph₃P also shows an upfield shift and for *p*-Tol₃P it is reversed; and finally (iv) for *meta*-carbons the trend is irregular and nearly unaffected.

3.1.1. Crystal and molecular structures

The atomic numbering schemes of [CuBr(η²-S-μ-C₅H₅NS)(*p*-Tol₃P)]₂ (**1**) and [CuCl(η¹-S-μ-C₅H₅NS)(Ph₃P)₂] (**4**) are shown in Figs. 1 and 2, respectively. The selected bond lengths and angles are given in Table 2. The basic structural unit of **1** is a centrosymmetric dimer with no interaction between the dimers and the S atoms of C₅H₅NS molecules bridge two Cu atoms forming a strictly planar Cu₂S₂ core. Each Cu atom is further bonded to a P atom of *p*-Tol₃P and one bromine atom and thus Cu acquires a distorted tetrahedral geometry. Two tetrahedra share a S–S edge and the *trans*-bromine atoms stabilise the dimer with strong intramolecular hydrogen bonds [N–H···Br, 3.319(5); H···Br, 2.41(5) Å and N–H–Br bond angle = 163(5)°] similar to those observed in literature [6,25]. The pyridyl ring of the thione ligand is planar and makes an angle of 63.66° with the plane of the Cu₂S₂ core.

The Cu–Br bond distance, 2.446 Å, is shorter than that (2.493 Å) in [Cu₂(C₅H₅NS)₂Br₂(*m*-Tol₃P)₂] (**14**) [33] (the sum of ionic radii, 2.73 Å) [50]. The two short and two longer Cu–S bonds, 2.389 and 2.415 Å form a parallelogram of the Cu₂S₂ core, similar to other dimeric Cu(I) complexes listed in Table 3 and bond lengths are similar in value. The Cu–P bond distance of 2.238 Å is

Table 3
Bond lengths (Å) and angles (°) for Cu₂S₂ core of dinuclear copper(I)-heterocyclic thione complexes

Compound	Cu···Cu	S···S	Cu–S _{br}	Cu–S–Cu	S–Cu–S	Reference
1	3.250	3.539	2.389, 2.415	85.14	94.9	this work
5	3.139		2.328, 2.577	79.4	96.1	[24]
6	4.506		2.204, 2.631	137.3		[25]
7	2.914		2.301, 2.572	73.2	106.8	[26]
8	2.861		2.377, 2.457	72.6	107.4	[27]
9	2.950		2.308, 2.498	74.3	105.7	[28,29]
10	2.907		2.297, 2.534	73.8	106.2	[28,29]
11	3.007	3.766	2.358, 2.459	77.2	110.1	[30]
12	2.686		2.362, 2.490	67.2	112.8	[31]
13	3.316	3.508	2.356, 2.470	86.7	93.2	[32]
14	2.691	4.005	2.335, 2.488	67.7	112.3	[33]
15	3.420	3.332	2.383, 2.392	91.5	88.5	[34]
16	3.263	3.545	2.393, 2.425	85.2	94.7	[6]
17	3.508		2.386, 2.470	87.5	92.5	[35]
18	3.308		2.243, 2.151	94.8		[36]

Table 4
¹H NMR data (δ ppm, J , Hz) for the compounds ^a

	CH ₃	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H
<i>p</i> -Tol ₃ P ^b	2.36s	7.23t (6H) (7.8, ³ <i>J</i> _{H-H} , ³ <i>J</i> _{H-P})	7.15d (6H) (7.3, ³ <i>J</i> _{H-H})	
Ph ₃ P		7.23m ^c		
1 ^b	2.27s	7.30dd (6H) (8.1, ³ <i>J</i> _{H-H} , 10.3, ³ <i>J</i> _{H-P})	7.07d (6H) (7.4, ³ <i>J</i> _{H-H})	
2		7.39–7.45m ^c	7.23–7.31m ^c	7.39–7.45m ^c
3		7.44–7.51m ^c	7.29–7.36m ^c	7.44–7.51m ^c
	H(6)	H(4)	H(3)	H(5)
1 ^b	7.71d (4.1, <i>J</i> ₅)	7.43td (8.9, <i>J</i> ₃ , <i>J</i> ₅ , 1.6, <i>J</i> ₆)	7.46d (7.3, <i>J</i> ₄)	6.84td (6.2, <i>J</i> ₄ , <i>J</i> ₆ , 2.0, <i>J</i> ₃)
2	7.70	^c	^c	6.81td (6.4, <i>J</i> ₄ , <i>J</i> ₆ , 1.6, <i>J</i> ₃)
3	7.70d (6.2, <i>J</i> ₅)	^c	^c	6.91td (5.9, <i>J</i> ₄ , <i>J</i> ₆ , 2.7, <i>J</i> ₃)
C ₅ H ₅ NS ^{b,d}	7.56ddd (6.3, <i>J</i> ₅ , 1.6, <i>J</i> ₄ , 0.8, <i>J</i> ₃)	7.34ddd (8.7, <i>J</i> ₃ , 7.0, <i>J</i> ₅ , 1.8, <i>J</i> ₆)	7.49dt (8.7, <i>J</i> ₄ , 0.8, <i>J</i> ₅ , <i>J</i> ₆)	6.73td (6.7, <i>J</i> ₄ , <i>J</i> ₆ , 1.2, <i>J</i> ₃)

^a d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; dt, doublet of triplets.

^b From Ref. [6].

^c Unresolved signals.

^d Unresolved signals δ_{NH} for **1–3** and ligand are 14.43, 14.92, 13.93, 13.40 ppm, respectively.

comparable to that (2.243 Å) in analogous [Cu₂(C₅H₅NS)I₂(*p*-Tol₃P)₂] (**16**) [6], but shorter than in monomeric tetrahedral complexes [12,33]. The C–S bond distance of 1.717 Å is longer than (1.690 Å) in analogous **16**, but close to those in **13** [32], **14** [33] and **15** [34]. The Cu–S–C angles (108.41°, 113.12°) are similar to those (107.0(4)°, 116.5(5)°) in analogous **16**.

The bond angles around Cu in compound **4** reveal a distorted tetrahedral geometry with different Cu–P and Cu–S bond distances unlike those observed in the dimer **1** (Table 2). The structural parameters are similar to the ones reported earlier in literature [12]. In **1**, the non-bonded H(1)···Br bond distance of 2.41(5) Å is longer than that (2.348(2) Å) in [Cu₂(C₅H₅NS)₂Br₂(*m*-Tol₃P)₂] (**14**) [33], but shorter than that (2.49 Å) in [Cu₂(C₅H₅NS)₂Br₂(PPh₃)₂] (**15**) [34]; all these are longer than that (2.39 Å) in the monomer [Cu(C₅H₅NS)Br(PPh₃)₂] (**22**) [34]. The H···Br separation is about 0.6 Å shorter than the sum of the van der Waals radii (3.00–3.45 Å) [50] and therefore fulfils Hamilton's criterion for hydrogen bond formation

[51]. The H···Cl bond separation of 1.94(12) Å in **4** is much shorter than that (2.23 Å) in analogous monomer [Cu(btztdtH)Cl(PPh₃)₂] (**23**) {btztdtH = benz-1, 3-thiazolidine-2-thione} [52] as well as that (2.30 Å) in the related dimer [Cu₂(pymtH)₂Cl₂(*p*-Tol₃P)₂] (**13**) {pymtH = pyrimidine-2-thione} [32].

From the reactions of copper(I) halides with tertiary phosphines reported to date, it is noted that there is no monomeric tetrahedral complex with a substituted tertiary phosphine; however monomeric trigonal planar copper(I) complexes, viz. [CuBr(*o*-tol₃P)(thiazolidine-2-thione)] [37], [CuCl(*o*-tol₃P)(pyrimidine-2-thione)] and [CuI(*o*-tol₃P)(pyridine-2-thione)] [38] have been reported. The large cone angles of substituted tertiary phosphines appear responsible for the different behaviour [39]. Our efforts to get tetrahedral or trigonal planar complexes using pyridine-2-thione and *m*- or *p*-tol₃P resulted in the formation of dinuclear copper(I) complexes [6]. However, copper(I) bromide with unsubstituted tertiary phosphines, e.g. triphenyl phosphine, formed both monomeric [Cu(C₅H₅NS)Br(PPh₃)₂] (**22**)

Table 5
¹³C NMR data (δ ppm, J , Hz) for the compounds

Compound	CH ₃	<i>i</i> -C (¹ <i>J</i> _{C-P})	<i>o</i> -C (² <i>J</i> _{C-P})	<i>m</i> -C (³ <i>J</i> _{C-P})	<i>p</i> -C (⁴ <i>J</i> _{C-P})
<i>p</i> -Tol ₃ P ^a	20.30	133.0 (8.8)	132.6 (19.5)	128.3 (7.2)	137.6
PPh ₃		132.5 (10.0)	134.2 (19.5)	128.9 (10.8)	129.1 (9.3)
1 ^a	20.38	131.0	132.8 (15.1)	128.4 (9.9)	138.9
2		131.7	132.9 (14.9)	129.5 (9.4)	128.8
3		131.9	133.0 (14.5)	127.6 (9.4)	128.9
	C(2)	C(6)	C(4)	C(5)	C(3)
1 ^a	171.5	137.8	136.0	128.7	114.6
2	173.3	137.6	136.2	131.0	114.4
3	170.6	137.8	136.2	131.3	114.6
C ₅ H ₅ NS ^a	175.6	137.0	135.9	132.8	113.4

^a From Ref. [6].

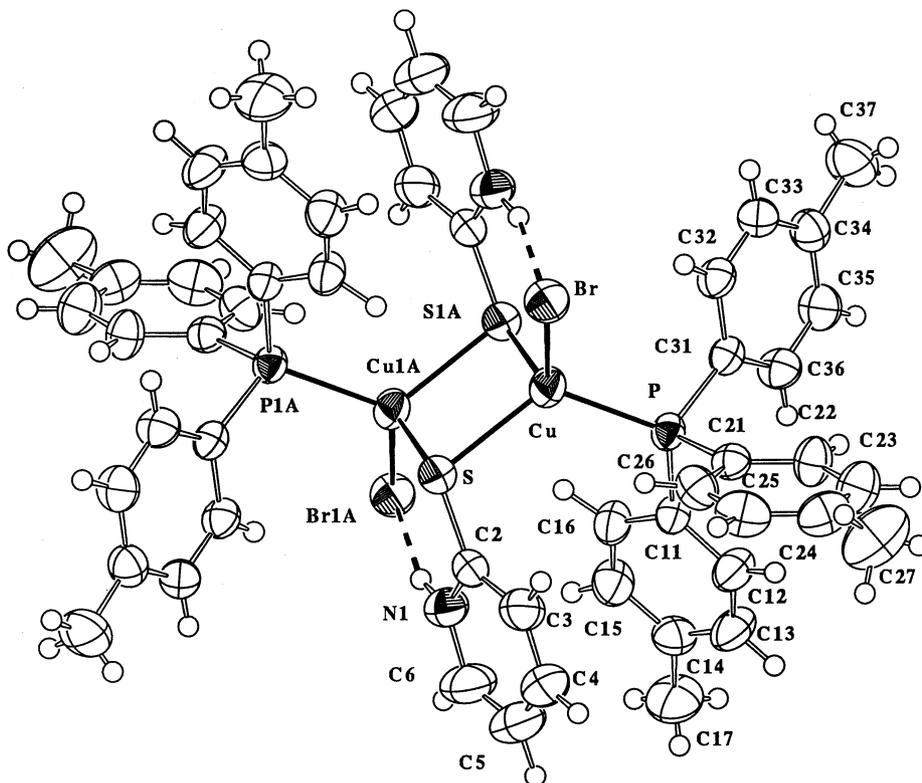


Fig. 1. A perspective view of the structure of compound 1 with atomic numbering scheme.

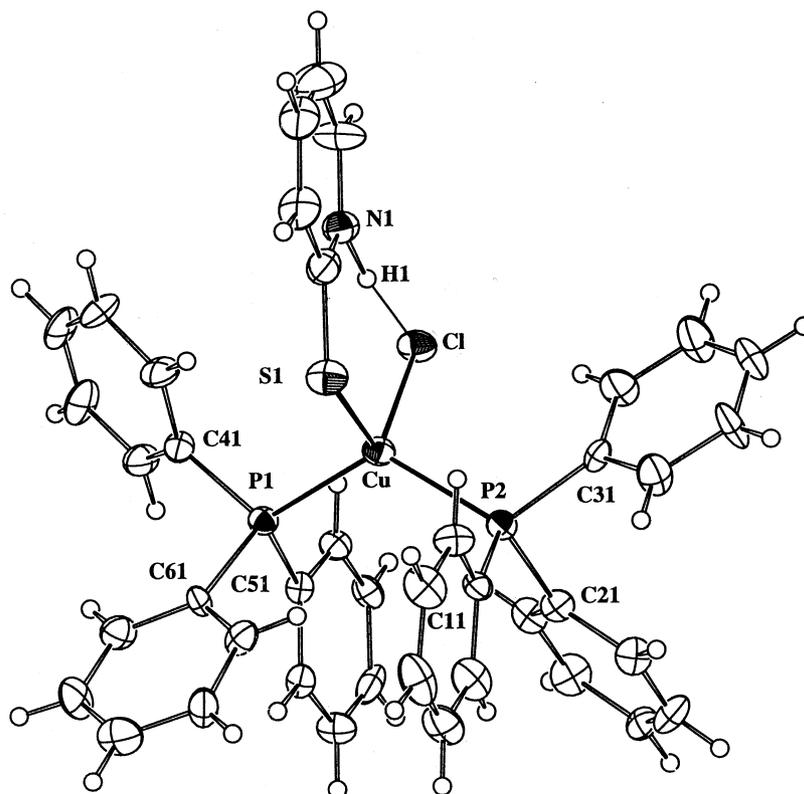


Fig. 2. A perspective view of the structure of compound 4 with atomic numbering scheme.

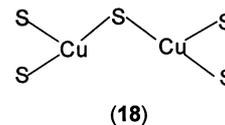
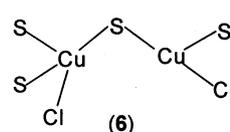
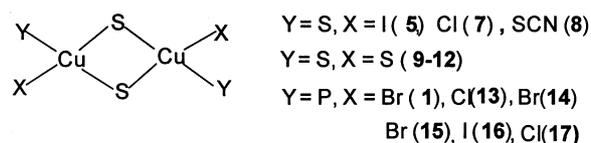
and dimeric $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{Br}_2(\text{PPh}_3)_2]$ (**15**) [34] complexes. Similarly, with copper(I) iodide there are monomeric $[\text{CuI}(\text{PPh}_3)_2(\text{pyrimidine-2-thione})]$ (**24**) with a $\text{NH}\cdots\text{I}$ separation of 2.65 Å [40] and probably dinuclear $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{I}_2(\text{PPh}_3)_2]$ (structurally uncharacterised) [34]. Whereas pyridine-2-thione with copper(I) chloride formed only the monomeric $[\text{Cu}(\text{C}_5\text{H}_5\text{NS})\text{Cl}(\text{PPh}_3)_2]$ complex [12], benzothiazole-2-thione however stabilised the dinuclear complex $[\text{CuCl}(\text{benzothiazole-2-thione})(\text{PPh}_3)_2]$ (**25**) [41]. Relatively strong $\text{NH}\cdots\text{Cl}$ hydrogen bonding in **4** favours the monomeric complex while dinuclear **25** has a $\text{NH}\cdots\text{Cl}$ separation of 2.169 Å indicating a weak interaction [41]. The analytical data of the stoichiometric reaction of copper(I) chloride with Ph_3P presumably showed the formation of a dinuclear complex (cf complex **2**, Section 2); however, the crystallisation of **2** led to the formation of the monomer **4** and it creates doubt about the existence of the dinuclear copper(I) chloride complex **2** [34]. It may be concluded from the above discussion that the intramolecular $\text{NH}\cdots\text{X}$ (halogen) bonding and nature of the heterocyclic thioamide both determine the formation of monomeric or dimeric copper(I) complexes.

3.2. $\text{Cu}\cdots\text{Cu}$ bond distances in homologous dinuclear copper(I) complexes

Table 3 contains a list of dinuclear copper(I) complexes with a series of heterocyclic-2-thiones namely pyridine-2-thione ($\text{C}_5\text{H}_5\text{NS}$), 1,3-imidazolidine-2-thione (imdtH₂), 1-methylimidazoline-2-thione (meimtH), pyrimidine-2-thione (pymtH) and 1,3-thiazolidine-2-thione (tzdtH) with tertiary phosphines as co-ligands in some cases. These compounds can be categorised into four types: (i) $[\text{Cu}_2(\mu\text{-S-NH})_2\text{X}_2]$ (**5**, **7**, **8**); (ii) $[\text{Cu}_2(\mu\text{-S-NH})_6\text{X}_2]$ (**9**, **10**, **11**, **12**); (iii) $[\text{Cu}_2(\mu\text{-S-NH})_2\text{X}_2\text{L}_2]$ (**1**, **13**, **14**, **15**, **16**, **17**); and (iv) $[\text{Cu}_2(\mu\text{-S-NH})(\text{S-NH})_3\text{Cl}_2]$ (**6**), $[\text{Cu}_2(\mu\text{-S-NH})(\text{S-NH})_4](\text{SO}_4)\cdot 3\text{H}_2\text{O}$ (**18**) { $\mu\text{-S-NH}$ indicates bridging S-bonding and S-NH indicates terminal S-bonding; X = halogen, and L = a tertiary phosphine}. Except in type (iv), all other complexes contain a Cu_2S_2 core with two heterocyclic-2-thione ligands bridging the Cu centres via S-donor atoms and in these compounds it can be noted that $\text{Cu}\cdots\text{Cu}$ and $\text{S}\cdots\text{S}$ distances (based on reported values) vary in a complementary manner. Generally a decrease in $\text{Cu}\cdots\text{Cu}$ bond distance is accompanied by an increase in $\text{S}\cdots\text{S}$ distance.

In the parallelogram Cu_2S_2 , the $\text{Cu}\cdots\text{Cu}$ bond distances vary with the change in ligand and the anion and in type (i) compounds (**5**, **7**, **8**), the shortest distance is observed in **8** with each copper bonded to four S atoms unlike three S and one halogen atom to each Cu in **5** and **7** (distances 2.861–3.139 Å). Thus the more polarisable SCN^- group has a strong influence in bringing two Cu atoms closer for interaction. In type

(ii) compounds, with each Cu bonded to four S atoms, the $\text{Cu}\cdots\text{Cu}$ distances (2.686–3.007 Å) vary in the sequence: **12** < **10** < **9** < **11** and it is certainly the



effect of the ligands and the non-bonded anions. It may be noted that the shortest $\text{Cu}\cdots\text{Cu}$ distance is observed in **12** among all the dinuclear compounds listed in Table 3. Similarly, in type (iii) compounds with each Cu bonded to two S, one P atom and one halogen atom, $\text{Cu}\cdots\text{Cu}$ distances fall in the range 3.250–3.508 Å except compound **14** which has a distance of 2.691 Å close to that in **12**. Finally in type (iv) compounds with one S atom bridging the two Cu atoms, the $\text{Cu}\cdots\text{Cu}$ distances (3.308–4.506 Å) are among the longest.

Some general trends in $\text{Cu}\cdots\text{Cu}$ bond distances are revealed as follows: (i) when each copper is bonded to four sulfur atoms, the $\text{Cu}\cdots\text{Cu}$ bond distances decrease (2.686–3.007 Å; compounds **8**, **9–12**) because the electron rich Cu atoms enhance metal–metal interaction; (ii) when each copper is bonded to two S, one P and one halogen atom, the $\text{Cu}\cdots\text{Cu}$ distances increase (3.250–3.508 Å; compounds **1**, **13–17**, except **14**) and this behaviour can be explained in terms of reduction in electron density at the Cu centres in view of pi-bonding from the metal to d-orbitals on phosphorus and this increases the $\text{Cu}\cdots\text{Cu}$ distance. Whereas complex **14**, having a *m*-tol₃P ligand, showed the short $\text{Cu}\cdots\text{Cu}$ distance of 2.691 Å, the same was not true for $[\text{Cu}_2\text{Br}_2(\text{thiazolidine-2-thione})_2(m\text{-tol}_3\text{P})_2]$ (**26**) [42] in which the $\text{Cu}\cdots\text{Cu}$ distance increased to 3.347 Å. It shows that $\text{Cu}\cdots\text{Cu}$ distance varies with the nature of the thione ligand and is independent of the substituent on the Ph group.

For compounds having three S atoms (2.914–3.139 Å; compounds **5**, **7**) and one halogen bonded to each Cu atom, though many examples are not available, the distances in between the two extremes are observed. Finally in type (iv) compounds (**6**, **18**), the $\text{Cu}\cdots\text{Cu}$ distance is longest (4.506 Å) in **6** because one Cu is bonded to three S and one halogen atom and the second Cu is bonded to two S and one halogen atom and this decreases electron density at the Cu centres thus weakening the $\text{Cu}\cdots\text{Cu}$ interaction. Interestingly in **18**, with each Cu bonded to three S atoms, the distance (3.308 Å) is quite short and comparable to that observed

in the compounds **1**, **13**–**17**. In short, an electron withdrawing halogen or a metal to ligand pi-bonding group decreases Cu···Cu interaction and an increase in number of sulfur groups bonded to Cu enhances Cu···Cu interaction.

The Cu–S–Cu and S–Cu–S bond angles in compounds with a Cu₂S₂ core vary with Cu···Cu distance. A shorter distance is accompanied by smaller Cu–S–Cu and larger S–Cu–S bond angles and vice versa and for *type (iv)* compounds the Cu–S–Cu bond angles are the largest. It is interesting to note that the angular flexibility at S is very large (67.2°–137.3°) and is of great consequence for controlling metal–metal interactions.

4. Supplementary material

Supplementary data are available from the Cambridge Crystallographic Data Centre, CCDC Nos. 164391–164390 for compounds **1** and **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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