

## Dichloro(2,2'-diamino-4,4'-bi-1,3-thiazole- $N^3,N^3'$ )copper(II)

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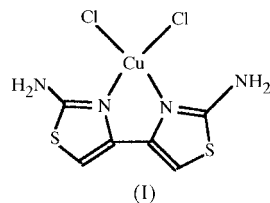
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The title complex,  $[\text{CuCl}_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)]$ , has a flattened tetrahedral coordination. The  $\text{Cu}^{\text{II}}$  atom is located on a twofold rotation axis and is coordinated by two N atoms from a chelating 2,2'-diamino-4,4'-bi-1,3-thiazole ligand and by two Cl atoms. Intramolecular hydrogen bonding exists between the amino groups of the 2,2'-diamino-4,4'-bi-1,3-thiazole ligand and the Cl atoms. The intermolecular separation of 3.425 (1) Å between parallel bithiazole rings suggests there is a  $\pi$ - $\pi$  interaction between them.

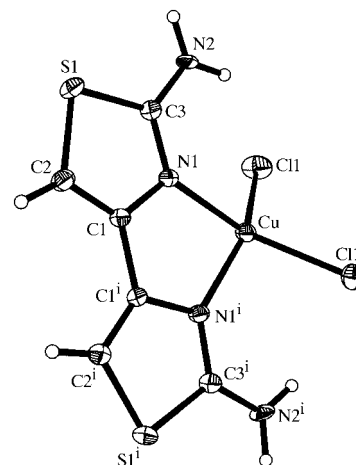
### Comment

Transition metal complexes with 2,2'-diamino-4,4'-bi-1,3-thiazole (DABT) or its derivatives show interesting properties and have potential applications in many fields. For example, a  $\text{Co}^{\text{II}}$  complex and an  $\text{Ni}^{\text{II}}$  complex with DABT have both been found to be effective inhibitors of DNA synthesis in tumour cells (Waring, 1981; Fisher *et al.*, 1985), and multinuclear  $\text{Fe}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes with a DABT Schiff base have been found to be excellent soft magnetic materials (Sun *et al.*, 1997; Liu *et al.*, 2001). Structural investigation of these complexes is helpful for understanding the relationship between properties and structures, and for designing useful new materials. However, only a few metal complexes with DABT have been reported so far (Tian *et al.*, 1996). We have prepared a new DABT complex of  $\text{Cu}^{\text{II}}$ , the title complex, (I), and have determined its structure by X-ray diffraction.



The molecular structure of (I) is shown in Fig. 1. The  $\text{Cu}^{\text{II}}$  atom lies on a twofold rotation axis. Together with the chelating DABT molecule, the two Cl atoms coordinate to the  $\text{Cu}^{\text{II}}$  to complete the four-coordinate geometry. A flattened tetrahedral coordination geometry (Gavel & Hodgson, 1979;

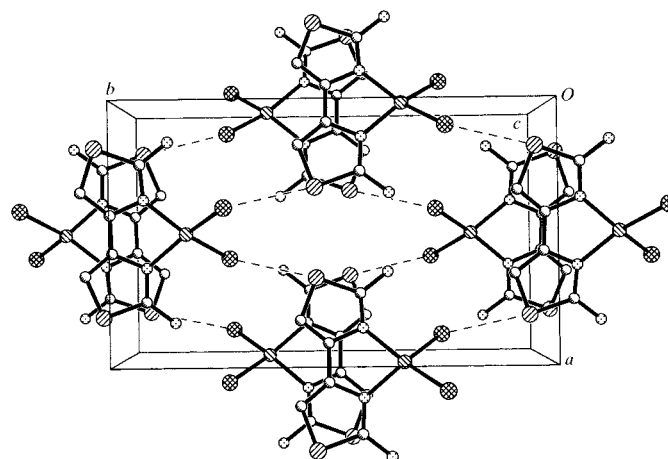
Valle *et al.*, 1991) is observed in the structure. The dihedral angle of  $39.17(6)^\circ$  between the  $\text{Cl1}-\text{Cu}-\text{Cl1}^i$  and  $\text{N1}-\text{Cu}-\text{N1}^i$  planes [symmetry code: (i)  $-x, y, \frac{1}{2}-z$ ], and the deviation of 1.058 (2) Å for Cl1 from the  $\text{N1}-\text{Cu}-\text{N1}^i$  plane, show that the coordination geometry is neither tetrahedral nor square planar. However, coordination bond angles near  $90^\circ$  (see Table 1) suggest that the coordination geometry is distorted square planar.



**Figure 1**

The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii [symmetry code: (i)  $-x, y, \frac{1}{2}-z$ ].

An intramolecular hydrogen bond is observed between Cl1 and N2 [ $\text{Cl1}\cdots\text{N2}$  3.158 (3) Å and  $\text{Cl1}\cdots\text{H2A}-\text{N2}$  149 (3) $^\circ$ ], which results in the coordination being distorted from a square plane. The deviation of Cl1 from the  $\text{N1}-\text{Cu}-\text{N1}^i$  plane shows less overlap between the atomic orbitals of Cl1 and Cu. However, the  $\text{Cu}-\text{Cl1}$  distance of 2.2392 (8) Å is shorter than the  $\text{Cu}^{\text{II}}-\text{Cl}$  distances found in other four-coordinate  $\text{Cu}^{\text{II}}$  complexes (2.244–2.302 Å; Gavel & Hodgson, 1979; Valle *et al.*, 1991; Weise & Willett, 1993; Bond & Willett, 1991). This fact might imply the existence of an electrostatic interaction in (I) between  $\text{Cu}^{\text{II}}$  and the Cl atoms.



**Figure 2**

The packing diagram for (I) viewed along the  $c^*$  axis. The dashed lines show the short contacts between neighbouring molecules.

Electron delocalization between the thiazole ring and the amino group is verified by identical bond distances [N1—C3 1.322 (3) Å and N2—C3 1.327 (4) Å]. Although no previous geometric data of the bithiazole complex of Cu<sup>II</sup> are available for comparison, the Cu—N1 distance of 1.990 (2) Å in (I) is comparable with Cu—N distances in the range 1.982 (3)–2.004 (6) Å in 2,2'-bipyridine complexes of Cu<sup>II</sup> (Xu *et al.*, 1996; Zhang *et al.*, 1997).

The molecular packing in (I) is illustrated in Fig. 2. The bithiazole rings of complex molecules related by an inversion centre are shown to overlap. The distance of 3.425 (1) Å between neighbouring parallel bithiazole rings suggests the existence of a  $\pi$ – $\pi$  interaction between them. The distance of 3.389 (1) Å between Cl1 and S1( $\frac{1}{2} - x, y - \frac{1}{2}, z$ ) is the shortest contact between neighbouring molecules.

## Experimental

Crystals of (I) were obtained by a solution diffusion method using an H-shaped glass tube. CuCl<sub>2</sub>·2H<sub>2</sub>O (0.85 g, 5 mmol) was dissolved in anhydrous methanol (50 ml; solution A), and 2,2'-diamino-4,4'-bi-1,3-thiazole (DABT; 0.99 g, 5 mmol) was dissolved in another 50 ml of hot anhydrous methanol (solution B) under a nitrogen atmosphere. Solution B was then introduced into one branch of the H-shaped tube and nitrogen was bubbled into the solution to drive off air. Solution A was introduced into the other branch of the H-shaped tube. The surfaces of both solutions were about 12 mm below the horizontal pass-through of the H-shaped tube. Next, air-free methanol was carefully introduced into the tube and layered above the two solutions as a diffusion medium. The tube was sealed with a piece of saran wrap and left at room temperature. Dark-green crystals of (I) were obtained after a week.

### Crystal data

[CuCl <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> S <sub>2</sub> )]	Mo K $\alpha$ radiation
$M_r = 332.71$	Cell parameters from 25 reflections
Orthorhombic, <i>Pbcn</i>	$\theta = 8\text{--}16^\circ$
$a = 9.494$ (2) Å	$\mu = 2.871$ mm <sup>-1</sup>
$b = 15.936$ (3) Å	$T = 293$ (2) K
$c = 7.1370$ (14) Å	Hexagonal prism, dark green
$V = 1079.8$ (4) Å <sup>3</sup>	$0.35 \times 0.35 \times 0.32$ mm
$Z = 4$	
$D_x = 2.047$ Mg m <sup>-3</sup>	

**Table 1**

Selected geometric parameters (Å, °).

Cu—N1	1.990 (2)	S1—C3	1.737 (3)
Cu—Cl1	2.2392 (8)	Cl1—C2	1.344 (4)
S1—C2	1.730 (3)	Cl1—Cl <sup>1</sup>	1.467 (5)
N1—Cu—N1 <sup>1</sup>	81.85 (12)	N1 <sup>1</sup> —Cu—Cl1	151.81 (6)
N1—Cu—Cl1	97.01 (6)	Cl1—Cu—Cl1 <sup>1</sup>	96.78 (5)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

### Data collection

Rigaku AFC-7S diffractometer	$\theta_{\max} = 25^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 11$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$k = 0 \rightarrow 18$
$T_{\min} = 0.361, T_{\max} = 0.399$	$l = 0 \rightarrow 8$
941 measured reflections	3 standard reflections
941 independent reflections	every 100 reflections
857 reflections with $I > 2\sigma(I)$	intensity decay: 0.5%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 1.149P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.153$	$\Delta\rho_{\max} = 0.39$ e Å <sup>-3</sup>
940 reflections	$\Delta\rho_{\min} = -0.37$ e Å <sup>-3</sup>
78 parameters	
Only coordinates of H atoms refined	

H atoms were located in a difference Fourier map and their coordinates were refined [N—H = 0.78 (4) and 0.84 (4) Å, and C—H = 0.84 (4) Å], with a fixed  $U_{\text{iso}}$  value of 0.06 Å<sup>2</sup>.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b); program(s) used to solve structure: *SHELXS93* (Sheldrick, 1993); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1305). Services for accessing these data are described at the back of the journal.

## References

- Bond, M. R. & Willett, R. D. (1991). *Acta Cryst.* **C47**, 1084–1087.
- Fisher, L. M., Kurod, R. & Sakai, T. (1985). *Biochemistry*, **24**, 3199–3207.
- Gavel, D. P. & Hodgson, D. J. (1979). *Acta Cryst.* **B35**, 2704–2707.
- Liu, J., Sun, W. & Lu, F. (2001). *J. Mater. Res.* In the press.
- Molecular Structure Corporation (1992a). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1992b). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1993). *SHELXS93* and *SHELXL93*. University of Göttingen, Germany.
- Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sun, W., Gao, X. & Lu, F. J. (1997). *Appl. Polym. Sci.* **64**, 2309–2315.
- Tian, Y., Yang, F. & Wang, H. (1996). *Polyhedron*, **15**, 2771–2776.
- Valle, G., Gonzalez, A. S. & Ettore, R. (1991). *Acta Cryst.* **C47**, 1392–1394.
- Waring, M. J. (1981). *Ann. Rev. Biochem.* **50**, 159–192.
- Weise, S. & Willett, R. D. (1993). *Acta Cryst.* **B49**, 283–289.
- Xu, D., Xie, A., Xu, Y., Zhang, C. & Chen, W. (1996). *J. Coord. Chem.* **39**, 273–280.
- Zhang, L., Xu, D., Xu, Y. & Gu, J. (1997). *Acta Cryst.* **C53**, 299–301.