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#### Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.032  
 $wR$  factor = 0.090  
 Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Di- $\mu$ -pyridine-2-thiolato-bis[chloro(triphenylphosphine)copper(I)]

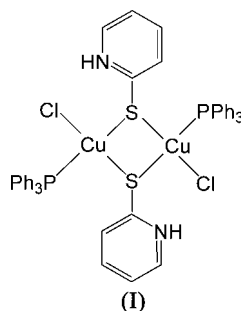
The structure of the title compound,  $[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{Cl}_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$ , shows two independent molecules, each a dimer bridged through a  $\text{Cu}_2\text{S}_2$  rectangular plane involving the two pyridinethione S atoms and lying about a centre of symmetry. The Cu atoms have a distorted tetrahedral geometry. There is intramolecular hydrogen bonding between the pyridinium H atoms and the Cl ligands.

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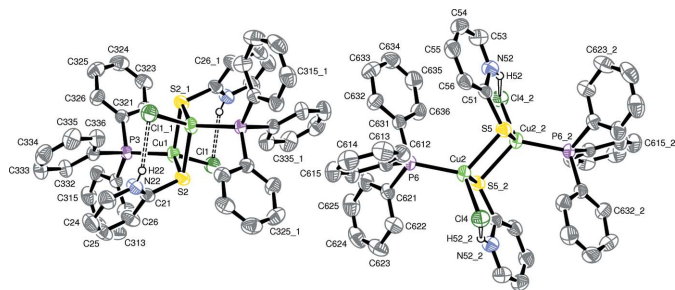
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#### Comment

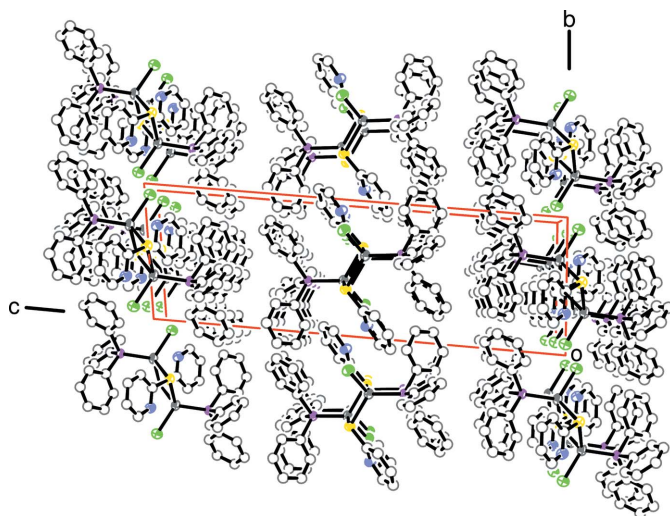
The dimeric title compound,  $[\{\text{CuCl}(\text{S}\{\text{C}_5\text{H}_5\text{N}\})(\text{P}\{\text{C}_6\text{H}_5\}_3)\}_2]$ , or  $[\{\text{CuCl}(\text{S}\{\text{C}_5\text{H}_5\text{N}\})(\text{PPh}_3)_2]$ , (I), has two half-molecules per asymmetric unit; the virtually identical molecules (Ia) and (Ib) each lie about a centre of symmetry (Fig. 1). At the core of each molecule there is a planar rectangular  $\text{Cu}_2\text{S}_2$  ring, in which the Cu atoms have distorted tetrahedral geometry and the S atoms show a trigonal pyramidal arrangement. The largest difference in bond lengths between the two molecules is 0.08 Å between the bonds C332—H332 in (Ia) and C632—H632 in (Ib), and the largest difference in bond angles is 5° between the angles C23—N22—H22 in (Ia) and C53—N52—H52 in (Ib).



The monomer  $[\text{CuCl}(\text{S}\{\text{C}_5\text{H}_5\text{N}\})(\text{PPh}_3)_2]$ , (II) (Lobana *et al.*, 1989), has previously been reported. On forming the dimer (I), the Cu—S' bond [where the prime (') indicates the symmetry-related atom] is significantly longer than the Cu—S bond; 2.374 (2) Å in (II) compared with 2.3745 (5) and 2.4375 (6) Å in (I). Several complexes analogous to (I) have been reported, and comparisons are made with the Br complex  $[\{\text{CuBr}(\text{S}\{\text{C}_5\text{H}_5\text{N}\})(\text{PPh}_3)_2]$ , (III) (Karagiannidis, 1989). In (III) there is a single centrosymmetric molecule which has dimensions (and distortions from ideal values) similar to those in (I), apart from the closer equivalence of the Cu—S and Cu—S' bonds [2.383 (1) and 2.392 (1) Å]. A third related structure,  $[\text{Cu}_2(\text{S}\{\text{C}_5\text{H}_5\text{N}\})_6]\text{Cl}_2$ , (IV) (Constable & Raithby, 1987), is also a dimer lying about a centre of symmetry, and has geometries in the  $\text{Cu}_2\text{S}_2$  core plane similar to those in the  $\text{Cu}_2\text{S}_2$  core of (I) [ $\text{Cu}-\text{S}_{\text{bridge}} = 2.308$  (2) and

**Figure 1**

A view of the two independent molecules of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms, except the pyridinium H atoms, have been omitted for clarity. [Symmetry codes: (–1)  $1 - x, 1 - y, -z$ ; (–2)  $1 - x, 1 - y, 2 - z$ .]

**Figure 2**

Packing diagram of (I), viewed along the crystallographic  $a$  axis. H atoms have been omitted for clarity.

2.498 (3) Å], but different geometries about the bridging S atoms [Cu–S–Cu' = 74.3 (1)°, compared with 90.64 (2) and 91.60 (2) in (I)].

Each Cu atom in (I) is in a distorted tetrahedral geometry, the major deviations from the ideal being the S–Cu–S'/S–Cu–P angles of 89.36 (2)/121.94 (2)° and 88.40 (2)/120.99 (2)° in (Ia) and (Ib), respectively (see Table 1), where ' indicates an atom related by an inversion centre. This distortion is similar to that found in (II) and (III), with that in (IV) being slightly less extreme [99.7 (1)/118.7 (1)°]. The bridging angles about the Cu atoms in (I), together with the Cu–S–Cu' angles, show a slightly distorted rectangular Cu<sub>2</sub>S<sub>2</sub> plane, which is similar to the slightly distorted square plane in (III) [S–Cu–S' = 88.5 (1)°] but different from the parallelogram formed in (IV) [S–Cu–S' = 105.7 (1)°].

The C<sub>5</sub>N groups are essentially planar with the N atoms lying furthest from the mean planes at 0.007 (3) Å in both (Ia) and (Ib). The pyridinium H atoms in both molecules lie 0.12 (3) Å from the respective planes. The S atoms lie 0.084 (3) and 0.109 (3) Å from the planes, which are tilted with respect to the Cu<sub>2</sub>S<sub>2</sub> planes; the angles between the normals to these planes are 119.55 (5) and 123.09 (5)° respectively. The CuCIP planes lie at approximate right angles to the Cu<sub>2</sub>S<sub>2</sub>

planes, with angles between the normals to the planes of 95.22 (2) and 94.27 (2)° in the two molecules. The P atoms also have distorted tetrahedral geometries, with angles in the ranges 102.76 (8)–120.59 (6)° in (Ia) and 102.59 (8)–120.54 (6)° in (Ib) (see Table 1); this is similar to structures (II) and (III), where the angles lie in the ranges 99.58 (9)–119.92 (12)° and 102.4 (3)–122.5 (2)° respectively. Other bond dimensions within the ligands of (I) are as expected.

There is intramolecular hydrogen bonding between the pyridinium N–H atoms and the Cl atoms at distances of 2.37 (3) and 2.30 (2) Å in (Ia) and (Ib), respectively. This is also evident in (II) and (III), with intermolecular hydrogen bonding present in (IV) between both pyridinium H atoms of the terminal S{C<sub>5</sub>H<sub>5</sub>N} ligands and two chloride ions (see Table 2).

In the crystal packing of (I), the (PPh<sub>3</sub>) phenyl groups lie in layers parallel to the crystallographic  $ab$  plane with normal van der Waals contacts between groups in neighbouring layers, the closest being C21...C25<sup>iii</sup> = 3.298 (3) Å and C51...C55<sup>iv</sup> = 3.303 (3) Å [symmetry codes: (iii)  $2 - x, 2 - y, 1 - z$ ; (iv)  $1 - x, -y, 2 - z$ ]; these layers alternate with the Cu<sub>2</sub>Cl<sub>2</sub>(S{C<sub>5</sub>H<sub>5</sub>N}) layers along the crystallographic  $c$  axis (Fig. 2). When viewed along the crystallographic  $c$  axis, the molecules form columns arranged with each column surrounded by six others. This arrangement is the same as that in (III) and similar to the packing of the monomer (II), where the full (PPh<sub>3</sub>) ligand forms layers alternating with the Cu<sub>2</sub>Cl<sub>2</sub>(S{C<sub>5</sub>H<sub>5</sub>N}) layers. It is also similar to the packing of (IV), where two (S{C<sub>5</sub>H<sub>5</sub>N}) ligands and the (C<sub>5</sub>H<sub>5</sub>N) groups of two further (S{C<sub>5</sub>H<sub>5</sub>N}) ligands form layers alternating with layers formed by the Cu atoms, the S atoms of two (S{C<sub>5</sub>H<sub>5</sub>N}) ligands and the remaining two (S{C<sub>5</sub>H<sub>5</sub>N}) ligands.

These results, with similarities in structure, hydrogen bonding and crystal packing between the title compound (I) and the reported structures (II), (III) and (IV), show that bond dimensions and geometries in (I) are not unusual.

## Experimental

The compound SC<sub>5</sub>H<sub>4</sub>NH (0.2 g, 2.5 mmol) was added, under a dinitrogen atmosphere, to a suspension of PPh<sub>3</sub> (0.65 g, 2.5 mmol) and CuCl (0.2 g, 2.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). The mixture was stirred for 2 h, then filtered. The solid was washed with CH<sub>2</sub>Cl<sub>2</sub> and dried *in vacuo*. The crude product was recrystallized from EtOH over CH<sub>2</sub>Cl<sub>2</sub>, giving crystals of [(CuCl(S{C<sub>5</sub>H<sub>5</sub>N})(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>)]<sub>2</sub> (0.15 g, 76%). IR: 1570 (s), 1430 (s), 1360 (m), 1125 (s), 1090 (w), 740 (s), 680 (s), 520 (m), 440 (w) cm<sup>–1</sup>.

### Crystal data

[Cu<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>NS)<sub>2</sub>Cl<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>]  
*M<sub>r</sub>* = 944.84  
 Triclinic,  $P\bar{1}$   
*a* = 9.7076 (6) Å  
*b* = 9.7875 (13) Å  
*c* = 26.348 (3) Å  
 $\alpha$  = 96.918 (11)°  
 $\beta$  = 91.942 (7)°  
 $\gamma$  = 119.488 (8)°  
*V* = 2150.7 (4) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.459 Mg m<sup>–3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 24 reflections  
 $\theta$  = 10–11°  
 $\mu$  = 1.32 mm<sup>–1</sup>  
*T* = 293 (2) K  
 Hexagonal plate, orange  
 0.51 × 0.33 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/\theta$  scans  
 Absorption correction:  $\psi$  scan (EMPABS; Sheldrick *et al.*, 1977)  
 $T_{\min} = 0.666$ ,  $T_{\max} = 0.709$   
 12901 measured reflections  
 12512 independent reflections  
 9568 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -1 \rightarrow 37$   
 3 standard reflections  
 frequency: 167 min  
 intensity decay: 3.3%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.090$   
 $S = 1.05$   
 12512 reflections  
 665 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.3413P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.007$   
 $\Delta\rho_{\text{max}} = 0.50 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—Cl1	2.3116 (6)	Cu2—Cl4	2.3127 (6)
Cu1—S2	2.3745 (5)	Cu2—S5	2.3838 (6)
Cu1—S2 <sup>i</sup>	2.4375 (6)	Cu2—S5 <sup>ii</sup>	2.4296 (5)
Cu1—P3	2.2344 (5)	Cu2—P6	2.2316 (5)
S2—C21	1.7184 (18)	S5—Cu2 <sup>ii</sup>	2.4296 (5)
P3—C311	1.8257 (17)	P6—C611	1.8232 (17)
P3—C321	1.8283 (17)	P6—C621	1.8269 (18)
P3—C331	1.8282 (17)	P6—C631	1.8263 (18)
P3—Cu1—Cl1	114.15 (2)	P6—Cu2—Cl4	114.24 (2)
P3—Cu1—S2	121.941 (19)	P6—Cu2—S5	120.99 (2)
Cl1—Cu1—S2	111.82 (2)	Cl4—Cu2—S5	112.23 (2)
P3—Cu1—S2 <sup>i</sup>	105.65 (2)	P6—Cu2—S5 <sup>ii</sup>	107.029 (19)
Cl1—Cu1—S2 <sup>i</sup>	110.26 (2)	Cl4—Cu2—S5 <sup>ii</sup>	110.30 (2)
S2—Cu1—S2 <sup>i</sup>	89.362 (19)	S5—Cu2—S5 <sup>ii</sup>	88.403 (19)
Cu1—S2—Cu1 <sup>i</sup>	90.638 (19)	Cu2—S5—Cu2 <sup>ii</sup>	91.598 (18)
C311—P3—C331	102.99 (8)	C611—P6—C631	102.77 (8)
C311—P3—C321	102.76 (8)	C611—P6—C621	102.59 (8)
C331—P3—C321	103.89 (8)	C631—P6—C621	104.63 (8)
C311—P3—Cu1	120.59 (6)	C611—P6—Cu2	120.54 (6)
C331—P3—Cu1	115.04 (6)	C631—P6—Cu2	113.53 (6)
C321—P3—Cu1	109.71 (6)	C621—P6—Cu2	111.10 (6)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 2$ .

Table 2

Comparison of hydrogen-bond dimensions (Å, °).

Complex	N—H	N···X	H···X	N—H···X
(Ia)	0.84 (3)	3.144 (2)	2.37 (3)	153 (2)
(Ib)	0.91 (2)	3.140 (2)	2.30 (2)	154 (2)
(II)	1.01	3.079 (7)	2.22	142
(III)	0.93	3.3082 (3)	2.49	147
(IV)	1.01	3.058 (7)	2.13	151
	1.01	3.132 (8)	2.19	155

X = Cl in (I), (II) and (IV), and Br in (III).

H atoms were included initially in idealized positions, except for the N-bonded H atom, which was located in a difference electron density map, and all were subsequently refined freely [N—H = 0.84 (3) Å and C—H = 0.85 (3)–1.00 (2) Å].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 Processing Program* (Hursthouse, 1976); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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