Two-Dimensional Coordination Polymer of 3-(Methylthio)-1-thiomorpholinopropan-1-one Propagated by Rhomboid Cu-I₂-Cu Linker

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The reaction of copper(I) iodide with 3-(methylthio)-1-thiomorpholinopropan-1-one (L) as an asymmetric dithia-ligand gave an elegant brick-wall-shaped coordination polymer, [CuIL]_n (**1**). The crystal structure of **1** demonstrates that the rhomboid Cu-I₂-Cu linker plays an essential role in the construction of such a supramolecular framework.

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The design and synthesis of metal-organic frameworks (MOFs) with beneficial properties remain an area of intense interest.¹ In view of the structural and photophysical properties, the chemistry of copper(I) coordination polymers built from amine functional group has been widely studied.² Our interest in coordination chemistry has been mainly on a new type of cyclic^{3,4} and acyclic⁵ ligands with soft donor atoms, since these are expected to exhibit novel coordination properties toward thiophilic metal species, such as silver(I) and copper(I) salts. As an extension of our programs, we are currently working on the synthesis of a novel sulfur-containing ligand system involving 3-(methylthio)-1-thiomorpholinopropan-1-one (L) as an asymmetric building block. Herein, we report on the preparation and crystal structure of the MOF assembled from L and copper(I) iodide.

The ligand L was synthesized by the chlorination of 3-methylthiopropionic acid with SOCl₂, followed by a reaction with thiomorpholine in the presence of triethylamine. The synthetic procedure will be presented elsewhere. An equimolar amount of copper(I) iodide and L was dissolved in acetonitrile. Vapor diffusion of diethyl ether into the acetonitrile solution of the reactants afforded a colorless X-ray quality crystalline product **1**. The crystal and experimental data are given in Table 1. The structure was solved by direct methods and refined with anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms were located from difference Fourier maps and were not refined. The atomic coordinates for non-hydrogen

atoms are listed in Table 2. The selected bond distances and bond angles are summarized in Table 3. The molecular structure with the atomic numbering is given in Fig. 2.

X-ray analysis revealed that the framework of the gross geometry of **1** can be described as an infinite brick-wall with Cu-I₂-Cu nodes, whose geometry resembles rhomboid with alternating vertices of copper(I) and iodide atoms. The asymmetric unit contains one molecule of L, one copper(I) and one iodide ions (Fig. 2). The framework contains four ligands bridged by the Cu-I₂-Cu linker, alternately resulting in an elongated rectangle. The copper(I) coordination sphere has a distorted tetrahedral shape, with “tetrahedral” angles falling in the range of 94.59(7)–124.17(7)°. The bond distances from copper to sulfur atoms [Cu-S1 2.320(2) and Cu-S2 2.345(2) Å] are reasonably similar and compare well to those found in other copper(I)-thiaether complexes.³ In the crystal lattice, no solvent molecule was observed inside and outside of the cavity. The 2-

Fig. 1 Chemical structure of [CuIL]_n (**1**).

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Table 1 Crystal and experimental data

Formula	C ₈ H ₁₅ NOS ₂ CuI
Formula weight	395.77
Temperature	173(2)K
Crystal system	monoclinic
Space group	P2 ₁ /c
Z	4
a	8.1449(9) Å
b	10.6519(11) Å
c	14.6161(15) Å
β	90.107(2)°
V	1268.1(2) Å ³
D _x	2.073 g/cm ³
2θ _{max}	56.56°
R	0.0673
wR	0.1025
No. of reflections used	2983
Diffractionmeter	Bruker SMART CCD system
Structure determination	SHELXTL
Refinement	full-matrix

CCDC 615567 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data/request/cif.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
I(1)	2170(1)	4491(1)	845(1)	24(1)
Cu(1)	340(1)	6332(1)	96(1)	25(1)
S(1)	1946(3)	7612(2)	-823(1)	21(1)
S(2)	10121(3)	7513(2)	-3544(2)	25(1)
O(1)	4538(8)	5441(6)	-3078(4)	30(2)
N(1)	6331(8)	7022(6)	-3385(5)	19(2)
C(1)	3634(10)	8005(9)	-91(6)	29(2)
C(2)	2992(10)	6614(8)	-1644(6)	21(2)
C(3)	4202(10)	7350(8)	-2227(5)	21(2)
C(4)	5031(10)	6507(8)	-2923(6)	20(2)
C(5)	7264(10)	6257(8)	-4027(6)	22(2)
C(6)	9000(11)	6064(8)	-3696(6)	26(2)
C(7)	8620(11)	8306(9)	-2833(6)	26(2)
C(8)	6924(10)	8302(8)	-3262(6)	22(2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

Table 3 Selected bond distances ($\text{\AA}$) and bond angles ($^\circ$)

I(1)-Cu(1) ⁱ	2.6126(13)	Cu(1)-S(2) ⁱⁱ	2.345(2)
I(1)-Cu(1)	2.6943(13)	Cu(1)-I(1) ^j	2.6126(13)
Cu(1)-S(1)	2.320(2)		
Cu(1) ⁱ -I(1)-Cu(1)	66.32(4)	I(1) ^j -Cu(1)-I(1)	113.68(4)
S(1)-Cu(1)-S(2) ⁱⁱ	103.04(9)	C(1)-S(1)-Cu(1)	103.0(3)
S(1)-Cu(1)-I(1) ^j	109.51(7)	C(2)-S(1)-Cu(1)	107.7(3)
S(2) ⁱⁱ -Cu(1)-I(1) ^j	124.17(7)	C(6)-S(2)-Cu(1) ⁱⁱⁱ	112.5(3)
S(1)-Cu(1)-I(1)	110.56(7)	C(7)-S(2)-Cu(1) ⁱⁱⁱ	107.1(3)
S(2) ⁱⁱ -Cu(1)-I(1)	94.59(7)		

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x - 1, -y + 3/2, z + 1/2$; (iii) $x + 1, -y + 3/2, z - 1/2$.

D layers are repeatedly packed and no significant interaction between adjacent layers was observed. A thermogravimetric analysis (TGA) curve shows that **1** is stable until *ca.* 170°C, and undergoes a gradual loss of 50.2% (calcd: 51.9%), corresponding to the ligand in the temperature range 180–300°C.

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Fig. 2 Crystal structure of **1**, showing a basic rectangular unit $[\text{L}_4(\text{Cu}-\text{I}_2-\text{Cu})_4]$ of the 2-D network. Fig. 3 Perspective drawing of the packing arrangement along the *a*-axis, showing a brick-wall type 2-D network.

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