Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis[1-hydroxypyridine-2(1*H*)-thionato-*S*,*O*]copper(II)

Andrew D. Bond,[a]* Neil Feeder,[a]† Simon J. Teat[b] and William Jones[a]

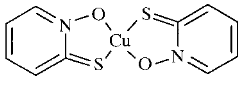
[a]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England, and [b]CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England
Correspondence e-mail: adb29@cam.ac.uk

Received 16 July 2001
Accepted 19 July 2001

The crystal structure of the widely used title fungicidal material, $[Cu(C_5H_4NOS)_2]$, has been determined at 150 (2) K from a microcrystalline fragment using synchrotron radiation. The molecule adopts a *trans*-square-planar configuration, with the Cu atom sited at a crystallographic centre of inversion.

Comment

Cyclic thiohydroxamic acids, such as 1-hydroxypyridine-2(1*H*)-thione (pyrithione), find extensive use as fungicides (Paulus, 1993). In particular, complexes of pyrithione with Zn and Cu are highly active broad-spectrum antimicrobial agents. Zinc pyrithione is the active ingredient in most antidandruff shampoos (Arch Chemicals, 2000*a*). Copper pyrithione is sold extensively (outside the USA) as a marine antifouling product; marine paints containing copper pyrithione are easy to formulate and show excellent stability even when subjected to extreme thermal conditions (Arch Chemicals, 2000*b*). The crystal structure of zinc pyrithione has been known for almost 25 years (Barnett *et al.*, 1977), and a considerable number of pyrithione complexes have been prepared and their crystal structures determined (Chen *et al.*, 1991; Hu *et al.*, 1991; Xu *et al.*, 1995; Wen *et al.*, 1996). Despite this extensive research, the crystal structure of copper pyrithione has remained elusive. This may undoubtedly be attributed to the fact that copper pyrithione does not readily form large single crystals suitable for diffraction analysis with laboratory instruments. We report here the crystal structure of copper pyrithione, (I), determined from a microcrystalline fragment using the additional brightness of the Synchrotron Radiation Source at Daresbury, England (Cernik *et al.*, 1997).



(I)

Compound (I) adopts a *trans*-square-planar arrangement, with Cu1 situated at a centre of inversion in the space group $P\bar{1}$ (Fig. 1). The Cu1—S1 and Cu1—O1 bond distances (Table 1) are shorter than those in zinc pyrithione [average 2.308 (3) and 2.115 (6) Å, respectively]. Molecules of (I) are linked into chains by C—H···O interactions, forming an $R_2^2(8)$ hydrogen-bond motif [H5···O1^{ii} 2.41 Å and C5—H5···O1^{ii} 164°; symmetry code: (ii) $-x$, $-1-y$, $-z$] (Fig. 2). The same motif exists in the divalent Ni complex of pyrithione (Chen *et al.*, 1991), in which a *cis*-square-planar geometry leads to the formation of discrete dimers rather than extended chains.

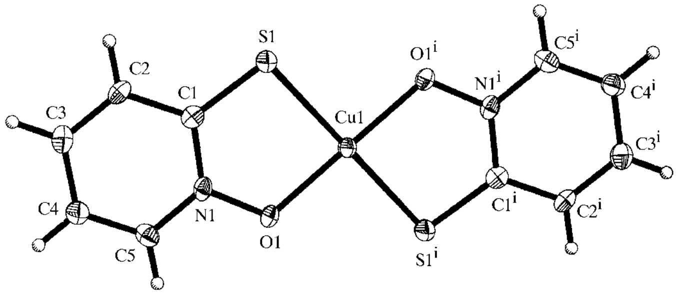


Figure 1
The molecular unit in (I), showing displacement ellipsoids at the 50% probability level and H atoms as small spheres of arbitrary radii [symmetry code: (i) $-x$, $-y$, $-z$].

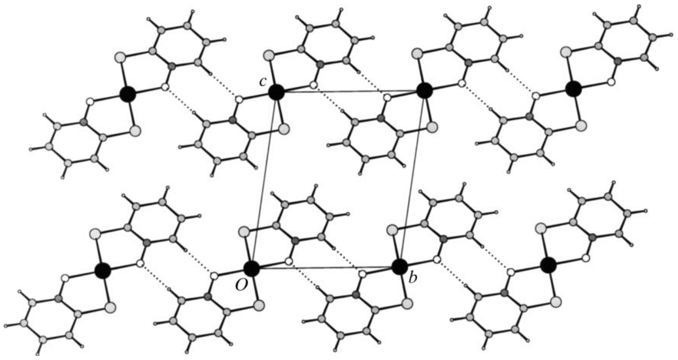


Figure 2
The projection onto (100) showing chains of (I) linked *via* C—H···O interactions.

Molecules of (I) in adjacent chains are stacked such that S1 in one molecule lies directly above Cu1 in an adjacent molecule, with Cu1···S1^{iii} = 3.4447 (13) Å [symmetry code: (iii) $1-x$, $-y$, $-z$]. The same arrangement exists below Cu1 [Cu1···S1^{iv}; symmetry code: (iv) $-1-x$, $-y$, $-z$], such that the coordination geometry around it may be considered to be a tetragonally distorted octahedron (Fig. 3), *i.e.* a Jahn–Teller-distorted octahedral geometry about Cu^{II} (d^9). Molecules of (I), therefore, form extended stacks containing edge-sharing octahedra along the [100] direction. Within these stacks, pyrithione rings of adjacent molecules are coplanar, with interplanar separations of 3.25 Å.

---

† Present address: Pfizer Global R&D, Ramsgate Road, Sandwich, Kent CT13 9NJ, England.

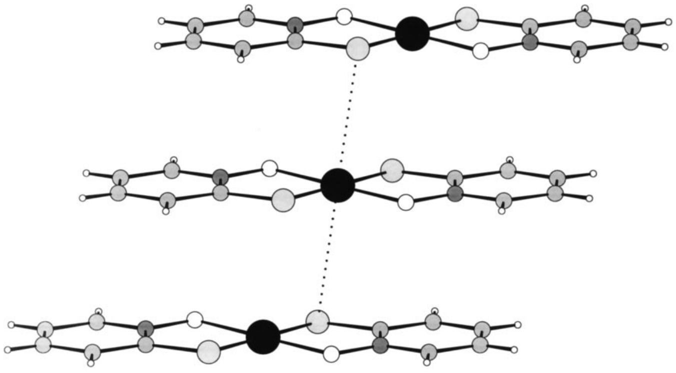


Figure 3
The coordination geometry around Cu1 illustrating the axial Jahn–Teller distortion.

Experimental

1-Hydroxypyridine-2(1*H*)-thione (HPT) was obtained as the hydrated sodium salt, Na(PT)·xH$_2$O, from Aldrich. The Cu^{II} complex was prepared by the combination of aqueous solutions of CuCl$_2$ and Na(PT) in a 1:2 molar ratio at room temperature. The resulting green precipitate was removed by filtration under gravity and dried in air at room temperature. Attempts to prepare single crystals of (I) suitable for X-ray diffraction using laboratory instruments were unsuccessful, since the material consistently crystallized as florets of fine needles. Data were therefore collected at Station 9.8, Daresbury SRS, England, from a needle cut from a floret grown by slow evaporation of a solution of (I) in dimethyl sulfoxide.

Crystal data

[Cu(C$_5$H$_4$NOS)$_2$]
M_r = 315.84
Triclinic, $P\overline{1}$
a = 4.0545 (7) Å
b = 7.5723 (12) Å
c = 9.0629 (14) Å
α = 81.096 (4)°
β = 86.190 (4)°
γ = 85.197 (4)°
V = 273.53 (8) Å^3
Z = 1

D_x = 1.917 Mg m^{-3}
Synchrotron radiation
λ = 0.6884 Å
Cell parameters from 1797 reflections
θ = 3.2–29.1°
μ = 2.37 mm^{-1}
T = 150 (2) K
Needle, green
0.04 × 0.02 × 0.01 mm

Data collection

Bruker SMART CCD diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min}$ = 0.911, $T_{\max}$ = 0.977
2505 measured reflections

1430 independent reflections
1074 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.044
$\theta_{\max}$ = 29.2°
$h = -5 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.161
S = 1.01
1430 reflections
79 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.011
$\Delta\rho_{\max}$ = 1.29 e Å^{-3}
$\Delta\rho_{\min}$ = −1.04 e Å^{-3}

Note that the transmission factors of the absorption correction are not real since they include corrections for beam decay and possibly crystal decay (the two cannot be distinguished). The numbers listed in the CIF are those calculated by *SHELXL*97 (Sheldrick, 1997). H atoms were placed geometrically and allowed to ride during subsequent refinement, with a C—H distance of 0.95 Å and an isotropic displacement parameter fixed at 1.2 times $U_{\rm eq}$ of the C atom to which they were attached. For subsequent discussion of the structure, the H-atom positions derived from the X-ray results were normalized to standard neutron-derived values (Allen *et al.*, 1987) along the C—H vector.

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.939 (3)	N1—C1	1.366 (6)
Cu1—S1	2.2445 (11)	C1—C2	1.405 (6)
S1—C1	1.703 (4)	C2—C3	1.365 (6)
O1—N1	1.354 (5)	C3—C4	1.405 (7)
N1—C5	1.362 (6)	C4—C5	1.356 (7)
O1^{i}—Cu1—S1^{i}	87.96 (9)	C1—S1—Cu1	95.67 (15)
O1—Cu1—S1^{i}	92.04 (9)	N1—O1—Cu1	115.7 (3)
O1^{i}—Cu1—S1	92.04 (9)	O1—N1—C5	116.6 (4)
O1—Cu1—S1	87.96 (9)	O1—N1—C1	120.6 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *LSCELL* (Clegg, 1997); data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *XP* in *SHELXTL* (Siemens, 1996) and *CAMERON* (Watkin *et al.*, 1996).

We thank the EPSRC and Avecia Ltd for funding to ADB *via* a CASE studentship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1171). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Arch Chemicals Inc. (2000*a*). For details see http://www.olinbiocides.com/Products/ZincOmadine.asp
Arch Chemicals Inc. (2000*b*). For details see http://www.olinbiocides.com/Products/Copper.asp
Barnett, B. L., Kretschmar, H. C. & Hartman, F. A. (1977). *Inorg. Chem.* **16**, 1834–1838.
Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cernik, R. J., Clegg, W., Catlow, C. R. A., Bushnell-Wye, G., Flaherty, J. V., Greaves, G. N., Burrows, I., Taylor, D. J., Teat, S. J. & Hamichi, M. (1997). *J. Synchrotron Rad.* **4**, 279–286.
Chen, X.-T., Hu, Y.-H., Wu, D.-X., Weng, L.-H. & Kang, B.-S. (1991). *Polyhedron*, **10**, 1651–1657.
Clegg, W. (1997). *LSCELL*. University of Newcastle-upon-Tyne, England.
Hu, Y.-H., Weng, L.-H., Huang, L.-R., Chen, X.-T., Wu, D.-X. & Kang, B.-S. (1991). *Acta Cryst.* C**47**, 2655–2656.
Paulus, W. (1993). *Microbicides for the Protection of Materials: A Handbook*. London: Chapman & Hall.
Sheldrick, G. M. (1997). *SHELXL*97, *SHELXS*97 and *SADABS*. University of Göttingen, Germany.
Siemens (1996). *XP* in *SHELXTL*. Version 5.06. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.
Wen, T.-B., Shi, J.-C., Liu, Q.-T., Kang, B.-S., Wu, B.-M. & Mak, T. C. W. (1996). *Acta Cryst.* C**52**, 1204–1206.
Xu, Y.-J., Kang, B.-S., Chen. X.-T. & Huang, L.-R. (1995). *Acta Cryst.* C**51**, 370–374.