Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

catena-Poly[[bis[μ-1-(2-pyridyl)pyridinium-2-thiolate]-κ^2N:S;κ^2S:N-dicopper(I)]-di-μ-chloro]

Phimphaka Harding,[a]* David J. Harding,[a] Chaveng Pakawatchai[b] and Hirihattaya Phetmung[c]

[a]Department of Chemistry, School of Science, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand, [b]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand, and [c]Department of Chemistry, Faculty of Science, Taksin University, Songkhla 90000, Thailand

Correspondence e-mail: kphimpha@wu.ac.th

Received 11 February 2006
Accepted 9 May 2006

The reaction of copper(II) chloride with pyridine-2-thiol affords the title complex, $[Cu_2Cl_2(C_{10}H_8N_2S)_2]_n$, in which two pyridine-2-thiol molecules have reacted to give a betain ligand and the copper centre has undergone reduction. The copper metal centre exhibits a distorted tetrahedral coordination geometry with bridging chloride and 1-(2-pyridyl)pyridinium-2-thiolate ligands, giving centrosymmetric dimers further linked into a polymeric chain.

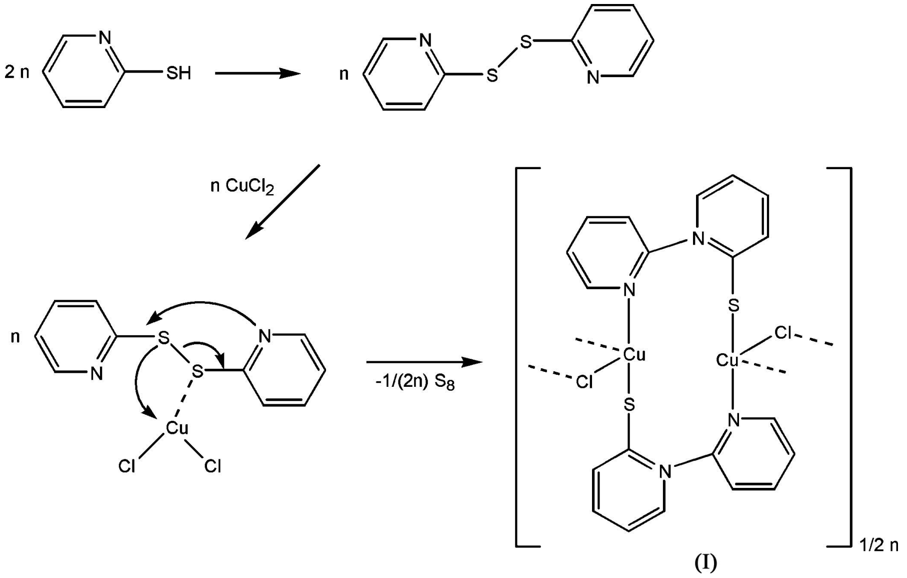
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.025
wR factor = 0.033
Data-to-parameter ratio = 8.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The synthesis of high nuclearity metal clusters as potential molecular magnets has been an intense area of research for many years (Hill *et al.*, 2003; Christou *et al.*, 2000). The synthetic procedure usually involves the reaction of an appropriate metal salt with one, or sometimes two, co-ligands (Winpenny *et al.*, 2002). The nature of these co-ligands is crucial for controlling the size and shape of the multinuclear cluster. Under these conditions, in most cases, cages and wheels are formed (Sessoli *et al.*, 1993; Taft *et al.*, 1994). To this end, we have recently been exploring the chemistry of pyridine-2-thiol and its use as a bridging ligand in metal clusters.



(I)

The reaction of $CuCl_2 \cdot 2H_2O$ with pyridine-2-thiol in the presence of a base in an ethanol solution initially gave a yellow solution. Slow evaporation of this solution over a period of many months yielded orange crystals. X-ray crystallographic analysis showed these to be copper(I)–1-(2-pyridyl)-pyridinium-2-thiolate (ppt) chloride $[Cu^I(\mu\text{-Cl})(\mu\text{-ppt})]_n$, (I). The compound is polymeric rather than the anticipated cage

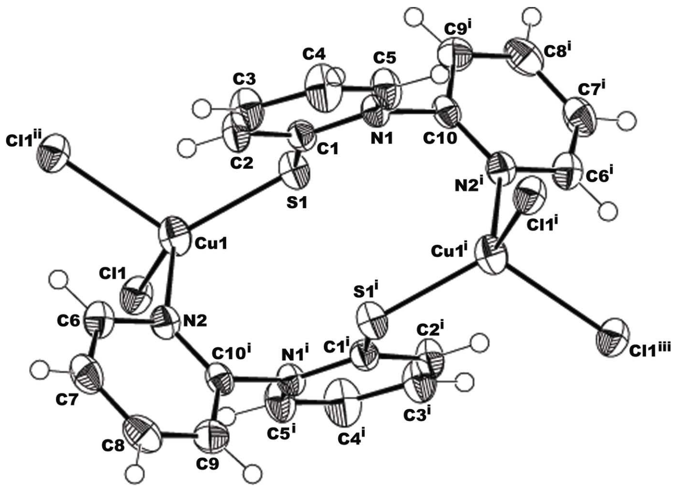


Figure 1

The centrosymmetric dimeric unit of the polymeric structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, -y, -z$; (iii) $x, y, 1 + z$.]

or wheel. In addition, the pyridine-2-thiol has been significantly modified and the copper centre reduced.

Although the compound is already known, no structural studies have been reported to our knowledge (Kinoshita *et al.*, 2003). Moreover, (I) was previously synthesized from 2,2′-dipyridyl disulfide (dpds) and $CuCl_2 \cdot 2H_2O$, not pyridine-2-thiol. Based on the proposed scheme for the formation of ppt from dpds, we suggest that 2,2′-dipyridyl disulfide is formed from two molecules of pyridine-2-thiol and then subsequently reacts to form ppt (see scheme). Formation of dpds from pyridine-2-thiol is known, in the case of cobalt (Harding *et al.*, 2005). This hypothesis is supported by the presence of elemental sulfur in the reaction solution.

The copper coordination in (I) is distorted tetrahedral with alternating bridging chloride and 1-(2-pyridyl)pyridinium-2-thiol ligands forming four-membered and twelve-membered rings, respectively (Fig. 1). The structure of (I) is very similar to the previously reported bromide derivative, in which the Cu—N [2.131 (2) Å] and Cu—S [2.2622 (8) Å] bond lengths are almost identical (Kinoshita *et al.*, 2003). The pyridine and pyridinium rings are almost perpendicular to one another. In addition, the pyridinium ring is planar, suggesting that the aromaticity of the ring is retained in the ppt ligand.

In conclusion, we report a novel synthesis of (I) and also its crystal structure. The crystal structure reveals a polymeric compound with tetrahedral copper(I) centres bridged by chloride and 1-(2-pyridyl)pyridinium-2-thiolate ligands.

Experimental

$CuCl_2 \cdot 2H_2O$ (0.120 g, 0.70 mmol) was dissolved in H_2O (3 ml). In a separate flask, pyridine-2-thiol (0.157 g, 1.41 mmol) was dissolved in EtOH (10 ml) and heated to 333 K. The copper salt solution was added dropwise, resulting in the formation of a yellow solid. The solution was stirred for 5 min and then cooled to room temperature. The solid was filtered, washed with cold EtOH (3 × 5 ml) and air-dried (0.130 g). Suitable crystals were obtained by allowing a concentrated solution of the solid in EtOH to evaporate slowly, yielding orange red crystals of the title compound (yield 0.097 g, 50%).

Crystal data

$[Cu_2Cl_2(C_{10}H_8N_2S)_2]$
$M_r = 574.50$
Triclinic, $P\overline{1}$
$a = 7.6268$ (11) Å
$b = 8.7596$ (13) Å
$c = 9.2748$ (14) Å
$\alpha = 72.340$ (2)°
$\beta = 70.924$ (2)°
$\gamma = 67.088$ (2)°
$V = 528.24$ (14) Å^3
$Z = 1$
$D_x = 1.806$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.48$ mm^{-1}
$T = 298$ K
Block, red
0.23 × 0.12 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan *SADABS* (Bruker, 1997)
$T_{min} = 0.700$, $T_{max} = 0.804$
4641 measured reflections
2619 independent reflections
1455 reflections with $F > 3.98\sigma(F)$
$R_{int} = 0.011$
$\theta_{max} = 28.3°$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.033$
$S = 1.09$
1455 reflections
169 parameters
All H-atom parameters refined
$w = 1/[\sigma^2|F_o|^2 + 0.005|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.033$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 3.9 (12) × 10^2

Table 1

Selected geometric parameters (Å, °).

Cu1—Cl1	2.3384 (10)	Cu1—N2	2.133 (3)
Cu1—S1	2.2518 (8)	Cu1—Cl1^{i}	2.4579 (8)
Cl1—Cu1—S1	119.35 (3)	S1—Cu1—Cl1^{i}	115.80 (3)
Cl1—Cu1—N2	110.16 (7)	N2—Cu1—Cl1^{i}	100.84 (6)
Cl1—Cu1—Cl1^{i}	98.71 (3)	Cu1—Cl1—Cu1^{i}	81.29 (3)
S1—Cu1—N2	110.08 (7)		

Symmetry code: (i) $-x + 1, -y, -z - 2$.

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95–0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *Xtal3.7* (Hall *et al.*, 2000); program(s) used to solve structure: *Xtal* 3.7; program(s) used to refine structure: *Xtal* 3.7; molecular graphics: *Xtal* 3.7; software used to prepare material for publication: *Xtal* 3.7.

We gratefully acknowledge financial support from the National Metal and Materials Technology Centre (MT-S45-POL-48–194-G) and Walailak University. CP thanks the Postgraduate Education and Research Program in Chemistry (PERCH) for partial support.

References

Bruker (1997). *SMART* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Christou, G., Gatteschi, D., Hendrickson, D. N. & Sessoli, R. (2000). *MRS Bull.* **25**, 66–71.

m1336 Harding *et al.* • $[Cu_2Cl_2(C_{10}H_8N_2S)_2]$ *Acta Cryst.* (2006). E**62**, m1335–m1337

Hall, S. R., King, G. S. D. & Stewart, J. M. (2000). *Xtal3.7 System*. University of Western Australia, Australia. (URL: http://*Xtal*.sourceforce.net/.)

Harding, P. & Harding, D. J. (2005). Unpublished results.

Hill, S., Edwards, R. S., Aliaga-Alcalde, N. & Christou, G. (2003). *Science*, **302**, 1015–1018.

Kinoshita, I., Wright, L. J., Kubo, S., Kimura, K., Sakata, A., Yano, T., Miyamoto, R., Nishioka, T. & Isobe, K. (2003). *Dalton Trans.* pp. 1993–2003.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Sessoli, R., Tsai, H.-L., Schake, A. R., Wang, S., Vincent, J. B., Folting, K., Gatteschi, D., Christou, G. & Hendrickson, D. N. (1993). *J. Am. Chem. Soc.* **115**, 1804–1816.

Taft, K. L., Delfs, C. D., Papaefthymiou, G. C., Foner, S., Gatteschi, D. & Lippard, S. J. (1994). *J. Am. Chem. Soc.* **116**, 823–832.

Winpenny, R. E. P. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1–10.

Acta Cryst. (2006). E**62**, m1335–m1337 Harding *et al.* • [$Cu_2Cl_2(C_{10}H_8N_2S)_2$] **m1337**