Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A twofold parallel interpenetration network from the assembly of a flexible spacer and CuI: poly[μ-iodido-μ-4,4′-(methylenedithio)dipyridine-κ^2N:N'-copper(I)]

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Received 5 November 2007
Accepted 30 November 2007
Online 12 January 2008

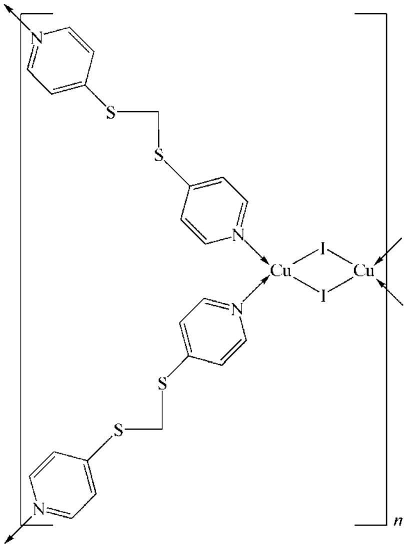
The title compound, $[\mathrm{CuI}(\mathrm{C}_{11}\mathrm{H}_{10}\mathrm{N}_2\mathrm{S}_2)]_n$, is built around centrosymmetric dinuclear $\mathrm{Cu}_2\mathrm{I}_2$ cores, each of which is linked to four neighboring $\mathrm{Cu}_2\mathrm{I}_2$ units *via* flexible dithioether ligands, *viz*. 4,4′-(methylenedithio)dipyridine, to form a two-dimensional grid containing rhombus-shaped cavities with diagonal distances of *ca* 15 and 22 Å. Two of these networks interpenetrate in a woven fashion, and the resulting structure does not possess any open channels or cavities. Each Cu atom is in a distorted tetrahedral coordination environment.

Comment

Recently, there has been much interest in the use of flexible bridging ligands in the construction of supramolecular architectures (Blake *et al.*, 1995; Bu *et al.*, 2002; Jaya Prakash & Radhakrishnan, 2006; Li *et al.*, 2003; Tong *et al.*, 1999; Wu *et al.*, 2006; Zhang *et al.*, 2006), because such ligands encode more variable chemical information, such as conformational freedom. These studies have shown that the nature of the anions, the terminal groups and the spacer length of potentially bridging ligands play fundamental roles in determining the structural types of the final assemblies.

Heterocyclic flexible thioethers containing N- and S-atom donors are well established ligands in coordination and metallosupramolecular chemistry. N and S atoms in such ligands have different donor properties which influence their abilities to coordinate to metal centers (Sharma *et al.*, 1998; Su *et al.*, 1999; Yang *et al.*, 1997). These properties, together with the relative numbers and orientations of the donor atoms, may give rise to interesting coordination architectures.

Previously, 2-pyridyl and 2-pyrimidinyl dithioether ligands with flexible spacers (alkane or arene) have been used successfully to construct metal complexes that exhibit various structures, including discrete molecules, and one- and two-dimensional coordination polymers (Bu *et al.*, 2003; Hong *et al.*, 2000; Peng *et al.*, 2006; Song *et al.*, 2003; Wang *et al.*, 2001; Xie & Bu, 2003; Xie, Du *et al.*, 2004; Xie, Zhang *et al.*, 2004; Xie *et al.*, 2005; Zheng *et al.*, 2003, 2005). However, complexes involving the 4,4′-(methylenedithio)dipyridine ligand are still comparatively rare (Amoedo-Portela *et al.*, 2005). We report here the crystal structure of the novel two-dimensional title Cu^{I} complex, (I).



(I)

Each Cu^{I} center in the title complex is four-coordinated by two N atoms from two different dithioether ligands and two iodide ligands (Table 1). The iodide ligand bridges, slightly asymmetrically, two Cu^{I} centers to give a doubly-bridged dinuclear centrosymmetric $\mathrm{Cu}_2\mathrm{I}_2$ unit. Each $\mathrm{Cu}_2\mathrm{I}_2$ core is connected by four ditopic 4,4′-(methylenedithio)dipyridine ligands to four neighboring $\mathrm{Cu}_2\mathrm{I}_2$ units, which generates a rhombus-shaped two-dimensional grid containing 52-membered metallocycles composed of four dithioether ligands, six Cu^{I} centers and two iodide ligands (Fig. 1). The grid lies parallel to the (100) plane. The metallocyclic cavities are so large that a second layer weaves through the first to form a two-dimensional parallel interpenetration network (Fig. 2). Weak intermolecular C—H$\cdots$I interactions (Table 2) exist between the two interpenetrating networks. The extent of interpenetration in this complex fills all the available voids, so no small molecules or solvent molecules are encapsulated.

The structures of the dichloro and dibromo Cu^{I} complexes with the same organic ligand as (I) have been reported by Amoedo-Portela *et al.* (2005). Those complexes are isostructural with one another, but not with (I), even though all three crystallize in the same space group and their unit-cell dimensions are similar. All three structures exhibit the same style of two-dimensional interpenetration networks, but the $\mathrm{Cu}_2\mathrm{I}_2$ cores present in (I) are replaced by mononuclear $\mathrm{Cu}X_2$ cores with terminal halide (X) ligands in the dichloro and dibromo complexes.

The topology of the two-dimensional network in (I) is also similar to the previously reported coordination polymer of

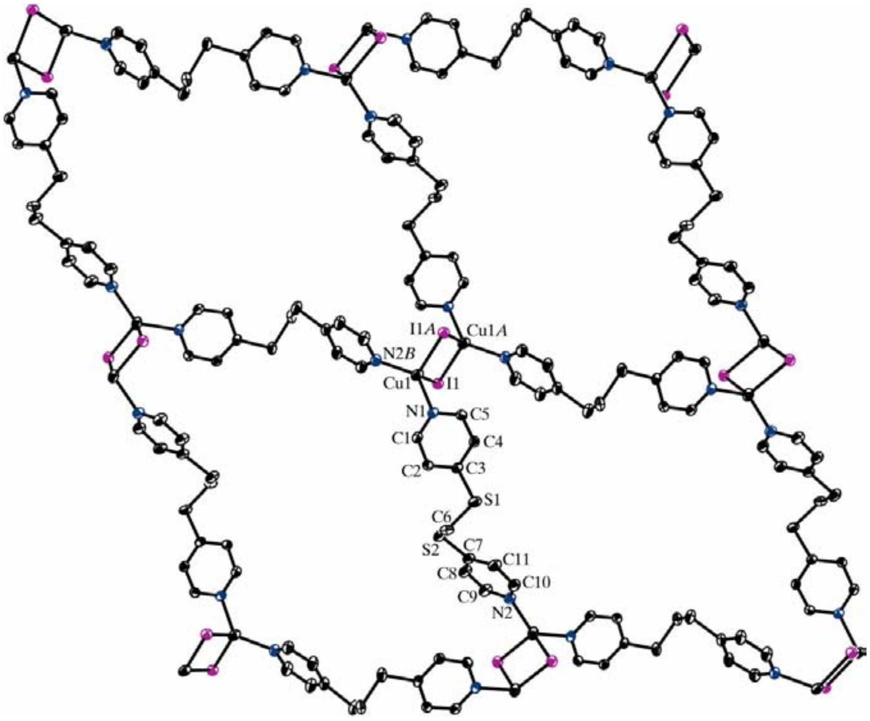


Figure 1
A section of the two-dimensional planar sheet structure of the title complex, with displacement ellipsoids drawn at the 30% probability level and H atoms omitted for clarity. [Symmetry codes: (A) $-x + 2, -y + 1, -z + 1$; (B) $-x + 2, y + 1, -z + \frac{1}{2}$.]

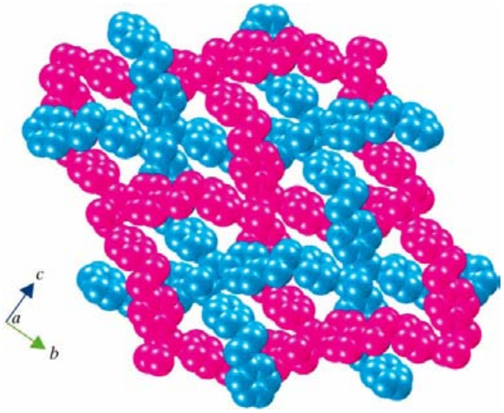


Figure 2
The packing of the twofold parallel interpenetrating sheets in the title complex.

$[Cu_2Br_2(bpe)_2]_n$ (bpe is 1,2-di-4-pyridylethane; Hu *et al.*, 2006), which contains 48-membered metallocycles. However, there is a significant difference in the way the networks interweave. In $[Cu_2Br_2(bpe)_2]_n$, two independent sets of two-dimensional square grids running in almost perpendicular directions interpenetrate to form a three-dimensional network. In (I), parallel networks interweave and these layers then stack upon one another. The ligand 1,3-bis(4-pyridyl)propane (bpp) is an analogue of 4,4′-(methylenedithio)dipyridine, but in the complex $[Cu_2Br_2(bpp)_2]_n$, the Cu_2Br_2 cores are linked by bpp ligands in two different conformations (*trans–trans* and *trans–gauche*) to form a one-dimensional double-stranded tubular chain. Such results reveal that flexible bridging ligands play fundamental roles in determining the structural topologies of their metal–organic architectures.

The dithioether ligand in (I) adopts a *trans–gauche* conformation, where the dihedral angle between the two pyridyl rings is 69.67 (11)°; this is comparable to that in the related $[CuX_2(C_{11}H_{10}N_2S_2)_2]_n$ (X = Cl and Br) analogues (Amoedo-Portela *et al.*, 2005). The torsion angles C3—S1—C6—S2 and C11—S2—C6—S1 are 70.2 (2) and 80.8 (2)°, respectively, which are about 10° larger than the corresponding torsion angles in the $[CuX_2(C_{11}H_{10}N_2S_2)_2]_n$ complexes.

Experimental

4,4′-(Methylenedithio)dipyridine was synthesized according to a reported procedure (Xu *et al.*, 1997). Equimolar quantities (0.025 mmol) of CuI (5.0 mg), 4,4′-(methylenedithio)dipyridine (6.1 mg) and acetonitrile (10 ml) in a 23 ml Teflon reactor were heated to 428 K for 3 d and then cooled to room temperature at a rate of 0.1 K min^{-1}. The precipitate was filtered off and the filtrate allowed to stand at room temperature for one week, after which time well shaped yellow crystals were obtained (m.p. 482 K; yield 2.1 mg, 20%).

Crystal data

$[CuI(C_{11}H_{10}N_2S_2)]$
$M_r = 424.77$
Monoclinic, $C2/c$
$a = 13.6695\ (9)$ Å
$b = 11.5996\ (8)$ Å
$c = 17.1524\ (12)$ Å
$\beta = 93.673\ (1)°$

$V = 2714.1\ (3)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 4.17\ mm^{-1}$
$T = 295\ (2)$ K
0.34 × 0.24 × 0.20 mm

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Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min} = 0.331$, $T_{\max} = 0.489$ (expected range = 0.294–0.434)
7375 measured reflections
2594 independent reflections
2362 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.056$
$S = 1.02$
2594 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.030 (2)	Cu1—I1$^{\text{ii}}$	2.7138 (5)
Cu1—N2$^{\text{i}}$	2.021 (2)	Cu1···Cu1$^{\text{ii}}$	2.7860 (9)
Cu1—I1	2.7737 (5)		
I1—Cu1—I1$^{\text{ii}}$	118.990 (17)	N2$^{\text{i}}$—Cu1—I1	103.84 (7)
N1—Cu1—I1	97.67 (6)	N2$^{\text{i}}$—Cu1—I1$^{\text{ii}}$	105.21 (7)
N1—Cu1—I1$^{\text{ii}}$	101.03 (7)	Cu1—I1—Cu1$^{\text{ii}}$	61.010 (17)
N1—Cu1—N2$^{\text{i}}$	131.66 (10)		

Symmetry codes: (i) $-x+2, y+1, -z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$.

Table 2
C—H···I interaction geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···I1$^{\text{iii}}$	0.93	3.15	3.922 (3)	142

Symmetry code: (iii) $-x+2, y, -z+\frac{1}{2}$.

H atoms were placed at calculated positions, with C—H distances of 0.93 (aromatic) or 0.97 Å (methylene), and refined as riding [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL7* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXTL*.

We thank Jiangxi Science and Technology Normal University for supporting this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3073). Services for accessing these data are described at the back of the journal.

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