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Crystal structure of the two-dimensional coordination polymer catena-bis-(μ_2 -bromo)-bis-(μ_2 -tetra-hydro-thio-phenes)-dicopper(I)

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Abstract

The polymeric title compound **CP1**, $C_8H_{16}Br_2Cu_2S_2 [Cu(\mu_2-Br)_2Cu](\mu_2-C_4H_8S)]_n$, represents an example of a two-dimensional coordination polymer resulting from reaction of CuBr with tetra-hydro-thio-phenes (THT) in MeCN solution. The 2D layers consist of two different types of rhomboid-shaped dinuclear $Cu(\mu_2-Br)_2Cu$ Secondary Building Units (SBUs); one with a quite loose $Cu \cdots Cu$ separation of 3.3348 (10) Å and a second one with a much closer inter-metallic contact of 2.9044 (9) Å. These SBUs are inter-connected through bridging THT ligands, in which the S atom acts as a 4-electron donor bridging each $Cu(\mu_2-Br)_2Cu$ unit in a μ_2 -bonding mode. In the crystal, the layers are linked by very weak $C-H \cdots Br$ hydrogen bonds with $H \cdots Br$ distances of 2.95 Å, thus giving rise to a three-dimensional supra-molecular network.

1. Chemical context

The five-membered heterocyclic ligand tetra-hydro-thio-phenes (THT) is known to form a great variety of molecular complexes and coordination polymers (CPs) with various transition metals. Also for the soft coinage metal ions Cu(I), Ag(I) and Au(I), numerous structurally characterized examples coordinated by terminal or bridging THT ligands are documented (Uson *et al.*, 1984; Noren & Oskarsson, 1985; Mälger *et al.*, 1992; Ahrlund *et al.*, 1993; Lopez-de-Luzuriaga *et al.*, 1997; Ahrens & Jones, 2000). The research group of Pike has shown that depending on the reaction conditions, the treatment of CuI with THT affords dinuclear $[(THT)_2Cu(\mu_2-I)_2Cu(THT)_2]$, the tetra-nuclear closed cubane-type cluster $[(Cu_4(\mu_3-I)_4(THT)_4)]$ or $[(CuI)_{10}(THT)_7(MeCN)]_n$ which contains the mixed motive $[(Cu_4I_4(THT))](\mu_2-THT)_2(Cu_2I_2)(\mu_2-THT)_2[Cu_4I_4(THT)]$ held together side-by-side by two μ_2 -THT assembling ligands to form a 1D ladder structure. Furthermore, the two-dimensional CP

$[(\text{CuI})_3(\text{THT})_3 \cdot \text{MeCN}]_n$ featuring a sheet structure in which $\text{Cu}_3(\text{THT})$ rings are linked in trigonal directions by rhomboid Cu_2I_2 dimers is literature-known. The luminescent product $[(\text{CuI})_4(\text{THT})_2]_n$ consisting of Cu_4I_4 cubane units knit into a 3D network by μ_2 -THT ligands is also known (Noren & Oskarsson, 1987; Henline *et al.*, 2014). A series of solvent-dependent 2D polymers results from treatment of $[\text{Cu}(\text{CO})\text{Cl}]_n$ with THT in THF, CH_2Cl_2 and DMF, exhibiting the composition $[(\text{CuCl})(\text{THT})]_n$ (THF), $[(\text{CuCl})(\text{THT})]_n$ (CH_2Cl_2), and $[(\text{CuCl})_3(\text{THT})_2]_n$ (DMF), respectively. The materials obtained in THF and CH_2Cl_2 are polymorphs (Solari *et al.*, 1996). A mono-dimensional ribbon $[(\text{CuCl})_2(\text{THT})_3]_n$ is generated by reaction of CuCl in neat THT (Mälger *et al.*, 1992). Even mixed-valence Cu(I)/Cu(II) compounds such as polymeric penta- μ -chloro-tris- μ -tetra-hydro-thio-phen-ene-tetra-copper(I,II) have been prepared (Ainscough *et al.*, 1985). Mälger *et al.* also showed that the treatment of CuBr in neat THT leads to the formation of a very labile rhomboid-based 1D polymer of the type $[(\text{CuBr})_2(\text{THT})_3]_n$ isostructural with its $[(\text{CuCl})_2(\text{THT})_3]_n$ analogue (Mälger *et al.*, 1992) (CSD JUDKOI). In the context of our research interest in the assembly of molecular cluster compounds and coordination polymers by complexation of di-alkyl sulfides $\text{R}-\text{S}-\text{R}$ or di-thiol-ane- and di-thiane-based thia-heterocycles on CuX salts (Knorr *et al.*, 2010; Lapprand *et al.*, 2013; Knorr *et al.*, 2016; Raghuvanshi *et al.*, 2017, 2019; Schlachter *et al.*, 2018; Knauer *et al.*, 2020), we have also investigated the complexation of THT on CuBr in aceto-nitrile as solvent (Scheme 1) and present here the crystal structure, which differs both in composition and dimensionality (two-dimensional *vs.* mono-dimensional) from the CP $[(\text{CuBr})_2(\text{THT})_3]_n$ reported by Mälger. Note that this colorless material crystallises easily in form of large well-shaped crystals which are stable in a THT-saturated environment, but decomposes rapidly by dissociation of volatile THT upon exposure to air.

2. Structural commentary

The crystal structure of **CP1** of composition $[(\text{CuBr})_2(\text{THT})_2]_n$ is built of $\text{Cu}(\mu_2\text{-Br})_2\text{Cu}$ rhomboids as SBUs and tetra-hydro-thio-phen ligands. The asymmetric unit contains two independent planar Cu_2Br_2 units placed over the symmetry centers at $1/2, 0, 0$ (Cu1Br1)₂ and $1, 0, 1/2$ (Cu2Br2)₂. They are connected through the sulfur atoms of thio-phen ligands acting, like in all bridging mono-thio-ethers, as 4-electron donors. (Fig. 1) The bridging S1 atoms develop the chains of alternating (Cu1Br1)₂ and (Cu2Br2)₂ SBUs parallel to one diagonal $[-1\ 0\ 1]$ direction of the *a0c* face of the unit cell (labelled on Fig. 2 from Cu2*h* to Cu2*i*), whereas the S2 atoms develop the analogous chains labelled from Cu2*e* to Cu2*f* parallel to the second diagonal $[1\ 0\ 1]$ direction of this face. The thus formed 2D layers lie over the $(0\ 1\ 0)$ planes (Fig. 2). This is the essential difference with the 1D polymer $[(\text{CuBr})_2(\text{THT})_3]_n$ described by Mälger (Mälger *et al.*, 1992) in which only one THT molecule acts as a bridging ligand, developing a chain in one direction, whereas the two other THT molecules are terminal. The outstanding feature of the structure of **CP1**

consists of largely different (0.43 Å) Cu⋯Cu distances in (Cu1Br1)₂ and (Cu2Br2)₂ units (3.3348 (10) Å vs. 2.9044 (9) Å) yet in similar chemical surroundings. Contrary to these metal—metal separations, the Cu—Br and Cu—S bond lengths are similar in both rhomboids. In the 1D polymer of Mälger, the Cu—Cu distance of 2.7784 (7) Å is significantly shorter than in **CP1**. Note that the presence of two independent Cu₂Br₂ SBUs has been also reported for the structure of Cu₂Br₂(1,4-oxa-thiane)₂ but the difference of the Cu—Cu distances therein is equal only to 0.12 Å (2.740 (3) Å vs. 2.865 (4) Å) (Barnes & Paton, 1982; CSD BOTIA). This difference is still smaller in two other CPs with different Cu₂Br₂ SBUs: [{Cu(μ₂-Br)₂Cu}{μ-PhS(CH₂)₃SPh}₂]_n (dCu⋯Cu 2.794 (1) and 2.776 (1) Å) (Knorr *et al.*, 2012; CSD ZEHREL) and in [{Cu(μ₂-Br)₂Cu}{μ-p-MeC₆H₄SCCH₂C≡CCH₂SC₆H₄Me-p}]_n dCu⋯Cu 2.9306 (14) and 2.9662 (14) Å) (Bonnot *et al.*, 2015; CSD QUPXOQ). These observations indicate a high flexibility of the Cu₂Br₂ units. It is worth noting that the Cu—Cu distances in coordination polymers containing di-bromo-dicopper units and bridging mono-thio-ethers were observed in the range from 2.740 (3) Å in Cu₂Br₂(1,4-oxa-thiane)₂ (Barnes & Paton, 1982) to 3.074 (1) Å at 115 K in [(Cu₂Br₂)(Cu₄Br₄)(SMeEt)₆]_n (Knorr *et al.*, 2010). Thus the Cu1—Cu1 distance of 3.3348 (10) Å in **CP1** is the longest one observed in Cu₂Br₂ CP's with bridging mono-thio-ethers. The coordination polyhedra of Cu1 and Cu2 atoms are best described as distorted tetra-hedral despite the values of four-coordinate geometry τ₄ indexes of Yang (Yang *et al.*, 2007) equal to 0.88 that argue for a trigonal pyramidal one (theoretical values are equal to 0.85 for C_{3v} and 1.0 for T_d symmetries). On the other hand, the tetra-hedral character THC_{DA} parameters of Höpfl (0.66 for Cu1 and 0.60 for Cu2) are closer to the tetra-hedral (THC = 1.0) than pyramidal (THC = 0) geometries (Höpfl, 1999). Moreover, the sums of all six bond angles around Cu1 (656.7°) and Cu2 (656.1°) are very close to the value expected for T_d symmetry (657°) and far from that of 630° in an ideal trigonal pyramidal geometry.

3. Supra-molecular features

The layers are built through dative Cu—S coordination bonds. There are also weak non-covalent CH⋯HC (d(H1A⋯H8AA) 2.36 Å) Van der Waals contacts and C—H⋯Br (d(Br2⋯H4B) 2.90 Å; d(Br2⋯H5B) 2.89 Å) hydrogen bonds within the layers (Fig. 3 and Supplementary Table). More inter-estingly, the inter-layer connectivity for building of a supra-molecular 3D structure is apparently limited only to very weak CH⋯Br hydrogen bonds (Fig. 4). The Br2⋯H7AA distance of 2.95 Å is only by 0.10 Å shorter than the sum of the Van der Waals radii (Bondi, 1964).

4. Database survey

The rich structural diversity of THT-ligated molecular and polymeric copper (I) halide compounds has already been presented in an exhaustive manner in the "Chemical Context" section. The three-dimensional

MOF [tris-(μ_2 -cyano)-tris-(μ_2 -THT)tricopper(I)]_n (CSD ITEZOX) has been isolated upon treatment of CuCN with THT (Dembo *et al.*, 2010). An example for a cationic dinuclear bi-pyridine-bridged complex is (μ -4,4'-bi-pyridine)-bis-(THT)-tetra-kis(tri-phenyl-phosphine)di-copperbis(tetra-fluoro-borate) (CSD MOJWOZ) (Rozman *et al.*, 2014). A molecular organometallic aryl complex (2,6-bis-(2,4,6-triisopropyl-phenyl)-phenyl)-(THT)-copper(I) (CSD DOPMUR) has been structurally characterized (Grosman & Holm, 2009). There is also the tetra-nuclear compound cyclo-(tetra-kis(μ_2 -mesityl-idene)-bis-(THT-copper)dicopper(I)) featuring bridging aryl groups and terminal bound THT ligands (Meyer *et al.*, 1989). For selected examples of molecular thio-ether-ligated complexes incorporating dinuclear $\text{Cu}(\mu_2\text{-Br})_2\text{Cu}$ SBUs see: $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{1\text{-oxa-4,7-di-thia-cyclo-nonane}\}_2]$ (Lucas *et al.*, 1997; CSD NONWOC, $d\text{Cu}\cdots\text{Cu}$ 2.852 (2) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\text{phenyl propargyl sulfide}\}_4]$ (Kokoli *et al.*, 2013; CSD VEQXUM, $d\text{Cu}\cdots\text{Cu}$ 3.0062 (7) Å). For selected examples of mono-dimensional thio-ether-assembled CPs incorporating dinuclear $\text{Cu}(\mu_2\text{-Br})_2\text{Cu}$ SBUs see: $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\mu\text{-PhSCH}_2\text{SPh}\}_2]_n$ (Knorr *et al.*, 2014; CSD FOWZIC, $d\text{Cu}\cdots\text{Cu}$ 2.9192 (8) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\mu\text{-PhS}(\text{CH}_2)_3\text{SPh}\}_2]_n$ (Knorr *et al.*, 2012; CSD ZEHREL, $d\text{Cu}\cdots\text{Cu}$ 2.794 (1) and 2.776 (1) Å); $[\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\{\mu\text{-}p\text{-EtSCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{SEt-}p\}_2]_n$ (Toyota *et al.*, 1996; CSD ZARYUMO1, $d\text{Cu}\cdots\text{Cu}$ 2.918 (11) Å); $[\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\{\mu\text{-O}_2\text{S}_2\text{-macrocycle}\}_2]_n$ (Park *et al.*, 2012; CSD GAXHIY, $d\text{Cu}\cdots\text{Cu}$ 2.927 (1) Å).

For selected examples of two-dimensional thio-ether-assembled CPs incorporating dinuclear $\text{Cu}(\mu_2\text{-Br})_2\text{Cu}$ SBUs see: $[\{\text{Cu}_2(\mu_2\text{-Br})_2\}(\text{tetra-thia-phthalazinophane})_2]_n$ (Chen *et al.*, 1993; CSD HANGUY, $d\text{Cu}\cdots\text{Cu}$ 3.06 (8) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}(\mu_2\text{-2-iso-butyl-1,3-di-thiane})_2]_n$ (Raguvanshi *et al.*, 2019; CSD JIZQOB, $d\text{Cu}\cdots\text{Cu}$ 2.9057 (8) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\mu\text{-PhCH}_2\text{S}(\text{CH}_2)_6\text{SCH}_2\text{Ph}\}_2]_n$ (Schlachter *et al.*, 2020; CSD IHIBUZ, $d\text{Cu}\cdots\text{Cu}$ 2.953 (3) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\mu\text{-PhCH}_2\text{S}(\text{CH}_2)_7\text{SCH}_2\text{Ph}\}_2]_n$ (Schlachter *et al.*, 2020; CSD IHICOU, $d\text{Cu}\cdots\text{Cu}$ 2.7081 (4) Å); $[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}(\mu\text{-1,2,4,5-tetra-methyl-mercapto-benzene})]_n$ (Suenaga *et al.*, 1997; CSD WIQMIS, $d\text{Cu}\cdots\text{Cu}$ 3.1073 (12) Å). These examples underpin that the $\text{Cu}\cdots\text{Cu}$ separations within these dinuclear $\text{Cu}(\mu_2\text{-Br})_2\text{Cu}$ SBUs are quite variable.

5. Synthesis and crystallization

To a solution of CuBr (1.43 g, 10.0 mmol) in MeCN (12 mL) was added neat THT (1.058 g, 12.0 mmol) via syringe. The solution turned brownish-red and a colourless microcrystalline material commenced to precipitate. The suspension was stirred at 20 °C for 2h, then heated 2 min to reflux until all product dissolved. Upon allowing to reach ambient temperature, colourless crystal formed progressively (Fig.5). After filtering off the product after 1d, stored the mother liquor in a refrigerator afforded a second crop of

CP1. Overall yield (1.80 g, 78% yield). Calc. for C₈H₁₆Br₂Cu₂S₂: C, 20.74 H, 3.48; S, 13.84. Found: C, 20.35; H, 3.28, S, 13.41%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in calculated positions and treated in a riding model. C—H distances were set to 0.99 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. The C7 atom in one of the THT ligands as well as the hydrogen atoms ridden on and on the neighboured C6 and C8 atoms are splitted between two sites. Their occupancy factors have been refined to 0.77 (1) and 0.23 (1).

Table 1

Hydrogen-bond geometry (Å, °) for (12mk2902)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C4—H4B···Br2 ^{iv}	0.99	2.90	3.566 (4)	125
C5—H5B···Br2 ⁱⁱ	0.99	2.89	3.556 (4)	126
C7A—H7AA···Br2 ^v	0.99	2.95	3.885 (6)	157

Symmetry codes: (ii) $-x+2, -y, -z+1$; (iv) $x-1, y, z$; (v) $x, y-1, z$.

Table 2

Experimental details

Crystal data	
Chemical formula	C ₈ H ₁₆ Br ₂ Cu ₂ S ₂
<i>M</i> _r	463.23
Crystal system, space group	Triclinic, <i>P</i> [−] 1
Temperature (K)	115
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.8076 (3), 9.7078 (4), 10.1579 (4)
α, β, γ (°)	75.804 (2), 89.845 (2), 89.594 (2)
<i>V</i> (Å ³)	650.79 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α ₁
μ (mm ^{−1})	9.69
Crystal size (mm)	0.25 × 0.15 × 0.1

Data collection	
Diffractionmeter	Nonius Kappa Apex II
Absorption correction	Multi-scan R.H. Blessing, <i>Acta Cryst.</i> (1995), a51, 33-38
T_{\min}, T_{\max}	0.024, 0.072
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5297, 2954, 2743
R_{int}	0.021
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.075, 1.09
No. of reflections	2954
No. of parameters	132
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e \AA^{-3})	0.82, -0.91

Computer programs: Collect (Bruker AXS BV, 1997-2004), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), *SIR97* (Burla *et al.*, 2007), *SHELXL* 2018/3 (Sheldrick, 2015), *OLEX2* 1.3 (Dolomanov *et al.*, 2009).

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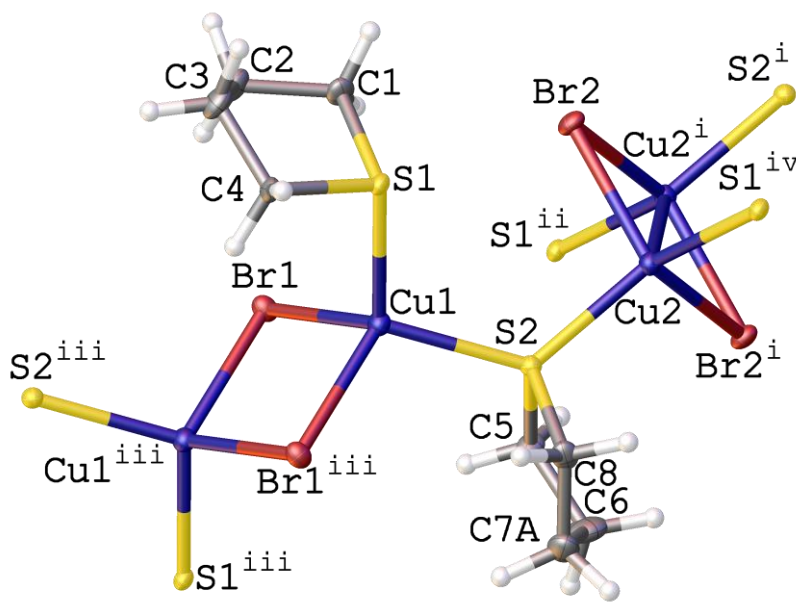


Figure 1

A view of the asymmetric unit of CP1 depicting the independent Cu_2Br_2 SBU's and THT ligands. Hydrogen atoms are omitted for clarity. Only the major component of disordered C7 atom is shown. Symmetry codes: i $-x+2, -y, -z+1$; ii $x+1, y, z$; iii $-x+1, -y, -z$; iv $-x+1, -y, -z+1$.

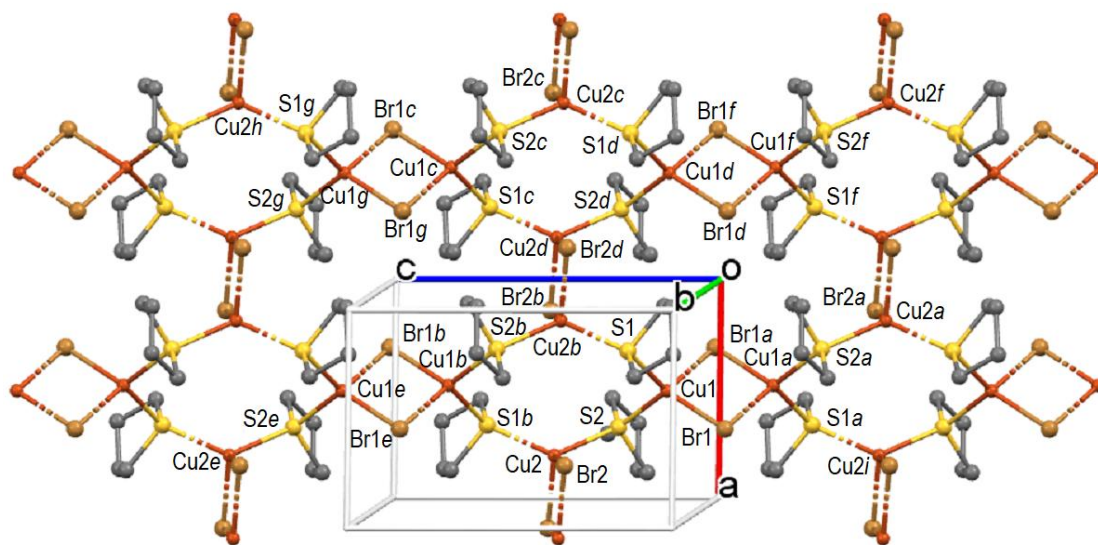


Figure 2

Projection of one layer on the $a0c$ plane in the structure of **1**. Hydrogen atoms are omitted for clarity. Only the major component of disordered C7 atom is shown. Symmetry codes: a $-x+1, -y, -z$; b $-x+1, -y+1, -z+1$; c $-x, -y, -z+1$; d $x-1, y, z$; e $x, y, z+1$; f $-x, -y, -z$; g $x-1, y, z+1$; h $-x, -y+1, -z+2$; i $x, y, z+1$; j $x, y, z-1$.

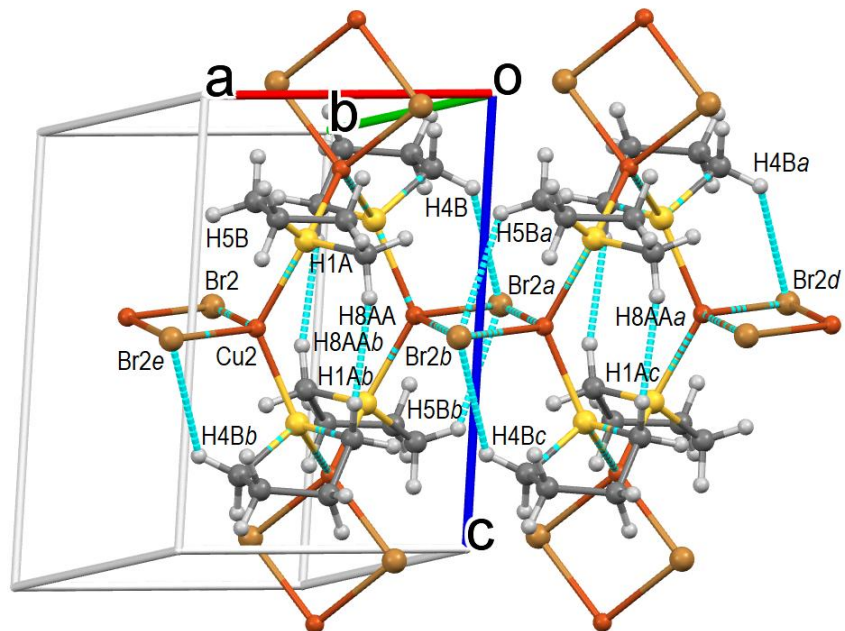


Figure 3

Intralayer CH...Br and CH...HC non-covalent interactions. Symmetry codes: *a* $x-1, y, z$; *b* $-x+1, -y, -z+1$; *c* $-x, -y, -z$; *d* $x-2, y, z$; *e* $-x+2, -y, -z$.

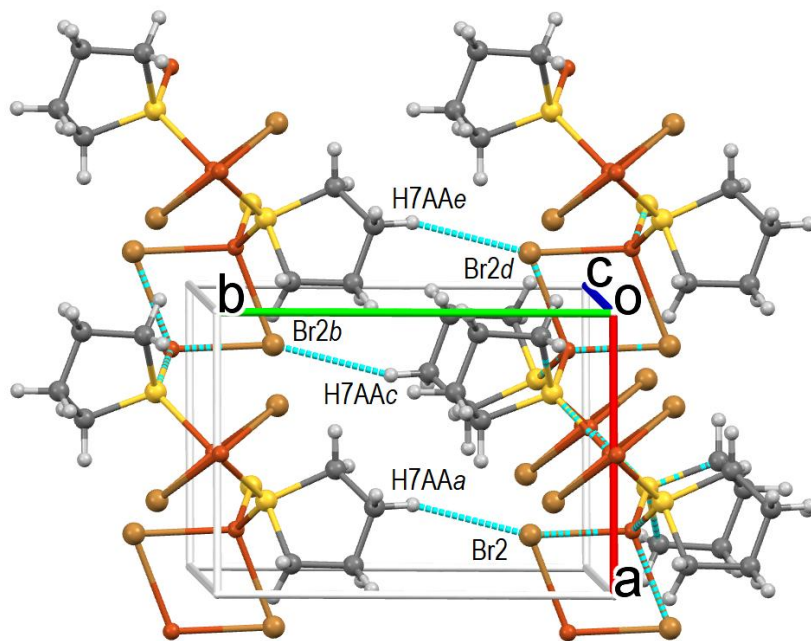


Figure 4

Interlayer CH \cdots Br hydrogen bonds. Symmetry codes: *a* $x, y+1, z$; *b* $-x+1, -y+1, -z+1$; *c* $-x+1, -y, -z+1$; *d* $x-1, y, z$; *e* $x-1, y+1, z$.

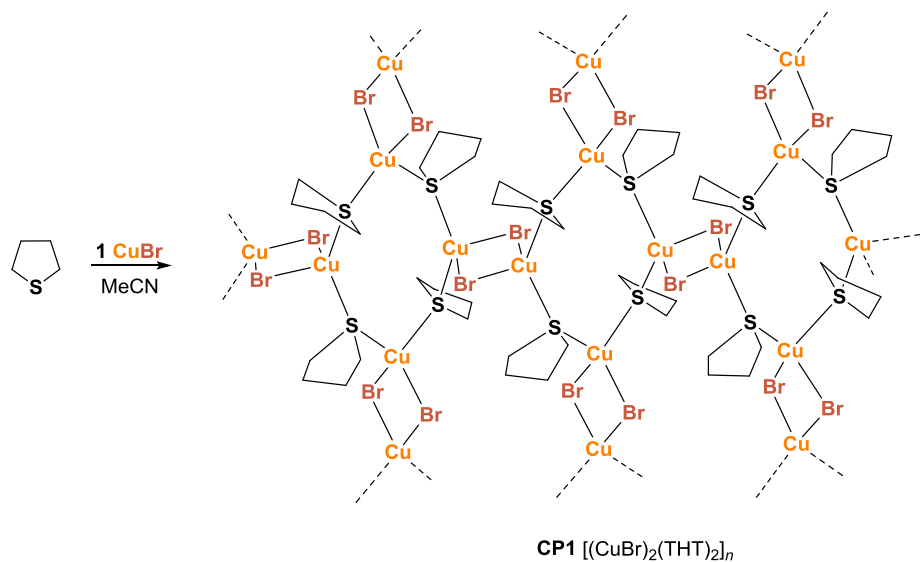


Figure 5

Reaction scheme for synthesis of **CP1**.

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supporting information

Crystal structure of the two-dimensional coordination polymer catena-bis-(μ_2 -bromo)-bis-(μ_2 -tetra-hydro-thio-phene)-dicopper(I)

Michael Knorr, Lydie Viau, Yoann Rousselin and Marek M. Kubicki*

Computing details

Data collection: Collect (Bruker AXS BV, 1997-2004); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997); program(s) used to solve structure: *SIR97* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL* 2018/3 (Sheldrick, 2015); molecular graphics: *OLEX2* 1.3 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* 1.3 (Dolomanov *et al.*, 2009).

(12mk2902)

Crystal data

$\text{C}_8\text{H}_{16}\text{Br}_2\text{Cu}_2\text{S}_2$	$Z = 2$
$M_r = 463.23$	$F(000) = 448$
Triclinic, $P\bar{1}$	$D_x = 2.364 \text{ Mg m}^{-3}$
$a = 6.8076 (3) \text{ \AA}$	Mo $K\alpha_1$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 9.7078 (4) \text{ \AA}$	Cell parameters from 2662 reflections
$c = 10.1579 (4) \text{ \AA}$	$\theta = 1.0\text{--}27.5^\circ$
$\alpha = 75.804 (2)^\circ$	$\mu = 9.69 \text{ mm}^{-1}$
$\beta = 89.845 (2)^\circ$	$T = 115 \text{ K}$
$\gamma = 89.594 (2)^\circ$	Prism, clear light colourless
$V = 650.79 (5) \text{ \AA}^3$	$0.25 \times 0.15 \times 0.1 \text{ mm}$

Data collection

Nonius Kappa Apex II diffractometer	2954 independent reflections
Radiation source: X-ray tube, Siemens KFF Mo 2K-180	2743 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.021$
Detector resolution: 9 pixels mm^{-1}	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 3.0^\circ$
ϕ and ω scans'	$h = -8 \rightarrow 8$

Absorption correction: multi-scan R.H. Blessing, Acta Cryst. (1995), a51, 33-38	$k = -12 \rightarrow 12$
$T_{\min} = 0.024$, $T_{\max} = 0.072$	$l = -12 \rightarrow 13$
5297 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H-atom parameters constrained
$wR(F^2) = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 2.0511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\max} < 0.001$
2954 reflections	$\Delta_{\max} = 0.82 \text{ e } \text{\AA}^{-3}$
132 parameters	$\Delta_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$
6 restraints	

Special details

<i>Geometry.</i> All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for (12mk2902)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.66540 (5)	0.15468 (4)	-0.03837 (3)	0.01461 (10)	
Br2	0.83088 (5)	0.17939 (4)	0.45014 (4)	0.01506 (10)	
Cu1	0.51313 (7)	-0.00292 (5)	0.16455 (5)	0.01505 (11)	
Cu2	0.82082 (6)	-0.08288 (5)	0.51958 (4)	0.01385 (11)	
S1	0.31065 (12)	0.13645 (9)	0.26538 (8)	0.01195 (17)	
S2	0.70032 (12)	-0.14665 (9)	0.33197 (9)	0.01222 (17)	
C1	0.4015 (6)	0.3198 (4)	0.2177 (4)	0.0192 (8)	
H1A	0.375096	0.368406	0.290963	0.023*	
H1B	0.544740	0.320766	0.200413	0.023*	
C2	0.2910 (6)	0.3928 (4)	0.0890 (4)	0.0206 (8)	
H2A	0.354608	0.371724	0.008315	0.025*	

H2B	0.289017	0.496987	0.077765	0.025*	
C3	0.0821 (6)	0.3339 (4)	0.1059 (4)	0.0226 (8)	
H3A	0.010384	0.370283	0.175423	0.027*	
H3B	0.009678	0.363357	0.018959	0.027*	
C4	0.0989 (6)	0.1729 (4)	0.1496 (4)	0.0163 (7)	
H4A	0.121252	0.132901	0.069998	0.020*	
H4B	-0.022152	0.131202	0.196654	0.020*	
C5	0.9163 (6)	-0.2030 (4)	0.2504 (4)	0.0179 (7)	
H5A	0.902627	-0.175035	0.150356	0.022*	
H5B	1.036738	-0.159227	0.275978	0.022*	
C6	0.9258 (7)	-0.3639 (5)	0.3012 (5)	0.0325 (10)	
H6AA	1.003988	-0.405261	0.237893	0.039*	0.771 (13)
H6AB	0.988725	-0.390717	0.391775	0.039*	0.771 (13)
H6BC	0.911154	-0.407662	0.223452	0.039*	0.229 (13)
H6BD	1.055839	-0.392163	0.342976	0.039*	0.229 (13)
C7A	0.7197 (8)	-0.4183 (6)	0.3098 (6)	0.0265 (16)	0.771 (13)
H7AA	0.716201	-0.518002	0.364131	0.032*	0.771 (13)
H7AB	0.669637	-0.415264	0.217672	0.032*	0.771 (13)
C7B	0.7690 (16)	-0.4178 (16)	0.4028 (15)	0.016 (5)*	0.229 (13)
H7BA	0.732673	-0.515246	0.398840	0.019*	0.229 (13)
H7BB	0.819357	-0.422099	0.495122	0.019*	0.229 (13)
C8	0.5925 (6)	-0.3246 (4)	0.3767 (4)	0.0188 (8)	
H8AA	0.591371	-0.362462	0.476472	0.023*	0.771 (13)
H8AB	0.455767	-0.321214	0.343042	0.023*	0.771 (13)
H8BC	0.508814	-0.337978	0.458646	0.023*	0.229 (13)
H8BD	0.513653	-0.342444	0.300886	0.023*	0.229 (13)

Atomic displacement parameters (\AA^2) for (12mk2902)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01355 (17)	0.01735 (19)	0.01357 (17)	-0.00288 (13)	0.00077 (13)	-0.00496 (14)
Br2	0.01333 (17)	0.01052 (18)	0.02045 (19)	0.00292 (13)	-0.00208 (13)	-0.00219 (14)
Cu1	0.0167 (2)	0.0148 (2)	0.0137 (2)	0.00320 (17)	-0.00176 (16)	-0.00354 (17)
Cu2	0.0162 (2)	0.0132 (2)	0.0120 (2)	0.00180 (17)	-0.00123 (16)	-0.00298 (17)
S1	0.0142 (4)	0.0100 (4)	0.0108 (4)	0.0027 (3)	-0.0016 (3)	-0.0010 (3)

S2	0.0140 (4)	0.0111 (4)	0.0119 (4)	0.0016 (3)	-0.0012 (3)	-0.0037 (3)
C1	0.0254 (19)	0.0107 (18)	0.0198 (18)	-0.0041 (15)	-0.0019 (15)	-0.0003 (14)
C2	0.0212 (19)	0.0146 (19)	0.0218 (19)	0.0013 (15)	-0.0009 (15)	0.0036 (15)
C3	0.0189 (18)	0.018 (2)	0.027 (2)	0.0055 (15)	-0.0040 (16)	0.0000 (16)
C4	0.0198 (17)	0.0151 (18)	0.0138 (16)	0.0055 (14)	-0.0060 (14)	-0.0030 (14)
C5	0.0190 (18)	0.0183 (19)	0.0159 (17)	0.0070 (14)	0.0055 (14)	-0.0033 (14)
C6	0.038 (3)	0.021 (2)	0.041 (3)	0.0089 (19)	0.007 (2)	-0.012 (2)
C7A	0.036 (3)	0.018 (3)	0.028 (3)	-0.002 (2)	-0.010 (2)	-0.009 (2)
C8	0.0243 (19)	0.0141 (19)	0.0171 (17)	-0.0067 (15)	-0.0020 (15)	-0.0018 (14)

Geometric parameters (Å, °) for (12mk2902)

Br1—Cu1	2.4755 (6)	C3—C4	1.520 (5)
Br1—Cu1 ⁱ	2.5000 (6)	C4—H4A	0.9900
Br2—Cu2 ⁱⁱ	2.5349 (6)	C4—H4B	0.9900
Br2—Cu2	2.4711 (6)	C5—H5A	0.9900
Cu1—Cu1 ⁱ	3.3348 (10)	C5—H5B	0.9900
Cu1—S1	2.3292 (9)	C5—C6	1.522 (6)
Cu1—S2	2.2991 (10)	C6—H6AA	0.9900
Cu2—Cu2 ⁱⁱ	2.9044 (9)	C6—H6AB	0.9900
Cu2—S1 ⁱⁱⁱ	2.2982 (9)	C6—H6BC	0.9900
Cu2—S2	2.2983 (9)	C6—H6BD	0.9900
S1—C1	1.837 (4)	C6—C7A	1.497 (7)
S1—C4	1.840 (4)	C6—C7B	1.488 (12)
S2—C5	1.831 (4)	C7A—H7AA	0.9900
S2—C8	1.833 (4)	C7A—H7AB	0.9900
C1—H1A	0.9900	C7A—C8	1.526 (6)
C1—H1B	0.9900	C7B—H7BA	0.9900
C1—C2	1.523 (5)	C7B—H7BB	0.9900
C2—H2A	0.9900	C7B—C8	1.484 (12)
C2—H2B	0.9900	C8—H8AA	0.9900
C2—C3	1.530 (5)	C8—H8AB	0.9900
C3—H3A	0.9900	C8—H8BC	0.9900
C3—H3B	0.9900	C8—H8BD	0.9900
Cu1—Br1—Cu1 ⁱ	84.167 (19)	S1—C4—H4A	110.7
Cu2—Br2—Cu2 ⁱⁱ	70.916 (19)	S1—C4—H4B	110.7
Br1—Cu1—Br1 ⁱ	95.832 (19)	C3—C4—S1	105.3 (3)

S1—Cu1—Br1	107.82 (3)	C3—C4—H4A	110.7
S1—Cu1—Br1 ⁱ	114.58 (3)	C3—C4—H4B	110.7
S2—Cu1—Br1	121.51 (3)	H4A—C4—H4B	108.8
S2—Cu1—Br1 ⁱ	108.88 (3)	S2—C5—H5A	110.6
S2—Cu1—S1	108.12 (3)	S2—C5—H5B	110.6
Br2—Cu2—Br2 ⁱⁱ	109.084 (19)	H5A—C5—H5B	108.7
Br2 ⁱⁱ —Cu2—Cu2 ⁱⁱ	53.516 (16)	C6—C5—S2	105.7 (3)
Br2—Cu2—Cu2 ⁱⁱ	55.568 (17)	C6—C5—H5A	110.6
S1 ⁱⁱⁱ —Cu2—Br2	105.18 (3)	C6—C5—H5B	110.6
S1 ⁱⁱⁱ —Cu2—Br2 ⁱⁱ	104.86 (3)	C5—C6—H6AA	110.2
S1 ⁱⁱⁱ —Cu2—Cu2 ⁱⁱ	116.52 (3)	C5—C6—H6AB	110.2
S2—Cu2—Br2	104.11 (3)	C5—C6—H6BC	109.3
S2—Cu2—Br2 ⁱⁱ	105.71 (3)	C5—C6—H6BD	109.3
S2—Cu2—Cu2 ⁱⁱ	116.35 (3)	H6AA—C6—H6AB	108.5
S2—Cu2—S1 ⁱⁱⁱ	127.13 (4)	H6BC—C6—H6BD	108.0
Cu2 ⁱⁱⁱ —S1—Cu1	128.70 (4)	C7A—C6—C5	107.7 (4)
C1—S1—Cu1	108.21 (14)	C7A—C6—H6AA	110.2
C1—S1—Cu2 ⁱⁱⁱ	111.26 (13)	C7A—C6—H6AB	110.2
C1—S1—C4	94.46 (18)	C7B—C6—C5	111.5 (6)
C4—S1—Cu1	102.71 (12)	C7B—C6—H6BC	109.3
C4—S1—Cu2 ⁱⁱⁱ	105.46 (13)	C7B—C6—H6BD	109.3
Cu2—S2—Cu1	125.08 (4)	C6—C7A—H7AA	110.0
C5—S2—Cu1	107.52 (13)	C6—C7A—H7AB	110.0
C5—S2—Cu2	104.92 (13)	C6—C7A—C8	108.3 (4)
C5—S2—C8	93.98 (19)	H7AA—C7A—H7AB	108.4
C8—S2—Cu1	108.84 (13)	C8—C7A—H7AA	110.0
C8—S2—Cu2	111.74 (13)	C8—C7A—H7AB	110.0
S1—C1—H1A	110.6	C6—C7B—H7BA	109.4
S1—C1—H1B	110.6	C6—C7B—H7BB	109.4
H1A—C1—H1B	108.7	H7BA—C7B—H7BB	108.0
C2—C1—S1	105.9 (3)	C8—C7B—C6	111.0 (9)
C2—C1—H1A	110.6	C8—C7B—H7BA	109.4
C2—C1—H1B	110.6	C8—C7B—H7BB	109.4
C1—C2—H2A	110.5	S2—C8—H8AA	110.4
C1—C2—H2B	110.5	S2—C8—H8AB	110.4
C1—C2—C3	106.3 (3)	S2—C8—H8BC	111.3
H2A—C2—H2B	108.7	S2—C8—H8BD	111.3

C3—C2—H2A	110.5	C7A—C8—S2	106.8 (3)
C3—C2—H2B	110.5	C7A—C8—H8AA	110.4
C2—C3—H3A	110.3	C7A—C8—H8AB	110.4
C2—C3—H3B	110.3	C7B—C8—S2	102.3 (6)
H3A—C3—H3B	108.5	C7B—C8—H8BC	111.3
C4—C3—C2	107.3 (3)	C7B—C8—H8BD	111.3
C4—C3—H3A	110.3	H8AA—C8—H8AB	108.6
C4—C3—H3B	110.3	H8BC—C8—H8BD	109.2
Cu1—S1—C1—C2	91.5 (3)	S2—C5—C6—C7B	-3.4 (8)
Cu1—S1—C4—C3	-123.6 (2)	C1—S1—C4—C3	-13.8 (3)
Cu1—S2—C5—C6	-128.8 (3)	C1—C2—C3—C4	-49.3 (4)
Cu1—S2—C8—C7A	103.2 (3)	C2—C3—C4—S1	37.6 (4)
Cu1—S2—C8—C7B	143.3 (6)	C4—S1—C1—C2	-13.4 (3)
Cu2 ⁱⁱⁱ —S1—C1—C2	-121.9 (2)	C5—S2—C8—C7A	-6.8 (3)
Cu2 ⁱⁱⁱ —S1—C4—C3	99.7 (3)	C5—S2—C8—C7B	33.3 (6)
Cu2—S2—C5—C6	96.1 (3)	C5—C6—C7A—C8	-45.0 (5)
Cu2—S2—C8—C7A	-114.6 (3)	C5—C6—C7B—C8	30.0 (12)
Cu2—S2—C8—C7B	-74.5 (6)	C6—C7A—C8—S2	30.3 (5)
S1—C1—C2—C3	37.0 (4)	C6—C7B—C8—S2	-40.9 (11)
S2—C5—C6—C7A	38.3 (4)	C8—S2—C5—C6	-17.7 (3)

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

Hydrogen-bond geometry (Å, °) for (12mk2902)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4 <i>B</i> ...Br2 ^{iv}	0.99	2.90	3.566 (4)	125
C5—H5 <i>B</i> ...Br2 ⁱⁱ	0.99	2.89	3.556 (4)	126
C7A—H7AA...Br2 ^v	0.99	2.95	3.885 (6)	157

Symmetry codes: (ii) $-x+2, -y, -z+1$; (iv) $x-1, y, z$; (v) $x, y-1, z$.

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