

# Synthesis, Structure and Optical Properties of Cupro-8-thioquinoline Coordination Polymer, $[\text{Cu}^{\text{I}}(\text{C}_9\text{H}_6\text{NS})]_n$

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A Cupro-8-thioquinoline coordination polymer,  $[\text{Cu}^{\text{I}}(\text{C}_9\text{H}_6\text{NS})]_n$ , was synthesized by methano-thermal reaction of CuCl and 8,8'-dithiodiquinoline (dtdq) in a molar ratio of 2:1 at 160 °C for 7 d. X-Ray single crystal structure determination revealed the formation of a one-dimensional structure belonging to monoclinic crystal system, space group  $P2_1/c$  with cell parameters  $a = 0.8043(1)$  nm,  $b = 1.8949(3)$  nm,  $c = 1.1048(1)$  nm,  $\beta = 110.109(4)^\circ$ ,  $V = 1.5810(4)$  nm<sup>3</sup> and  $Z = 4$ . The crystal was found to be stable up to approximately 300 °C by thermal analysis and have an energy gap ( $E_g$ ) of 2.0 eV exhibited by UV-Vis-NIR reflectance spectrum.

**Keywords** coordination polymer, cupro-8-thioquinoline complex, synthesis, crystal structure

## Introduction

A variety of functional coordination polymers were synthesized in recent years for their diversified structures<sup>1</sup> and considerable applications in the fields such as catalysis,<sup>2</sup> non-linear optics,<sup>3</sup> molecular magnetic materials<sup>4</sup> and electric conductors.<sup>5</sup> Frameworks of coordination polymers are constructed with metal cations as templating species and polytopic organic ligands as building blocks.

Recently, we found that 8,8'-dithiodiquinoline (dtdq) was decomposed to give 8-thioquinoline under solvo-thermal conditions. The bidentate 8-thioquinoline was released to coordinate to transition metal ion in control from decomposition of 8,8'-dithiodiquinoline which was used as starting reagent in a solvo-thermal reaction. Up to now, no metal-organic coordination polymers containing 8-thiodiquinoline ligand have been reported except for its metal chelates.<sup>6</sup> Herein, studies on synthesis, crystal structure and optical property of a novel cupro-8-thioquinoline coordination polymer,  $[\text{Cu}(\text{C}_9\text{H}_6\text{NS})]_n$ , are described.

## Experimental

### Synthesis

All chemicals and solvents used in the synthesis were of

reagent grade and without further purification.

A mixture of CuCl (0.099 g, 1.0 mmol) and dtdq (0.1602 g, 0.5 mmol) in a molar ratio of 2:1 was placed in a 25-mL Teflon-lined stainless steel Parr bomb containing methanol (11.2 mL) and water (2.8 mL), heated at 160 °C for 7 d, and followed by cooling to room temperature. Deep purplish red crystals were isolated and washed thoroughly with water, ethanol and ether, and air-dried to give the product in 65% yield.

### X-Ray diffraction

The single crystal (0.5 mm × 0.25 mm × 0.10 mm) was selected for X-ray diffraction measurement. Intensity data were collected using a Rigaku R-AXIS RAPID image plate diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm). A total of 13327 reflections were measured, of which 3609 reflections were unique with  $R_{\text{int}} = 0.0689$ , and 2485 observed reflections had  $I > 2\sigma(I)$ , within the limit  $5.40^\circ \leq 2\theta \leq 54.98^\circ$ . The raw data were corrected for Lp factors and empirical absorption. The structure was solved by the direct methods<sup>7</sup> and all non-H atoms were refined anisotropically with full-matrix least-squares on  $F^2$ .<sup>8</sup> H atoms were added at calculated positions on the relevant atoms. Computations were performed using the SHELX-97 program package. Crystal drawings were produced with the SCHAKAL92.<sup>9</sup>

### Thermal analysis

Thermogravimetric analysis for the title compound was performed on a Rigaku TG analyzer. The single-phase (11.50 mg) was loaded into alumina pan and heated in air with a ramp rate of 8 °C/min from room temperature to 500 °C.  $\alpha\text{-Al}_2\text{O}_3$  was selected as the reference.

### Reflectance spectrum

Reflectance spectrum of the crystal was taken on a UV-3100 recording spectrophotometer from 250 nm to 2500 nm.

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Specimen was prepared by the reported method.<sup>10</sup>

## Results and discussion

### Description of the crystal structure

$[\text{Cu}^{\text{I}}(\text{C}_9\text{H}_6\text{NS})]_n$  crystallized in the monoclinic crystal

system, space group  $P2_1/c$  with the cell parameters,  $a = 0.8043(1)$  nm,  $b = 1.8949(3)$  nm,  $c = 1.1048(1)$  nm,  $\beta = 110.109(4)^\circ$ ,  $V = 1.5810(4)$  nm<sup>3</sup> and  $Z = 4$ . The crystallographic data, atomic coordinates, and selected bond lengths and angles are listed in Tables 1, 2 and 3, respectively.

**Table 1** Crystal data and structure refinement

Empirical formula	$\text{C}_{18}\text{H}_{12}\text{Cu}_2\text{N}_2\text{S}_2$
Formula weight	447.50
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 0.8043(1)$ nm, $b = 1.8949(3)$ nm, $c = 1.1048(1)$ nm, $\beta = 110.109(4)^\circ$
Volume	$1.5810(4)$ nm <sup>3</sup>
$Z$ , Calculated density	4, 1.880 Mg/m <sup>3</sup>
Absorption coefficient	$2.954$ mm <sup>-1</sup>
$F(000)$	896
Crystal size	$0.50$ mm $\times$ $0.25$ mm $\times$ $0.10$ mm
$\theta$ range for data collection	$2.70^\circ$ to $27.49^\circ$
Index ranges	$-10 \leq h \leq 9$ , $-24 \leq k \leq 24$ , $-14 \leq l \leq 14$
Reflections collected/unique	13327/3609 [ $R_{\text{int}} = 0.0689$ ]
Completeness to $2\theta = 27.49^\circ$	96.1%
Absorption correction	Empirical
Max. and min. transmission	0.7442 and 0.3353
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3609/0/217
Goodness-of-fit on $F^2$	0.951
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0387$ , $wR_2 = 0.0912$
[all data]	$R_1 = 0.0639$ , $wR_2 = 0.1001$
Largest diff. peak and hole	758 and $-735$ e/nm <sup>3</sup>

**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $10^5$  nm<sup>2</sup>)

Atom	$x$	$y$	$z$	$U_{\text{eq}}$	Atom	$x$	$y$	$z$	$U_{\text{eq}}^a$
Cu(1)	3731(1)	5531(1)	4751(1)	46(1)	C(7)	6108(6)	7201(2)	7488(4)	63(1)
Cu(2)	1552(1)	4880(1)	5914(1)	48(1)	C(8)	5810(5)	6648(2)	6586(3)	48(1)
S(1)	766(1)	5820(1)	4136(1)	40(1)	C(9)	2762(4)	6787(2)	5950(3)	39(1)
S(2)	4478(1)	4549(1)	6433(1)	38(1)	C(11)	5313(4)	5087(2)	7820(3)	34(1)
N(1)	4214(3)	6440(1)	5849(2)	38(1)	C(12)	7112(4)	5125(2)	8510(3)	46(1)
N(2)	2346(3)	5460(1)	7576(3)	36(1)	C(13)	7757(5)	5525(2)	9645(4)	57(1)
C(1)	1029(4)	6554(2)	5172(3)	39(1)	C(14)	6649(6)	5890(2)	10099(4)	56(1)
C(2)	$-407(5)$	6908(2)	5275(4)	55(1)	C(15)	4804(5)	5885(2)	9411(3)	44(1)
C(3)	$-171(6)$	7484(2)	6133(5)	71(1)	C(16)	3590(6)	6278(2)	9812(4)	57(1)
C(4)	1436(7)	7708(2)	6889(4)	69(1)	C(17)	1833(6)	6252(2)	9096(4)	58(1)
C(5)	2968(5)	7359(2)	6826(3)	50(1)	C(18)	1268(5)	5838(2)	7993(3)	48(1)
C(6)	4705(6)	7542(2)	7605(3)	63(1)	C(19)	4127(4)	5479(2)	8269(3)	34(1)

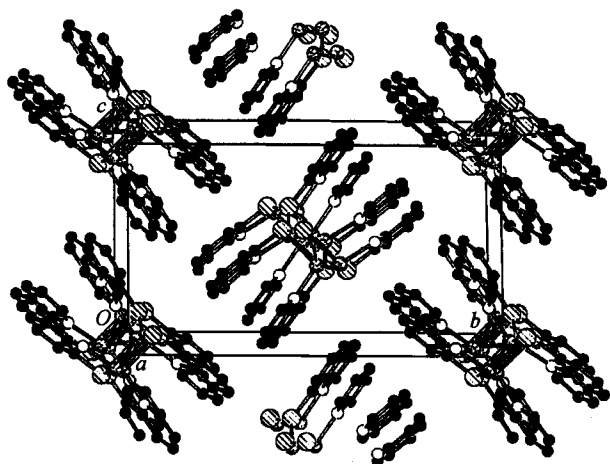
<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 3** Selected bond lengths (nm) and angles ( $^{\circ}$ )

Cu(1)—N(1)	0.2066(3)	S(2)—Cu(1)—Cu(2)	97.07(3)
Cu(1)—S(2a)	0.22590(10)	Cu(1a)—Cu(1)—Cu(2)	50.95(3)
Cu(1)—S(1)	0.23100(11)	N(2)—Cu(2)—S(1b)	109.63(8)
Cu(1)—S(2)	0.25507(10)	N(2)—Cu(2)—S(2)	86.93(8)
Cu(1)—Cu(1a)	0.27830(10)	S(1b)—Cu(2)—S(2)	127.27(4)
Cu(1)—Cu(2)	0.27922(8)	N(2)—Cu(2)—S(1)	103.47(8)
Cu(2)—N(2)	0.2045(3)	S(1b)—Cu(2)—S(1)	113.70(4)
Cu(2)—S(1b)	0.22721(10)	S(2)—Cu(2)—S(1)	109.89(4)
Cu(2)—S(2)	0.23085(11)	N(2)—Cu(2)—Cu(2b)	120.81(8)
Cu(2)—S(1)	0.25647(10)	S(1b)—Cu(2)—Cu(2b)	62.14(3)
Cu(2)—Cu(2b)	0.26563(13)	S(2)—Cu(2)—Cu(2b)	147.83(4)
S(1)—C(1)	0.1769(3)	S(1)—Cu(2)—Cu(2b)	51.56(3)
S(1)—Cu(2b)	0.22721(10)	N(2)—Cu(2)—Cu(1)	97.12(7)
S(2)—C(11)	0.1770(3)	S(1b)—Cu(2)—Cu(1)	152.38(3)
S(2)—Cu(1a)	0.22590(10)	S(2)—Cu(2)—Cu(1)	59.10(3)
		S(1)—Cu(2)—Cu(1)	50.87(3)
N(1)—Cu(1)—S(2a)	111.57(7)	Cu(2b)—Cu(2)—Cu(1)	98.55(3)
N(1)—Cu(1)—S(1)	86.68(8)	C(1)—S(1)—Cu(2b)	112.92(11)
S(2a)—Cu(1)—S(1)	130.19(4)	C(1)—S(1)—Cu(1)	96.56(11)
N(1)—Cu(1)—S(2)	103.34(8)	Cu(2b)—S(1)—Cu(1)	128.66(5)
S(2a)—Cu(1)—S(2)	109.59(3)	C(1)—S(1)—Cu(2)	96.17(10)
S(1)—Cu(1)—S(2)	110.33(4)	Cu(2)—S(1)—Cu(2)	66.30(4)
N(1)—Cu(1)—Cu(1a)	120.65(8)	Cu(1)—S(1)—Cu(2)	69.67(3)
S(2a)—Cu(1)—Cu(1a)	59.71(3)	C(11)—S(2)—Cu(1a)	114.34(10)
S(1)—Cu(1)—Cu(1a)	147.37(4)	C(11)—S(2)—Cu(2)	96.31(11)
S(2)—Cu(1)—Cu(1a)	49.88(3)	Cu(1a)—S(2)—Cu(2)	132.31(4)
N(1)—Cu(1)—Cu(2)	96.84(7)	C(11)—S(2)—Cu(1)	97.78(10)
S(2a)—Cu(1)—Cu(2)	149.64(3)	Cu(1a)—S(2)—Cu(1)	70.41(3)
S(1)—Cu(1)—Cu(2)	59.46(3)	Cu(2)—S(2)—Cu(1)	69.94(3)

Symmetry transformations used to generate equivalent atoms: a:  $(-x+1, -y+1, -z+1)$ ; b:  $(-x, -y+1, -z+1)$ .

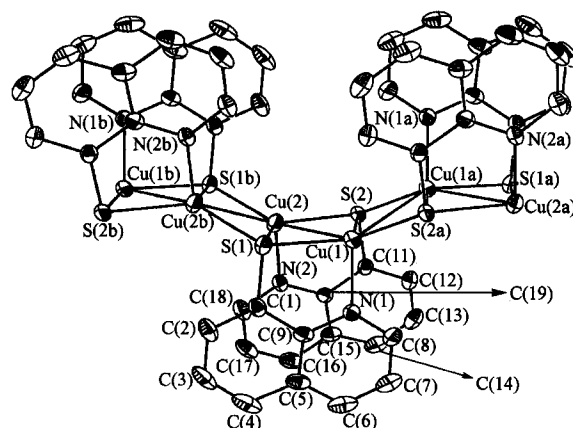
The crystal structure is constructed by packing of  $[\text{Cu}^{\text{I}}(\text{C}_9\text{H}_6\text{NS})]_n$  chains running parallel to the  $a$ -axis as depicted in Fig. 1.



**Fig. 1** Crystal packing view along the  $a$ -axis. The double shaded circles are for Cu, single shaded circles for S, open circles for N, and solid circles for C atoms. The unit cell is outlined.

In the chain, the centers of Cu(1)—Cu(1a) and Cu(2)—Cu(2b) bonds are centers of symmetry. The asym-

metric unit contains two Cu atoms, Cu(1) and Cu(2), and two 8-thioquinoline ligands which are referred to as **L1** and **L2**, respectively. Both Cu(1) and Cu(2) are coordinated by one N and three S atoms in distorted tetrahedral geometry, Cu(1)—N(1)—S(1)—S(2)—S(2a) and Cu(2)—N(2)—S(2)—S(1)—S(1b), respectively, as shown in Fig. 2.



**Fig. 2** ORTEP drawing for  $[\text{Cu}(\text{C}_9\text{H}_6\text{NS})]_n$  with 50% probability ellipsoids, showing the atomic numbering scheme.

Cu(1) is coordinated by **L1** via N(1) and S(1) to form a five-membered ring, Cu(1)—S(1)—C(1)—C(9)—N(1), in

the molecular plane of **L1**. In the same way, Cu(2) forms a five-membered ring, Cu(2)-S(2)-C(11)-C(19)-N(2), with **L2**. Cu-S edges of the two five-membered rings are parallel to each other and bridged through other two Cu-S bonds to construct a parallelogram, Cu(1)-S(1)-Cu(2)-S(2), with the mean bond length 0.2310 nm for Cu(1)-S(1) and Cu(2)-S(2), 0.2555 nm for Cu(1)-S(2) and Cu(2)-S(1), and mean bond angle 110.11° for S(1)-Cu(1)-S(2) and S(2)-Cu(2)-S(1), 69.80° for Cu(1)-S(1)-Cu(2) and Cu(2)-S(2)-Cu(1). **L1** and **L2** are located in the same side of the parallelogram. The dihedral angle between the molecular planes of **L1** and **L2** is approximately 26°.

The asymmetric unit is reversed by the symmetric centers at the centers of Cu(1)-Cu(1a) and Cu(2)-Cu(2b) bonds, respectively, to form a rack-shaped chain extending along the *a*-axis, with **L1** and **L2** ligands standing on two sides of the chain. In the chain, each Cu(1)-S(1)-Cu(2)-S(2) parallelogram is linked to its two adjacent centrically symmetric relatives through Cu(1)-S(2a), S(2)-Cu(1a) bonds to set up a new parallelogram Cu(1)-S(2a)-Cu(1a)-S(2), and through Cu(2)-S(1b), S(1)-Cu(2b) bonds to set up another new parallelogram Cu(2)-S(1b)-Cu(2b)-S(1), respectively. The dihedral angle between Cu(1)-S(1)-Cu(2)-S(2) and each of the two new parallelograms is about 150°.

There is a Cu-Cu bond between the two Cu atoms at trans-corners of each parallelogram with Cu(1)-Cu(2) [0.27922(8) nm] for Cu(1)-S(1)-Cu(2)-S(2), Cu(1)-Cu(1a) [0.27830(10) nm] for Cu(1)-S(2a)-Cu(1a)-S(2) and Cu(2)-Cu(2b) [0.26563(13) nm] for Cu(2)-S(1b)-Cu(2b)-S(1).

The [Cu<sup>I</sup>(C<sub>9</sub>H<sub>6</sub>NS)]<sub>n</sub> chains are packed by molecular interactions along the *b*-axis and *c*-axis to construct the crystal structure (Fig. 1).

#### Optical property and thermal stability

The Kubelka-Munk function (*F*) is converted from the diffuse reflectance data.  $F = (1 - R_{\infty})^2 / 2R_{\infty}$ , where *R*<sub>∞</sub> is the relative diffuse reflectance of an infinitely thick layer.<sup>11</sup>

The *F* function versus the energy were plotted in Fig. 3. The reflectance spectra of the compound display strong absorption in the range from 1.1 eV to 3.2 eV, where a strong absorption in UV-Vis region shows an energy gap (*E<sub>g</sub>*) of about 2.0 eV.<sup>12</sup> The crystal must be a semiconductor with the energy gap resulting from the Cu-Cu bonding. We adopted an empirical and convenient method quantitatively to calculate absorption ability to solar radiation from the diffuse reflectance data for the material.<sup>10</sup> The mean absorp-

tion coefficient  $\epsilon$  to solar radiation equals to 0.0217  $\mu\text{m}^{-1}$ .

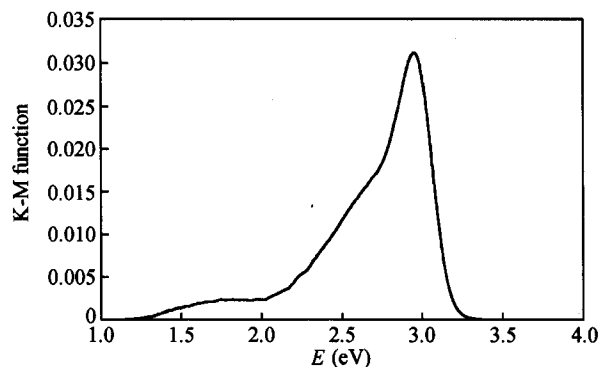


Fig. 3 Plot of K-M function vs. energy (eV) for [Cu<sup>I</sup>(C<sub>9</sub>H<sub>6</sub>NS)]<sub>n</sub>.

The result of thermal analysis indicated that the coordination polymer crystal should be thermally stable up to 300 °C based on the temperature at which the first weight loss occurred in the weight loss curve (W%-°C).

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