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A Ring-Like Coordination Structure Constructed by Cu(II) and Bis(2-(Pyridin-2-ylthio)ethyl)ether Ligand[1]

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Abstract—The reaction of bis(2-(pyridin-2-ylthio)ethyl)ether (L) with $CuCl_2$ in $CH_3OH/CHCl_3$ solution gives a novel 24-membered ring-like coordination structure which has been characterized by elemental analysis, IR, and X-ray single-crystal diffraction. The X-ray diffraction analysis reveals that $[Cu_2L_2Cl_4]$ crystallizes in the triclinic, space group $P\bar{1}$. The ring-like structure is consisted of two ligands with two copper ions coordinated to the pyridyl nitrogen atoms from two ligands respectively. The largest diameters of the planar-shaped dinuclear ring are about 12.7 Å. The adjacent ring-like units are linked via C—H···O hydrogen bonds to generate an infinite linear chain, which are further linked by C—H···Cl hydrogen bonds and weak intermolecular interactions to form a three-dimensional network.

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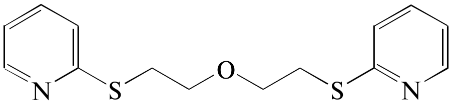
INTRODUCTION

Much attention has been given to the copper complexes for their great importance in bioinorganic chemistry, magnetochemistry, materials chemistry, and solid-state chemistry [1–4]. Ligands containing thioether groups are well established sources for structurally diverse and biologically active supramolecular complexes. Reports on the bioactivities of these kinds of complexes have also increased in recent years, and they show considerable antibacterial, antifungal and pesticide activities [5–7]. Referring to some reported heterocyclic N- and S-ligands [8–10], we designed a series of flexible dithioethyl ligands, like bis(2-(pyridin-2-ylthio)ethyl)ether (L)



Some mono- or multinuclear Ag(I) complexes were obtained using such ligands which showing obvious inhibitory effect toward marine *Phaeodactylum tricornutum* [11]. To further investigate the coordinate mode of L with transition metals, we report herein the synthesis and structure of its Cu(II) complex.

EXPERIMENTAL

Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. L was obtained from the reaction of bis(2-chloroethyl)ether and pyridine-2-thiol with the same procedure as described in our previous paper [11]. The C, H, and N elemental analysis were carried out with an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Vertex 70 spectrometer.

Synthesis of $[Cu_2L_2Cl_4]$. A solution of $CuCl_2 \cdot 2H_2O$ (17.1 mg, 0.1 mmol) in MeOH (1 mL) was added to a solution of L (29.2 mg, 0.1 mmol) in $CHCl_3$ (5 mL) in a 25 mL flask and white powder formed immediately. The yield was 56%. Single crystals suitable for X-ray analysis were obtained by recrystallization the powder from MeOH–$CHCl_3$–DMF. The complex is insoluble in water and slightly soluble in common organic solvents, such as methanol, ethanol, and acetone.

For $C_{28}H_{32}N_4O_2S_4Cl_4Cu_2$			
anal. calcd., %:	C, 39.39;	H, 3.78;	N, 6.56.
Found, %:	C, 39.32;	H, 3.91;	N, 6.43.

IR spectrum (ν, cm^{-1}): 1142 v.s, 1421 v.s, 1455 s, 1589 v.s.

X-ray crystal determination. Single-crystal X-ray diffraction measurements were carried out at 293(2) K using an Oxford Xcalibur S diffractometer with CuK_α radiation (λ = 1.54184 Å). Data collection, integration and scaling of the reflections were performed by means of the CryAlis suite of programs. The structure was solved by direct methods with SHELXS-97 and refined by the full-matrix least-squares method on all F^2 data suing the SHELXL-97 program [12–14]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were added theoretically and riding on the concerned at-

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Table 1. Crystallographic parameters and summary of data collection for $[Cu_2L_2Cl_4]$

Parameter	Value
Formula weight	853.70
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	8.080(2)
b, Å	8.700(2)
c, Å	12.660(3)
α, deg	75.45(3)
β, deg	88.80(3)
γ, deg	76.63(3)
Volume, Å^3	837.4(3)
Z	2
ρ_{calcd}, g/cm^3	1.693
Crystal size, mm	0.25 × 0.21 × 0.17
F(000)	434
μ, mm^{-1}	1.873
θ range for data collection, deg	3.605–72.126
Limiting index ranges	$-7 \le h \le 9$, $-10 \le k \le 10$, $-15 \le l \le 15$
Type of scan	Multi-scan
Reflections collected	3225
Reflections unique (R_{int})	2683 (0.0195)
Parameters	199
S on F^2	1.081
R_1 ($I > 2\sigma(I)$)*	0.0572
wR_2 ($I > 2\sigma(I)$)*	0.1595
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	1.33 and –0.39

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)\ ]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg) for $[Cu_2L_2Cl_4]$

Bond	d, Å	Bond	d, Å
Cl(1)–Cu(1)	2.2836(14)	Cu(1)–N(1)	2.021(3)
Cl(2)–Cu(1)	2.2705(14)	Cu(1)–N(2)	2.028(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
Cl(2)Cu(1)Cl(1)	175.66(4)	N(2)Cu(1)Cl(2)	90.41(9)
N(1)Cu(1)N(2)	171.54(13)	N(1)Cu(1)Cl(1)	91.55(10)
N(1)Cu(1)Cl(2)	87.97(10)	N(2)Cu(1)Cl(1)	90.68(9)

Table 3. Geometric parameters of hydrogen bonds for $[Cu_2L_2Cl_4]$*

Contact D–H···A	Distance, Å			Angle D–H...A, deg
	D–H	H···A	D···A	
C(1)–(1*B*)···O(1)	0.97	2.60	3.536	162
C(6)–(6)···Cl(1)^i	0.93	2.81	3.602	143

* Symmetry code: ^{i} $2 - x, 2 - y, -z$.

oms. Crystallographic data and experimental details for structure analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2. Hydrogen bonding geometric data are listed in Table 3. Supplementary data have been deposited with the Cambridge Crystallographic Data Centre (no. 847615; deposit@ccdc.cam.ac.uk or ttp://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of L with $CuCl_2$ leads to the formation of 24-membered ring-like coordination structure (Fig. 1). In each dinuclear unit, each Cu(II) is coordinated to two pyridyl nitrogen atoms from two ligands respectively and form a planar tetrahedron geometry together with two chloride anions. The bond lengths range from 2.021(3) to 2.2836(14) Å. The bond angles ranging from 87.97(10)° to 175.66(4)°. The distance between Cu···Cu in one dinuclear unit is 12.058 Å. There exists a central symmetry in the complex molecule. The

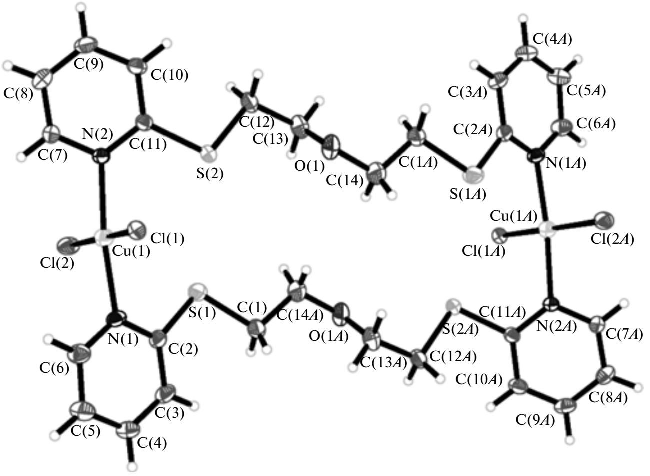

Fig. 1. The structure of [$Cu_2L_2Cl_4$], showing 50% thermal ellipsoids.

Fig. 2. Fragment of the hydrogen bonded 1D chain structure.

adjacent dinuclear units are linked via C–H···O hydrogen bonds to generate an infinite linear chain (Fig. 2), which are further linked by C–H···Cl hydrogen bonds and weak intermolecular interactions to form a three-dimensional network (Fig. 3).

The IR spectrum of free L shows bands at 1122 cm^{-1} which may be assigned to ν(C–O–C). In the IR spectra of the copper complex, the band shift by 20 cm^{-1} towards higher wave numbers, which may be caused by the deformation of the flexible chain or by the hydrogen bond. The larger shifts for ν(C=C), ν(C=N) in the spectra of the complexes exhibit that the nitrogen atom of the pyridine ring coordinate to the copper ion (Fig. 4).

In general, a new Cu(II) complex [$Cu_2L_2Cl_4$] has been successfully synthesized. The dithioethyl ligand adopt bidentate coordination mode to connect two copper ions to form a ring-like structure. A three-dimensional network is linked via strong hydrogen bonds and weak intermolecular interactions.

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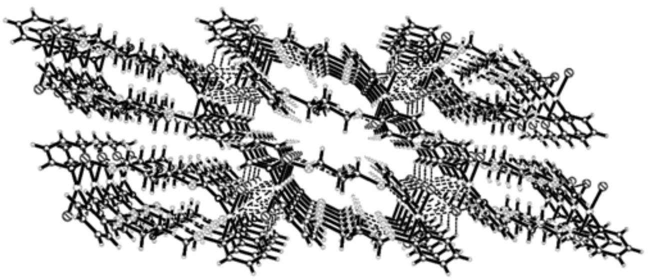

Fig. 3. Fragment of the 3D network.

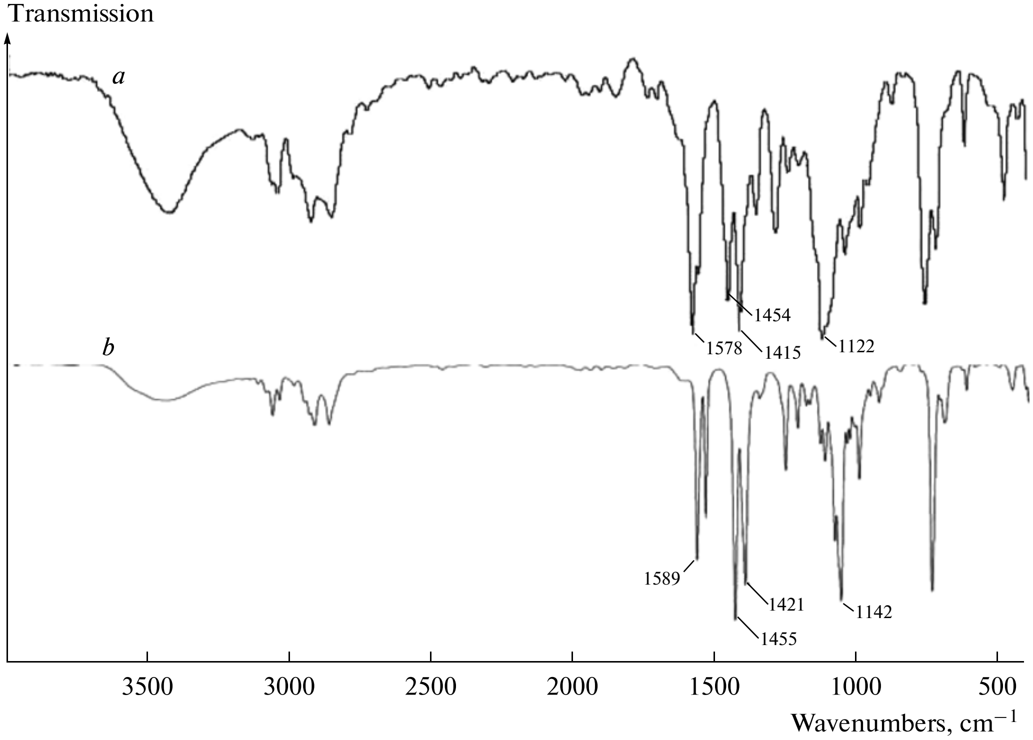

Fig. 4. IR spectrum of free L (*a*) and the complex [$Cu_2L_2Cl_4$] (*b*).

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