Data reduction was performed with the *XP*2_1 program (Pavelčík, 1987). The structure was solved by the Patterson method and refined by block-diagonal least-squares methods. H atoms were placed at calculated positions and their coordinates and displacement parameters were fixed. Calculations were performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4′-Bithiazole and Bis(2,4′-bithiazole)bis(dimethyl sulfoxide)copper(II) Diperchlorate

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Abstract

The synthesis and crystal structure of 2,4′-bithiazole, $C_6H_4N_2S_2$ (I), and its copper complex $[Cu(C_6H_4N_2S_2)_2(C_2H_6OS)_2](ClO_4)_2$ (II) are presented. The bithiazole molecules are planar in both compounds. The 2,4′-bithiazole (I) molecule is located on a symmetry center and the structure was solved by the introduction of disorder between the S atom and its neighbour S/C2, which caused a small deviation in the S—C and C—C bond distances. Other bond distances and angles are as expected. In the copper complex (II), the Cu atom is hexacoordinated and the 2,4′-bithiazole moiety again presents statistical disorder giving the ligand a local mirror symmetry.

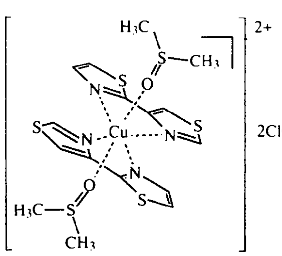
Comment

2,4′-Bithiazole was isolated for the first time by Erlenmeyer, Weber, Schmidt, Kung, Zinsstay & Prijs (1948) from a Hantzsch cyclization. This molecule is of great interest because it is the chromophoric group of bleomycine which causes the degradation of DNA in a process that requires iron(II) and dioxygen (Riordan & Sakai, 1981; Zeen-Cheen & Cheng, 1970; Riordan, Glickson & Sakai, 1982; Aogagi, Suguna, Murugesa, Ehernfeld, Chang, Ohgi, Shekhani, Kirkup & Hecht, 1982; Levin, Subrahananion, Katz, Smith, Burlett & Hecht, 1980). In fact, it is only derivatives of 2,4′-bithiazole that have been studied by X-ray diffraction (Trowitzsch, Höfle & Sheldrick, 1981; Koyama, Nakamura, Muraoku, Takita, Maeda & Umezawa, 1968). More recently, π-accepting ligands such as bithiazole have been of considerable interest because they tend to stabilize a particular electronic configuration of the associated metal (Cu, Rh, Ni, Pd). This interaction generates metal–ligand excited transfer states which can be studied through their photoluminescent properties (Krause, Krause & Lamtruong, 1988). We prepared 2,4′-bithiazole as a model compound in order to obtain precise intercycle geometric parameters for comparison with extended Hückel theory (Hoffmann, 1963) and molecular-mechanics calculations previously carried out on this compound (Baudrion, 1992).

For compound (I), the helicoidal 2_1 axis is determined by four non-observed reflections; $0k0$, $k = 1, 3, 5$ and 7. Refinement in the non-centrosymmetric space group Pc gives rise to a molecular inversion center; therefore, the structure has been solved in space group $P2_1/c$.

2,4′-Bithiazole, which does have an inversion center, is located on the crystallographic symmetry center $\frac{1}{2}$,0,0, and because of this it is not possible to distinguish between positions 1 and 5 of the heterocycle. The structure has been solved by considering S/C [$\frac{1}{2}$(S + C)] as a hybrid atom on these positions. In other words, the crystal structure can be considered to be the result of the packing of two molecules *A* and B having two different orientations but in equal proportions, as shown in Fig. 1.

The complex molecule (II) is centrosymmetric with the Cu atom located at the special position 4(*e*) (0, *y*, $\frac{1}{4}$) and the bidentate ligand atoms in general positions. However, the bithiazole moiety has a local pseudo mirror due to a stacking fault similar to that found for (I). The observed structure is a statistical average between two orientations A and B of the 2,4′-bithiazole, and positions 1 and 5 of the heterocycle are neither C nor S but a hybrid atom (S/C) composed of 50% S and 50% C as deduced from least-squares calculations. It is interesting to note that the type of disorder observed in the complex crystal is different from that described for (I) with the *cis* orientation of the N atoms allowing them to be linked to the Cu atom.



(II)

The disorder observed in compounds (I) and (II) seems to be a common feature of 2,4′-bithiazole molecules. It was first observed by Trowitzsch and co-workers (Trowitzsch, Höfle & Sheldrick, 1981) in the study of myxothiazol. The authors noted that the solution and refinement of the structure were complicated by the fact that the atom positions within the bithiazole chromophore are related by a pseudo-center of symmetry. Despite various treatments, the R factor remained relatively high; 0.083 for 1761 reflections.

For compound (II), the Cu atom is centrosymmetrically coordinated with four N atoms in equatorial positions, the Cu—N distances [Cu—N 2.012 (7) and Cu—N′ 2.023 (7) Å] being similar to those found in the literature, and two O atoms of DMSO in axial positions, the long Cu—O [2.435 (5) Å] distance having also been observed in other copper complexes (Kitajima & Moro-oka, 1993).

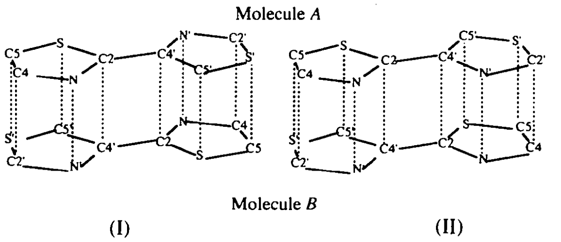
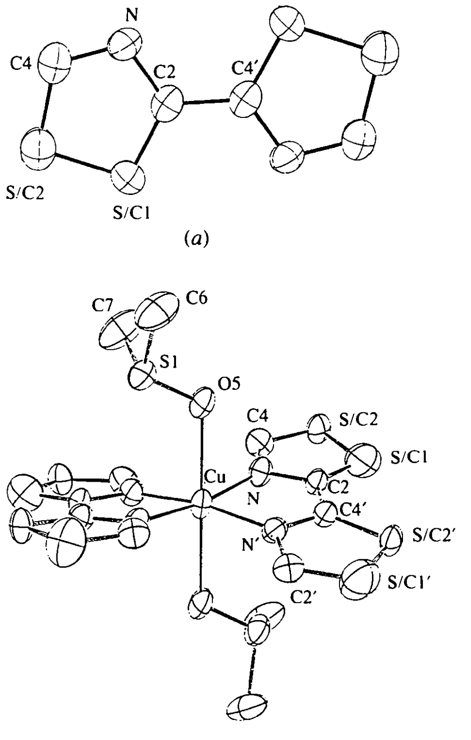


Fig. 1. Stacking of 2,4′-bithiazole molecules in crystals (I) and (II).



(*a*)

(*b*)

Fig. 2. *ORTEP* plots (Johnson, 1976) of the title compounds with the atomic numbering schemes: (*a*) (I) and (*b*) (II). Displacement ellipsoids are at the 50% probability level.

Experimental

2,4′-Bithiazole (I) was separated by a two-step reaction. Firstly, a diazonium salt of 2-aminothiazole was synthesized and reduced to 2-chlorothiazole by a Sandmeyer reaction. During this manipulation two other compounds were isolated, namely, 2-chloro-2′,5-bithiazole and 2-chloro-2,4′-bithiazole. Then, a second reaction allowed the isolation of 2,4′-bithiazole by reduction of the chloro compound in acetic acid with zinc metal. 2,4′-Bithiazole crystallizes after 1 d in CCl_4 and its melting point is about 391 K. The copper complex (II) was obtained by the reaction in ethanol of 2,4′-bithiazole and copper(II) diperchlorate hexahydrate. A greenish solid appeared and was separated by filtration. This complex crystallizes after 1 month in dimethyl sulfoxide.

Compound (I)

Crystal data

$C_6H_4N_2S_2$	Mo $K\alpha$ radiation
$M_r = 168.24$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	$\theta = 14$–$16°$
$a = 5.673$ (2) Å	$\mu = 0.636$ mm^{-1}
$b = 6.172$ (2) Å	$T = 293$ K
$c = 11.507$ (1) Å	Prism
$\beta = 61.79°$	

$V = 355.0$ (4) Å^3
$Z = 2$
$D_x = 1.574$ Mg m^{-3}

0.5 × 0.4 × 0.3 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1244 measured reflections
954 independent reflections
579 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 24°$
$h = 0 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -13 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.040$
$S = 0.465$
579 reflections
55 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$[Cu(C_6H_4N_2S_2)_2(C_2H_6OS)_2]$-$(ClO_4)_2$
$M_r = 755.19$
Monoclinic
$C2/c$
$a = 19.249$ (2) Å
$b = 10.073$ (2) Å
$c = 14.701$ (1) Å
$\beta = 97.93$ (2)°
$V = 2838.5$ (4) Å^3
$Z = 4$
$D_x = 1.767$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14$–$16°$
$\mu = 1.44$ mm^{-1}
$T = 293$ K
Rectangular
0.3 × 0.3 × 0.3 mm
Green

Data collection

Enraf–Noinus CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2463 measured reflections
2167 independent reflections
1891 observed reflections [$F > 3\sigma(F)$]

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.076$
$wR = 0.077$
$S = 2.34$
1891 reflections
186 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Compound (I)				
S/C1	0.2509 (2)	0.2048 (2)	0.9682 (1)	3.67 (3)
N	0.7424 (4)	0.1914 (4)	0.8835 (2)	3.40 (5)
C4	0.7037 (6)	0.3645 (5)	0.8246 (3)	3.81 (7)
S/C2	0.3976 (3)	0.4186 (2)	0.8571 (1)	4.54 (3)
C2	0.5077 (5)	0.0965 (4)	0.9625 (2)	3.07 (6)
Compound (II)				
Cu	1/2	−0.0052 (1)	1/4	2.83 (3)
S/C1	0.6158 (2)	0.1616 (3)	0.0403 (2)	3.10 (6)
S/C1′	0.5532 (2)	−0.3209 (3)	0.0528 (2)	3.40 (7)
N	0.5452 (3)	0.1232 (6)	0.1717 (4)	2.8 (1)
N′	0.5286 (3)	−0.1359 (6)	0.1580 (4)	3.0 (1)
C4	0.5632 (4)	0.2550 (8)	0.1764 (5)	3.4 (2)
C4′	0.5622 (4)	−0.0779 (8)	0.0924 (5)	2.7 (2)
S/C2	0.6025 (2)	0.3070 (5)	0.1012 (3)	6.3 (1)
S/C2′	0.5869 (2)	−0.1697 (4)	0.0186 (3)	5.6 (1)
C2	0.5715 (4)	0.0648 (8)	0.1012 (5)	2.9 (2)
C2′	0.5207 (5)	−0.2659 (8)	0.1417 (6)	3.8 (2)
S1	0.3223 (1)	0.0095 (2)	0.1969 (2)	4.09 (5)
O5	0.3877 (3)	0.0006 (6)	0.1515 (4)	4.5 (1)
C6	0.2888 (5)	−0.1547 (1)	0.1961 (9)	6.5 (3)
C7	0.2548 (5)	0.0815 (7)	0.1155 (8)	5.8 (3)
Cl	0.3581 (1)	0.5072 (2)	0.6366 (5)	4.32 (5)
O1	0.3705 (8)	0.4673 (8)	0.7241 (6)	10.1 (3)
O2	0.3541 (6)	0.4145 (8)	0.5711 (6)	11.1 (3)
O3	0.3489 (7)	0.6367 (1)	0.6135 (7)	14.3 (4)
O4	0.2829 (8)	0.5236 (8)	0.63667 (7)	12.9 (7)

Table 2. *Selected geometric parameters* (Å, °)

Compound (I)			
N—C2	1.340 (4)	C2—C4′	1.450 (4)
N—C4	1.345 (5)		
C2—N—C4	110.1 (2)	N—C4—S/C2	117.4 (3)
Compound (II)			
Cu—N	2.012 (7)	C2—C4′	1.45 (1)
Cu—N′	2.023 (7)	S1—O5	1.497 (6)
Cu—O5	2.435 (5)	S1—C6	1.78 (1)
N—C2	1.35 (1)	S1—C7	1.80 (1)
N′—C2′	1.34 (1)	N′—C4′	1.37 (1)
N—C4	1.37 (1)		
N—Cu—N′	81.5 (3)	C6—S1—O5	105.7 (6)
N—Cu—O5	93.4 (2)	C7—S1—O5	107.4 (3)
N′—Cu—O5	85.1 (2)	N′—C2′—S/C1′	115.6 (7)
C4—N—C2	109.9 (7)	C2′—N′—C4′	110.1 (7)
C6—S1—C7	97.7 (4)		

All non-H atoms were found by direct methods (Frenz, 1978) and both structures were successfully refined with a full-matrix least-squares procedure using anisotropic displacement parameters for all non-H atoms. For compound (I), two atoms were located on a difference Fourier map and included in the refinement. The weighting scheme used was derived from: $\sigma(I_{\rm obs}) = [\sigma^2(I_{\rm obs})^2]^{1/2}$.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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