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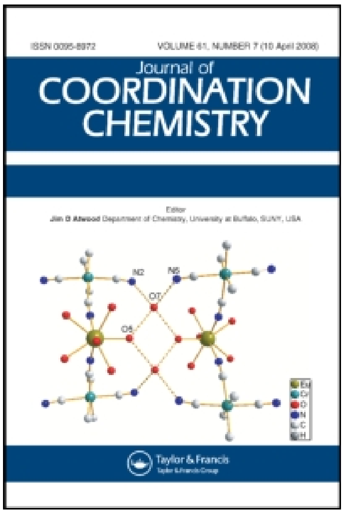

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Linear oxalato- and 4,4'-dipyridyldisulfide-bridged copper(II) coordination polymer involving <i>in situ</i> ligand synthesis

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Linear oxalato- and 4,4′-dipyridyldisulfide-bridged copper(II) coordination polymer involving *in situ* ligand synthesis

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The reaction of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one with $Cu(ClO_4)_2 \cdot 6H_2O$ gave a new complex $\{[Cu_2(4PDS)_2(ox)(H_2O)_4](ClO_4)_2\}_n$ (4PDS = 4,4′-dipyridyldisulfide, ox = oxalate), with 4PDS and ox being created by the Cu(II)-assisted oxidation of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one. The complex determined by X-ray crystallography is a 1D polymer, in which metallacycles formed by two 4PDS and two Cu(II) ions are further bridged through ox anions. It crystallizes in the orthorhombic system, space group *Fddd*, with lattice parameters $a = 15.106(2)$, $b = 23.667(4)$, $c = 27.637(3)$ Å and $Z = 8$.

Keywords: Copper(II) complex; Situ ligand synthesis; Single crystal structure

1. Introduction

Copper complexes with a wide variety of supporting ligands have been exploited in coordination chemistry. Particular attention has focused on the interconversion between disulfides RSSR and corresponding thiolates 2RS – a very important redox process relating to functional materials and many biological systems [1, 2]. Very recently, Itoh's group investigated the mechanism of C–S bond formation between phenolate and disulfide-bridged dicopper(I) complexes, ligand effects on the structures and redox reactivities of copper complexes, and the selective generation of disulfide-dicopper(I) or *bis*(*u*-thiolato)dicopper(II) compounds [3, 4], but interconversion between dithioether and disulfide has rarely been reported. We herein communicate the Cu(II)-assisted situ synthesis of the disulfide ligand 4,4′-dipyridyldisulfide (4PDS) derived from dithioether ligand 1,3-*bis*(pyridyl-4-ylthio)propan-2-one, and the crystal structure of the resultant complex $\{[Cu_2(4PDS)_2(ox)(H_2O)_4](ClO_4)_2\}_n$ (ox = oxalate).

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2. Experimental section

Warning! Although we experienced no problems in handling these perchlorate compounds, they should be treated with great caution due to their potential for explosion.

2.1. *General remarks*

Except for 1,3-*bis*(pyridyl-4-ylthio)propan-2-one being prepared by our previous method [5], all other reagents and solvents were commercially purchased and used as received. Elemental analyses of C, H, N and S were carried out by an Elemental Vario ELIII microanalyzer. IR spectra were recorded on a Magna750 FT–IR spectrophotometer using KBr pellet technique in a range of 4000–400 cm^{-1}.

2.2. *Synthesis of* $\{[Cu_2(4PDS)_2(ox)(H_2O)_4](ClO_4)_2\}_n$

A mixture of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one (0.055 g, 0.2 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.037 g, 0.1 mmol) and acetone (10 mL) immediately gave blue precipitate. IR (KBr): $\nu = 3068$ (w), 2931 (w), 1725 (vs), 1591 (s), 1534 (w), 1486 (s), 1416 (s), 1220 (m), 1110 (s), 1065 (m), 942 (w), 807 (m), 723 (m), 497 (m) cm^{-1}. The precipitate was easily dissolved in 5 mL dimethylformamide, and the resulting green solution swiftly turned dark, concomitant with dark precipitate. After filtration, slow diffusion of diethyl ether (30 mL) into the filtrate for two weeks created yellow green crystals suitable for single-crystal X-ray diffraction (0.015 g, 32%). IR (KBr): $\nu = 3411$ (br), 3097 (w), 1665 (s), 1596 (s), 1549 (s), 1486 (s), 1445 (m), 1420 (s), 1373 (s), 1215 (m), 1152 (m), 1108 (s), 1026 (w), 981 (w), 802 (s), 772 (m), 717 (s), 495 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{24}Cl_2Cu_2N_4O_{16}S_4$ (926.67): C 28.51, H 2.61, N 6.05, S 13.84, found: C 28.60, H 2.71, N 6.17, S, 13.67.

2.3. *Crystallographic measurement*

Single-crystal data were collected on a Rigaku Mercury-CCD diffractometer at 293 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using the CrystalClear program for the area detector [6]. Cell refinement and data reduction were carried out by the CrystalClear package [7]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXTL software suite [8]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions except water molecules. Counterion perchlorate shows severe disorder. A summary of the key crystallographic information is given in table 1, and the selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis and IR spectrum*

The reaction of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one with $Cu(ClO_4)_2 \cdot 6H_2O$ in acetone formed blue precipitate containing 1,3-*bis*(pyridyl-4-ylthio)propan-2-one characterized by IR. However, as further dissolved in dimethylformamide to foster single crystals,

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Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{22}H_{24}Cl_2Cu_2N_4O_{16}S_4$
Formula weight	926.67
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	*Fddd*
a (Å)	15.106(2)
b (Å)	23.667(4)
c (Å)	27.637(3)
V (Å^3)	9880(2)
Z, ρ_{Calcd} (Mg m^{-3})	8, 1.246
μ (Mo-Kα) (mm^{-1})	1.191
Crystal size (mm^3)	0.20 × 0.20 × 0.20
$F(000)$	3744
θ range (°)	3.07–25.03
Reflections collected/unique	13572/1988 (R (int) = 0.0466)
Observed reflections ($I > 2\sigma(I)$)	1694
Goodness-of-fit on F^2	1.175
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0807$, $wR_2 = 0.1991$
R indices (all data)	$R_1 = 0.0942$, $wR_2 = 0.2095$
Largest diff. peak and hole (e Å^{-3})	0.650 and −0.316

Table 2. Selected bond lengths (Å) and angles (°) for the title compound.

Cu1–N1	1.975(4)	Cu1–O1	1.986(4)
Cu1–N1A	1.975(4)	Cu1–O1A	1.986(4)
Cu1–O2	2.435(10)	Cu1–O2A	2.435(10)
N1–Cu1–N1A	94.0(2)	N1A–Cu1–O1A	174.1(2)
N1–Cu1–O1	174.1(2)	O1–Cu1–O1A	83.8(2)
N1A–Cu1–O1	91.18(17)	N1–Cu1–O2A	93.9(2)
N1–Cu1–O1A	91.18(17)	N1A–Cu1–O2A	90.4(2)
O1–Cu1–O2A	88.8(3)	O1–Cu1–O2	86.5(3)
O1A–Cu1–O2A	86.5(3)	O1A–Cu1–O2	88.8(3)
N1–Cu1–O2	90.4(2)	O2A–Cu1–O2	173.7(4)
N1A–Cu1–O2	93.9(2)		

Symmetry transformations used to generate the equivalent atoms A: x, $-y+1/4$, $-z+1/4$.

the green solution swiftly turned dark with dark precipitate. We speculated that a redox reaction occurred with the dissolving process. Through slow diffusion of diethyl ether into the filtrate, luckily, yellow green crystals were obtained.

In the IR spectrum of the resulting crystals, the prominent multiple peaks of 1108, 1026 and 981 cm^{-1} are assigned to free ClO_4^-, while the broad absorption centered at 3411 cm^{-1} indicates the presence of coordinated water [10]. Strangely, the very strong absorption at 1730 cm^{-1} for the carbonyl of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one has not been observed [5, 9], whereas two new strong absorptions centered at 1665 and 1373 cm^{-1}, appear. In combination with elemental and single-crystal structural analysis, the broad and strong absorption at 1665 cm^{-1} and the strong absorption at 1373 cm^{-1} are considered as a superposition of two asymmetric out-of-phase stretching vibrations of the carbonyl groups of the same oxalates and a mode coupling of the symmetric stretching vibrations of the bridging carbonyls with the C–C stretching vibrations, respectively [11]. Accordingly, it suggested that decomposition of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one occurred in dimethylformamide where

1,3-*bis*(pyridyl-4-ylthio)propan-2-one was oxidized into 4,4′-dipyridyldisulfide and oxalate by air. In comparison with stabilization of cobalt(II) compounds of 1,3-*bis*(pyridyl-4-ylthio)propan-2-one in dimethylformamide [5, 9], this redox process was probably assisted by Cu(II).

3.2. *Crystal structure description*

$\{[Cu_2(4PDS)_2(ox)(H_2O)_4](ClO_4)_2\}_n$ determined by single-crystal X-ray diffraction is a 1D polymer with an asymmetric unit consisting of one-half copper(II) ion and 4PDS molecule, one-half perchlorate, one-quarter ox anion and one coordination water (figure 1). Every Cu(II) is ligated by two N atoms from two 4PDS and two O atoms from different carboxyl groups of the same ox anion in the equatorial plane and two water molecules at the axial sites. The bond lengths of Cu–N and Cu–O in the equatorial plane are 1.975(4) and 1.986(4) Å, respectively. However, the Cu–O [2.435(10) Å] distance at the axial sites is considerably longer than in the equatorial plane due to the strong Jahn–Teller effect. Thus the coordination symmetry of Cu(II) is a sharply distorted, axial-elongated octahedron.

4PDS has two enantiomeric conformers and has been extensively used to assemble with transition metals [12–20]. As shown in figure 1, one of each enantiomer bridges two Cu(II) ions to form a meso-metallacycle with dimensions of the internal cavity being 9.9 Å (Cu1–Cu1A distance) and 9.7 Å (S1–S1A distance), slightly different from the previously published rhomboids [12]. In the compound the 4PDS presenting the usual gauche conformation has a dihedral angle of 72.1° between the disulfide units, notably different from idealized dihedral angles (C–SS–C) of 90° observed in the analogues [12–14]. Due to the *bis*-bidentate coordination of ox [10, 21], those metallacycles are further bridged into a 1D charged chain which is very different from the helix and double-stranded chain structures constructed by 4PDS and Cu(II) [12, 13]. Those 1D chains extend along the *a*-axis, and perchlorate anions in the crystal lattice further link the 1D arrays into a hydrogen-bound 3D supramolecule through weak (pyridyl) C–H ··· O hydrogen bonding (seen in figure 2).

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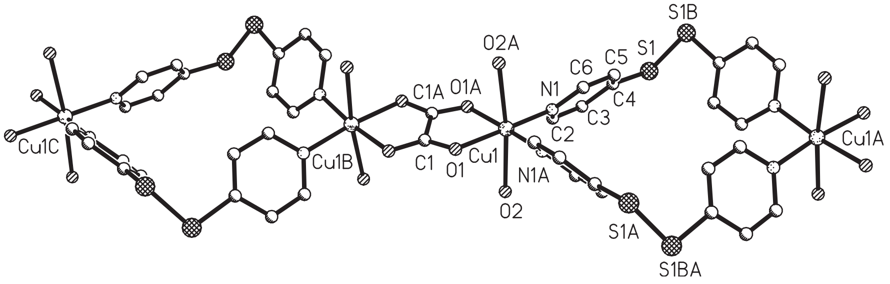

Figure 1. View of a 1D charged chain in the title complex (showing ox-bridged metallacycles formed by two 4PDS and two Cu(II) ions).

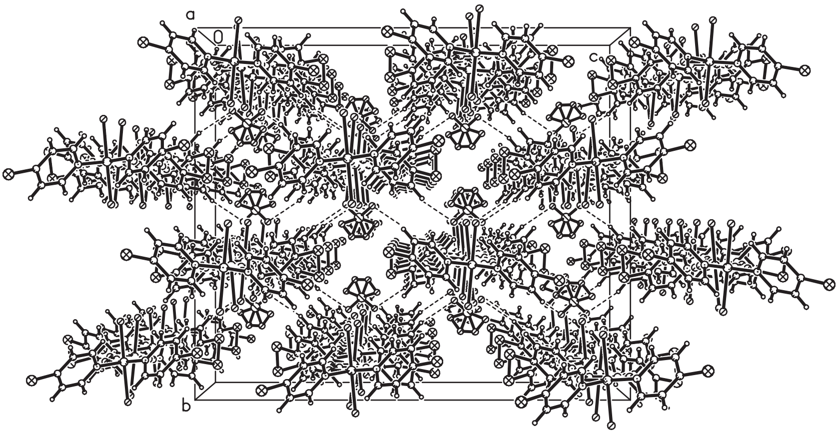

Figure 2. Packing structure of the title compound (showing weak hydrogen bond interactions between perchlorate anions and 1D chains).

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Supplementary data

The crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 602809. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

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