

Katayoun Marjani,^a Sian C. Davies,^{b*} Marcus C. Durrant,^c David L. Hughes^d and Nejat Khodamorad^a

^aFaculty of Chemistry, Teacher Training University, PO Box 15614, Tehran, Iran,

^bDepartment of Biological Chemistry, John Innes Centre, Colney, Norwich NR4 7UH, England,

^cSchool of Applied Sciences, Northumbria University, Ellison Building, Newcastle upon Tyne NE1 8ST, England, and ^dSchool of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, England

Correspondence e-mail: sianc.davies@bbsrc.ac.uk

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>.

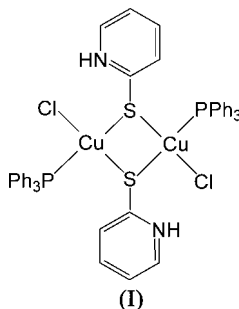
Di- μ -pyridine-2-thiolato-bis[chloro(triphenylphosphine)copper(I)]

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 Cu_2S_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.

Received 21 February 2006
 Accepted 22 February 2006

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 Cu_2S_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 Cu_2S_2 core plane similar to those in the Cu_2S_2 core of (I) [$\text{Cu}-\text{S}_{\text{bridge}} = 2.308$ (2) and

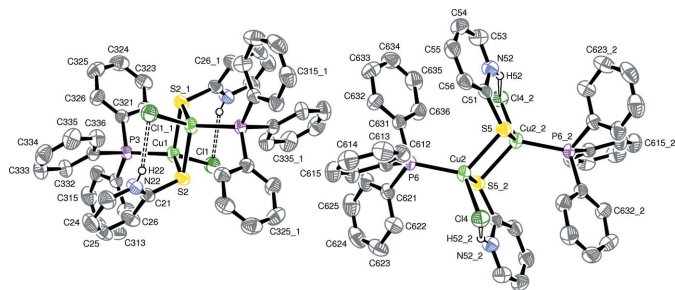


Figure 1

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) $1 - x, 1 - y, 2 - z$.]

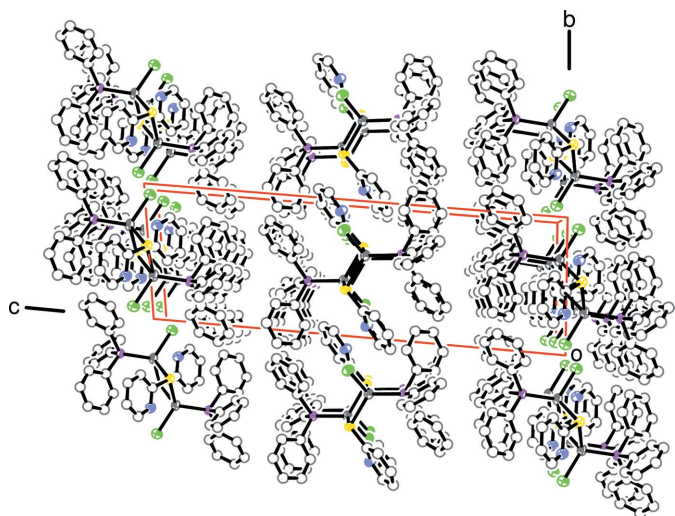


Figure 2

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 [$\text{Cu}-\text{S}-\text{Cu}' = 74.3 (1)^\circ$, 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 $\text{S}-\text{Cu}-\text{S}'/\text{S}-\text{Cu}-\text{P}$ angles of $89.36 (2)/121.94 (2)^\circ$ and $88.40 (2)/120.99 (2)^\circ$ 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 [$99.7 (1)/118.7 (1)^\circ$]. The bridging angles about the Cu atoms in (I), together with the $\text{Cu}-\text{S}-\text{Cu}'$ angles, show a slightly distorted rectangular Cu_2S_2 plane, which is similar to the slightly distorted square plane in (III) [$\text{S}-\text{Cu}-\text{S}' = 88.5 (1)^\circ$] but different from the parallelogram formed in (IV) [$\text{S}-\text{Cu}-\text{S}' = 105.7 (1)^\circ$].

The C_5N 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_2S_2 planes; the angles between the normals to these planes are $119.55 (5)$ and $123.09 (5)^\circ$ respectively. The CuClP planes lie at approximate right angles to the Cu_2S_2

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

There is intramolecular hydrogen bonding between the pyridinium N–H 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 $\text{S}\{\text{C}_5\text{H}_5\text{N}\}$ ligands and two chloride ions (see Table 2).

In the crystal packing of (I), the (PPh_3) 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 $\text{C}21 \cdots \text{C}25^{\text{iii}} = 3.298 (3)$ Å and $\text{C}51 \cdots \text{C}55^{\text{iv}} = 3.303 (3)$ Å [symmetry codes: (iii) $2 - x, 2 - y, 1 - z$; (iv) $1 - x, -y, 2 - z$]; these layers alternate with the $\text{Cu}_2\text{Cl}_2(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ 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_3) ligand forms layers alternating with the $\text{Cu}_2\text{Cl}_2(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ layers. It is also similar to the packing of (IV), where two $(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ ligands and the $(\text{C}_5\text{H}_5\text{N})$ groups of two further $(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ ligands form layers alternating with layers formed by the Cu atoms, the S atoms of two $(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ ligands and the remaining two $(\text{S}\{\text{C}_5\text{H}_5\text{N}\})$ 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 $\text{SC}_5\text{H}_4\text{NH}$ (0.2 g, 2.5 mmol) was added, under a dinitrogen atmosphere, to a suspension of PPh_3 (0.65 g, 2.5 mmol) and CuCl (0.2 g, 2.5 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 2 h, then filtered. The solid was washed with CH_2Cl_2 and dried *in vacuo*. The crude product was recrystallized from EtOH over CH_2Cl_2 , giving crystals of $[\{\text{CuCl}(\text{S}\{\text{C}_5\text{H}_5\text{N}\})(\text{P}(\text{C}_6\text{H}_5)_3)_2\}]_2$ (0.15 g, 76%). IR: $1570 (s)$, $1430 (s)$, $1360 (m)$, $1125 (s)$, $1090 (w)$, $740 (s)$, $680 (s)$, $520 (m)$, $440 (w) \text{ cm}^{-1}$.

Crystal data

$[\text{Cu}_2(\text{C}_5\text{H}_5\text{NS})_2\text{Cl}_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$
 $M_r = 944.84$
 Triclinic, $P\bar{1}$
 $a = 9.7076 (6)$ Å
 $b = 9.7875 (13)$ Å
 $c = 26.348 (3)$ Å
 $\alpha = 96.918 (11)^\circ$
 $\beta = 91.942 (7)^\circ$
 $\gamma = 119.488 (8)^\circ$
 $V = 2150.7 (4)$ Å³

$Z = 2$
 $D_x = 1.459 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 10$ – 11°
 $\mu = 1.32 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Hexagonal plate, orange
 $0.51 \times 0.33 \times 0.26 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/θ scans
 Absorption correction: ψ 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 ⁱ	2.4375 (6)	Cu2—S5 ⁱⁱ	2.4296 (5)
Cu1—P3	2.2344 (5)	Cu2—P6	2.2316 (5)
S2—C21	1.7184 (18)	S5—Cu2 ⁱⁱ	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 ⁱ	105.65 (2)	P6—Cu2—S5 ⁱⁱ	107.029 (19)
Cl1—Cu1—S2 ⁱ	110.26 (2)	Cl4—Cu2—S5 ⁱⁱ	110.30 (2)
S2—Cu1—S2 ⁱ	89.362 (19)	S5—Cu2—S5 ⁱⁱ	88.403 (19)
Cu1—S2—Cu1 ⁱ	90.638 (19)	Cu2—S5—Cu2 ⁱⁱ	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*.

We thank the Chemical Database Service, Science and Engineering Research Council, Daresbury Laboratory, England.

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