

## 4,4'-Thiodipyridinium tetrachloro-copper(II)

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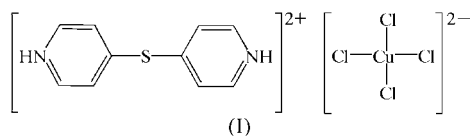
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The title compound,  $(C_{10}H_{10}N_2S)[CuCl_4]$ , was obtained by the reaction of cupric chloride with pyridine-4-thiol in a mixture of acetonitrile and tetrahydrofuran, suggesting that the desulfurization and coupling reactions of pyridine-4-thiol occurred in the presence of the  $Cu^{2+}$  ion. X-ray diffraction analysis reveals the presence of one 4,4'-thiodipyridinium cation,  $H_2bps^{2+}$ , and one  $[CuCl_4]^{2-}$  anion. The cations interact with the anions *via*  $N-H \cdots Cl$  hydrogen-bonding interactions to form a closed 'chair' conformation.

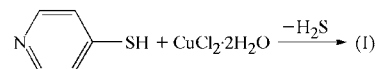
### Comment

Thiopyridines, as *N,S*-donor-containing ligands, have been extensively investigated in coordination chemistry because of their varied coordination modes and interesting reactivity. A large number of one-, two- and three-dimensional coordination polymers containing pyridine-2-thiol have been synthesized (Hong *et al.*, 1999; Kato *et al.*, 2002; Wen *et al.*, 2004). However, only a small number of analogues containing pyridine-4-thiol have been reported (Nunokawa *et al.*, 2001; Anjali *et al.*, 2003). We are interested in investigating the thiopyridine-copper halide system because of its potentially interesting reaction chemistry (Cheng *et al.*, 2004). We report here the synthesis and crystal structure of the title compound, (I), containing the 4,4'-thiodipyridinium cation ( $H_2bps^{2+}$ ) and the tetrachlorocopper(II) dianion.

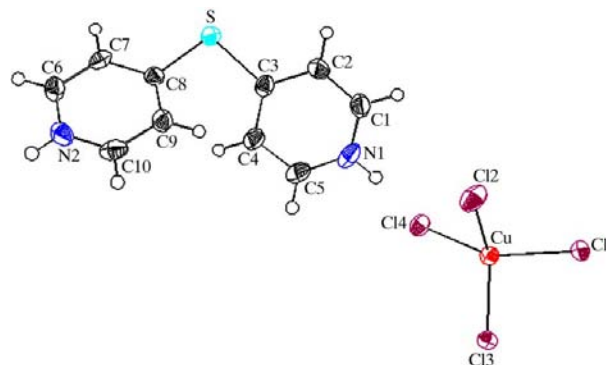


As illustrated in Fig. 1, the asymmetric unit of the crystal structure of (I) contains one  $H_2bps^{2+}$  cation and one  $[CuCl_4]^{2-}$  anion. The anion exhibits a flattened tetrahedral geometry with approximate  $D_{2d}$  symmetry, and the  $Cu^{II}$  ion is surrounded by four Cl atoms, with Cu—Cl distances ranging from 2.226 (3) to 2.284 (2) Å and Cl—Cu—Cl angles ranging

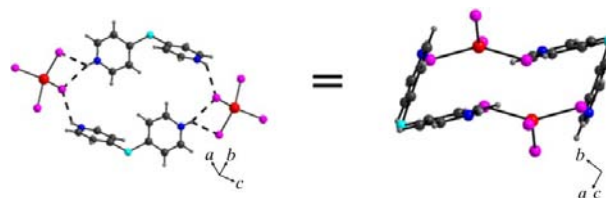
from 94.84 (9) to 147.18 (12)° (Table 1). The mean Cu—Cl bond length [2.247 (2) Å] is close to those observed in similar



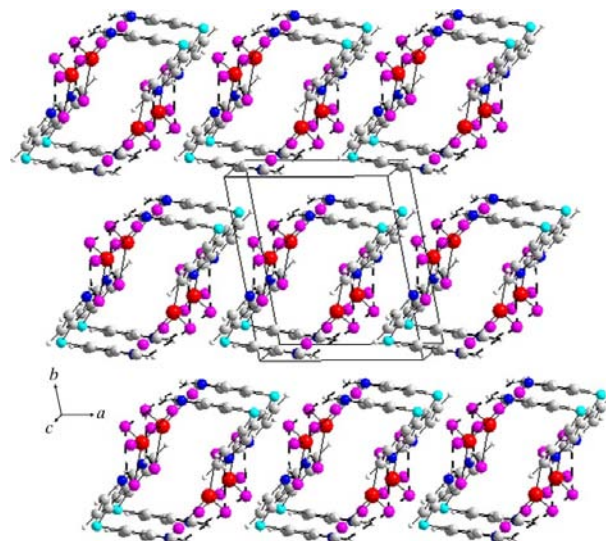
complexes, *e.g.*  $(C_{10}H_{16}N_2)[CuCl_4]$  [2.24659 (18) Å; Choi *et al.*, 2002]. The cation is formed *via* the desulfurization and coupling of pyridine-4-thiol ligands and concomitant release of hydrogen sulfide (see scheme above). The cation is proton-



**Figure 1**  
A view of (I), shown with 30% probability displacement ellipsoids.



**Figure 2**  
The closed 'chair' conformation of (I). Hydrogen bonds are depicted as dashed lines.



**Figure 3**  
A packing diagram of the title compound viewed along the *c* direction.

ated at atoms N1 and N2. To the best of our knowledge, although complexes containing the 4,4'-dipyridyl sulfide ligand have been reported (Su *et al.*, 2002), no structurally characterized example of a 4,4'-thiodipyrindinium perhalometallate complex obtained *via* the desulfurization and coupling of pyridine-4-thiol has been documented to date.

In (I), there are N—H...Cl hydrogen-bonding interactions between the cations and the anions (Fig. 2 and Table 2). Protonated atom N1 forms a three-center interaction with two *cis* Cl atoms of one [CuCl<sub>4</sub>]<sup>2-</sup> unit, with N1...Cl2 and N1...Cl4 distances of 3.316 (9) and 3.248 (8) Å, respectively. Protonated atom N2 forms a two-center hydrogen bond with one Cl atom of another [CuCl<sub>4</sub>]<sup>2-</sup> unit, with an N2...Cl4 distance of 3.388 (9) Å [symmetry code: (i)  $-x + 1, -y + 1, -z$ ]. As a result, two H<sub>2</sub>bps<sup>2+</sup> cations and two [CuCl<sub>4</sub>]<sup>2-</sup> anions are held together by hydrogen-bonding interactions to form a closed 'chair' conformation. The molecules of (I) are arranged regularly, as depicted in Fig. 3, parallel to the *c* axis, with dimensions of about 5.33 × 8.68 Å.

## Experimental

A mixture of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.170 g, 1 mmol) and pyridine-4-thiol (0.111 g, 1 mmol) was dissolved in a CH<sub>3</sub>CN–tetrahydrofuran mixture (1:1 *v/v*, 20 ml), stirred at room temperature (298 K) for 1 h and then filtered. The filtrate was allowed to stand at room temperature for two weeks, yielding blue crystals of (I).

### Crystal data

(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> S)[CuCl <sub>4</sub> ]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 395.62	<i>D<sub>x</sub></i> = 1.805 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.2442 (14) Å	Cell parameters from 1200 reflections
<i>b</i> = 9.4534 (16) Å	<i>θ</i> = 2.1–25.1°
<i>c</i> = 9.5475 (15) Å	<i>μ</i> = 2.36 mm <sup>-1</sup>
<i>α</i> = 92.594 (3)°	<i>T</i> = 293 (2) K
<i>β</i> = 94.243 (3)°	Prism, blue
<i>γ</i> = 100.571 (3)°	0.38 × 0.34 × 0.20 mm
<i>V</i> = 728.1 (2) Å <sup>3</sup>	

### Data collection

Siemens SMART CCD area-detector diffractometer	2598 independent reflections
<i>φ</i> and <i>ω</i> scans	1667 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> <sub>int</sub> = 0.042
<i>T</i> <sub>min</sub> = 0.425, <i>T</i> <sub>max</sub> = 0.624	<i>θ</i> <sub>max</sub> = 25.1°
3836 measured reflections	<i>h</i> = -9 → 9
	<i>k</i> = -11 → 6
	<i>l</i> = -10 → 11

**Table 1**

Selected geometric parameters (Å, °).

Cu—Cl2	2.226 (3)	Cu—Cl4	2.284 (2)
Cu—Cl1	2.228 (2)	S—C3	1.776 (9)
Cu—Cl3	2.251 (2)	S—C8	1.781 (8)
Cl2—Cu—Cl1	96.91 (11)	Cl1—Cu—Cl4	138.68 (11)
Cl2—Cu—Cl3	147.18 (12)	Cl3—Cu—Cl4	95.67 (9)
Cl1—Cu—Cl3	94.84 (9)	C3—S—C8	102.8 (4)
Cl2—Cu—Cl4	95.44 (10)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H8A...Cl4 <sup>i</sup>	0.86 (9)	2.67 (7)	3.388 (9)	142 (9)
N1—H3A...Cl4	0.86 (8)	2.57 (7)	3.248 (8)	136 (9)
N1—H3A...Cl2	0.86 (8)	2.63 (7)	3.316 (9)	138 (9)

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 3.8146P]$
$R[F^2 > 2\sigma(F^2)] = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.178$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.63 \text{ e \AA}^{-3}$
2598 reflections	$\Delta\rho_{\min} = -0.60 \text{ e \AA}^{-3}$
169 parameters	
H atoms treated by a mixture of independent and constrained refinement	

H atoms bonded to C atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)]. H atoms bonded to N atoms were located from difference maps and refined with the N—H distances restrained to 0.86 (2) Å [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N)].

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: XPREP in SHELXTL (Siemens, 1994) and SAINT; program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1093). Services for accessing these data are described at the back of the journal.

## References

- Anjali, K. S., Vittal, J. J. & Dean, P. A. W. (2003). *Inorg. Chim. Acta*, **351**, 79–88.
- Cheng, J.-K., Yao, Y.-G., Zhang, J., Li, Z.-J., Cai, Z.-W., Zhang, X.-Y., Chen, Z.-N., Chen, Y.-B., Kang, Y., Qin, Y.-Y. & Wen, Y.-H. (2004). *J. Am. Chem. Soc.* **126**, 7796–7797.
- Choi, S.-N., Lee, Y.-M., Lee, H.-W., Kang, S. K. & Kim, Y.-I. (2002). *Acta Cryst.* **E58**, m583–m585.
- Hong, M., Su, W., Cao, R., Zhang, W. & Lu, J. (1999). *Inorg. Chem.* **38**, 600–602.
- Kato, M., Omura, A., Toshikawa, A., Kishi, S. & Sugimoto, Y. (2002). *Angew. Chem. Int. Ed.* **41**, 3183–3185.
- Nunokawa, K., Onaka, S., Tatematsu, T., Ito, M. & Sakai, J. (2001). *Inorg. Chim. Acta*, **322**, 56–64.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1994). *SAINTE* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Su, X.-C., Guo, Y.-H., Zhu, S.-R. & Lin, H.-K. (2002). *J. Mol. Struct.* **643**, 147–153.
- Wen, Y.-H., Zhang, J., Cheng, J.-K., Li, Z.-J., Qin, Y.-Y., Kang, Y., Hu, R.-F. & Yao, Y.-G. (2004). *Acta Cryst.* **C60**, m248–m249.