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Crystal structure of the coordination polymer catena-(tris((μ_2 -1,3-dithiolane-*S,S,S'*)-(acetonitrile)-copper(I)hexafluorophosphate)

Lena Knauer,^a Michael Knorr,^{b*} Lydie Viau^b and Carsten Strohmann^{*a}

^aAnorganische Chemie, Technische Universität Dortmund, Otto-Hahn-Strasse 6, D-44227 Dortmund, Germany, and ^bInstitut UTINAM UMR 6213 CNRS, Université Bourgogne Franche-Comté, 16 Route de Gray, 25030 Besançon Cedex, France

Correspondence e-mail: michael.knorr@univ-fcomte.fr; carsten.strohmann@tu-dormund.de

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Abstract

The polymeric title compound, [Cu₂(C₂H₃N)₂(C₃H₆S₂)₂](PF₆)₂, represents an example of a one-dimensional coordination polymer resulting from the reaction of [Cu(MeCN)₄][PF₆] with 1,3-dithiolane. The cationic one-dimensional ribbon consists of two copper(I) centers each ligated by one acetonitrile molecule and interconnected through two bridging 1,3-dithiolane ligands. One S-donor site of each ligand is κ^1 -bound to Cu, whereas the second S atom acts as a four-electron donor, bridging two Cu atoms in a κ^4 -bonding mode. The positive charge of each copper cation is compensated for by a hexafluoridophosphate counter-ion. In the crystal, the polymer chains are linked by a series of C—H...F hydrogen bonds, forming a supramolecular framework.

1. Chemical Context

The five-membered heterocyclic ligand tetrahydrothiophene (THT) is known to form a great variety of molecular complexes and coordination polymers (CPs) with various transition metals. Notably, 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 (Ahrland *et al.*, 1993; Dembo *et al.*, 2010; Noren & Oskarsson, 1985; Mälger *et al.*, 1992; Uson *et al.*, 1984). Even mixed-valence Cu(I)-Cu(II) compounds such as polymeric penta- μ -chloro-

tris- μ -tetrahydrothiophene-tetracopper(I,II) have been prepared (Ainscough *et al.*, 1985). In the case of the five-membered heterocycle 1,2-dithiolane, in which one CH₂-unit is replaced by a second sulfur atom, there is one report on its coordination to Hg₂(NO₃)₂ yielding the Hg(I) adduct 1,2-dithiolane • Hg₂(NO₃)₂ (Brodersen & Rölz, 1977). Furthermore, the dinuclear organometallic species $[\eta^5\text{-CpMn}(\text{CO})_2(\mu_2\text{-1,2-dithiolane})]_2$ has been crystallographically characterized (Braunwarth *et al.*, 1991). The fluxional complexes $[\text{M}(\text{CO})_5(1,3\text{-dithiolane})]$ (M = Cr, Mo, W) ligated by the isomeric heterocycle 1,3-dithiolane (1,3-dithiacyclopentane) have been investigated by NMR spectroscopy (Abel *et al.*, 1990). In a comparative study with respect to our previous work on the coordination chemistry of the open-chain dithioether analogues RS-CH₂-SR (Chaabéne *et al.*, 2016; Knorr *et al.*, 2014; Peindy *et al.*, 2007) and in part to fill the gap between the versatile coordination chemistry of THT (see above) and the almost unexplored coordination chemistry of 1,3-dithiolane, we recently described in detail the construction and structural features of molecular clusters and coordination networks, with dimensionalities varying from 0D-2D by reacting 1,3-dithiolane and its ferrocenyl derivative substituted at the 2-position with CuX salts (X = Cl, Br, I) (Raghuvanshi *et al.*, 2017). But surprisingly, a survey of the CSD Database reveals that apart from our CuX • 1,3-dithiolane compounds no other unsubstituted 1,3-dithiolane complexes have been structurally characterized. We have now extended our project on the coordination chemistry of this cyclic dithioether using $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ as reactant to obtain an ionic salt-like material, which could be interesting for electrochemical investigation.

2. Structural commentary

We have previously described the structural features of the ribbon-like structures of compounds $[\{\text{Cu}(\mu_2\text{-Br})\}(\mu_2\text{-L1})]_n$ and $[\{\text{Cu}(\mu_2\text{-Cl})\}(\mu_2\text{-L1})]_n$, formed upon treatment of CuBr and CuCl with 1,3-dithiolane **L1** (Raghuvanshi *et al.*, 2017). The title complex salt, a ribbon of composition $[\text{Cu}(1,3\text{-dithiane})(\text{MeCN})]_n^+$ (**CP1**) also results from the reaction of $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ with **L1**, but its architecture is quite different. The molecular structure of the asymmetric unit of the title complex is illustrated in Fig. 1, and selected bond lengths and bond angles are given in Table 1. The ribbon-like structure is built upon individual Cu^I atoms, each ligated by a datively bound MeCN ligand and interconnected to the neighbouring metal centers by two bridging dithiolane ligands (Fig. 2). Overall, the architecture of **CP1** is quite reminiscent of that of the 1D polymeric tetrafluoroborate salt $[\text{Cu}(1,3\text{-dithiane})(\text{MeCN})]_n^+$ (Knaust & Keller, 2003). Nevertheless, there is one difference. Whereas the asymmetric unit of the latter salt (crystallizing in the orthorhombic Sohncke space group $P2_12_12_1$) contains three unique

copper(I) centers, that of **CP1** (crystallizing in the orthorhombic non-centrosymmetric space group $Pna2_1$) contains only two unique Cu^I atoms. Each displays a CuNS₃ four-coordinate environment; see Table 1 [L —Cu— L angles: 99.97 (7) to 119.47 (11)° for Cu1, and 99.29 (11) to 118.69 (4)° for Cu2]. The τ_4 descriptor for fourfold coordination is = 0.89 for both atoms Cu1 and Cu2, indicating that each have a trigonal-pyramidal geometry ($\tau_4 = 1$ for a perfect tetrahedral geometry, = 0 for a perfect square planar geometry and = 0.85 for a perfect trigonal-pyramidal geometry; Yang *et al.*, 2007). The coordination environment for each of the Cu^I centers includes three bridging dithiolane ligands and one terminal acetonitrile ligand. All Cu—S bond lengths are in the range 2.2630(10)–2.3367(11) Å, the mean Cu—S bond length of 2.314(12) Å is quite similar to that in [Cu(1,3-dithiane)(MeCN)]_n⁺. In addition, the mean Cu—N bond distance matches well with that of [Cu(1,3-dithiane)(MeCN)]_n [1.979 (4) *versus* 1.984 (7) Å]. The three dithiolane ligands each have one S atom that is a two-electron donor and one S atom that is a μ_2 -four-electron donor. The Cu⋯Cu separations of *ca* 3.689–3.852 Å are far above the sum of the van der Waals radii of two Cu atoms (2.8 Å), excluding any bonding interaction. These two bonding modes lead to the formation of a ribbon-like coordination polymer, which runs parallel to the *a* axis, where each copper(I) center is bonded to two μ_2 -S atoms and one μ_1 -S atom (Fig. 2 and Table 1).

Table 1 Selected geometric parameters (Å, °)

Cu1—N1	1.973(3)	Cu2—N2	1.980(3)
Cu1—S1	2.2630(10)	Cu2—S3	2.2886(11)
Cu1—S2 ⁱ	2.3305(9)	Cu2—S4 ⁱ	2.3281(9)
Cu1—S4 ⁱ	2.3367(11)	Cu2—S2	2.3357(11)
N1—Cu1—S1	119.47(11)	N2—Cu2—S4 ⁱ	99.29(11)
N1—Cu1—S2 ⁱ	99.97(9)	S3—Cu2—S4 ⁱ	118.69(4)
S1—Cu1—S2 ⁱ	115.68(4)	N2—Cu2—S2	106.03(13)
N1—Cu1—S4 ⁱ	105.68(12)	S3—Cu2—S2	115.99(4)
S1—Cu1—S4 ⁱ	110.65(4)	S4 ⁱ —Cu2—S2	102.03(4)
S2 ⁱ —Cu1—S4 ⁱ	103.69(4)	Cu1 ⁱⁱ —S2—Cu2	111.28(4)
N2—Cu2—S3	112.75(12)	Cu2 ⁱⁱ —S4—Cu1 ⁱⁱ	104.54(4)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z$.

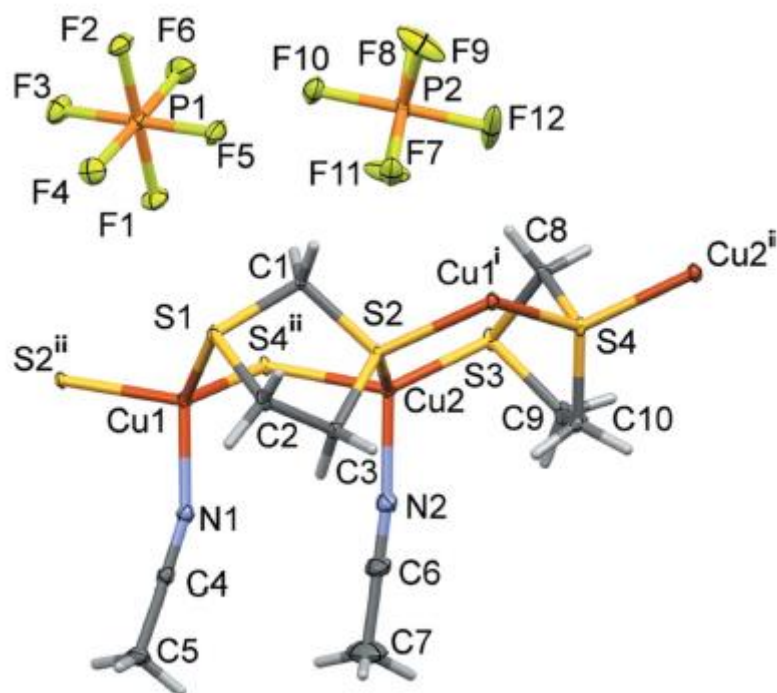


Figure 1. A view of the asymmetric unit of the title compound, with atom labelling [symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$]. Displacement ellipsoids are drawn at the 30% probability level

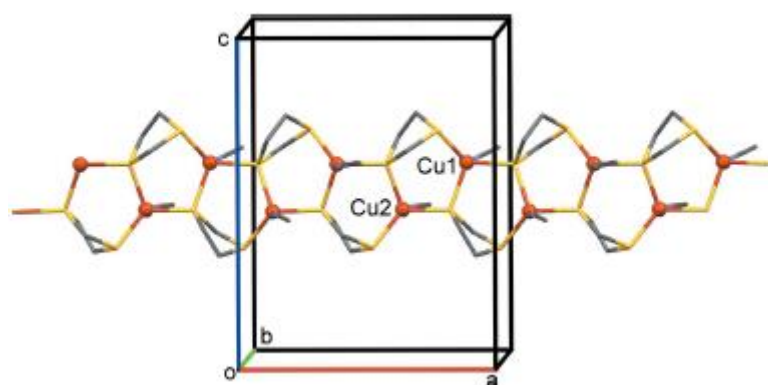


Figure 2. A partial view along the b axis of the crystal packing of the title compound. For clarity, the H atoms and the PF_6^- anions have been omitted.

3. Supramolecular features

The crystal packing of the title compound is illustrated in Fig.3, and shows the ribbon-like structures, propagating along the a -axis direction, that are linked by a number of C—H \cdots F hydrogen bonds, forming a supramolecular framework (Fig 3 and Table 2).

Table 2. Hydrogen-bond geometry (Å, °)

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C1—H1A···F9 ⁱⁱⁱ	0.99	2.55	3.264(4)	129
C1—H1A···F12 ⁱⁱⁱ	0.99	2.40	3.277(5)	147
C2—H2A···F9 ⁱⁱⁱ	0.99	2.50	3.287(5)	136
C3—H3B···F4 ⁱⁱ	0.99	2.42	3.376(5)	161
C5—H5C···F6 ^{iv}	0.98	2.54	3.426(6)	151
C8—H8A···F11	0.99	2.34	3.186(5)	143
C8—H8B···F2 ^v	0.99	2.46	3.323(5)	145
C10—H10A···F7 ⁱⁱ	0.99	2.31	3.221(5)	152
C10—H10B···F1 ⁱⁱ	0.99	2.48	3.264(5)	136

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (iii) $-x + 1, -y + 1, z + \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x + 1, -y + 1, z - \frac{1}{2}$.

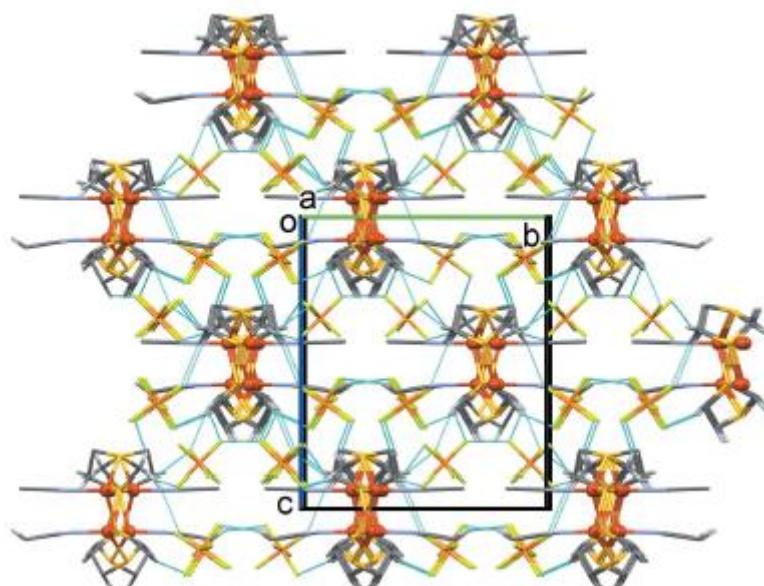


Figure 3. A view along the *a* axis of the crystal packing of the title compound. The C—H···F hydrogen bonds (Table 2) are shown as dashed lines. For clarity, only the H atoms involved in these interactions have been included.

4. Data survey

Other examples of crystallographically characterized 1,3-dithiolane complexes substituted at the 2 position found in the Cambridge Structural Database include catena-[(μ_5 -1,3-Dithiolane-2-carboxylato)-(μ_4 -1,3-dithiolane-2-carboxylato)-(μ_2 -trifluoromethanesulfonato-O,O')-tri-silver(I)] (FAQIPY; Gondi *et al.*, 2011), catena-((μ_3 -1,3-Dithiolane-2-methanol-S,S,S')-(nitrate-O)-silver(I)) (HESLUN; Zhang *et al.* 2006), Chloro-triphenylphosphine-(2,5-bis(1,3-

dithiolan-2-yl)phenyl-S)- palladium(II) (IVUFEK; Vicente *et al.* 2004), rac-trans-Dichloro-bis((2-(1,3-dithiolan-2-yl)phenyl)(diphenyl)phosphine)- ruthenium(II) chloroform solvate (TUMOK; Bayly *et al.* 2009). Other examples of related 1,3-dithiane copper (I) coordination polymers have also been reported (Raghuvanshi *et al.* 2019).

5. Synthesis and crystallization

The reaction scheme for the synthesis of the title compound is illustrated in Fig. 4. To a solution of $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (372 mg, 0.1mmol) in CH_2Cl_2 (10ml) was added an equimolar amount of 1,3-dithiolane (**L1**) *via* a syringe. The solution was stirred at 293K for 2h, then layered with Et_2O (10ml) and stored in a refrigerator for 2 days. Colourless block-like crystals formed progressively (245 mg, 68% yield). Elemental analysis Calculated. for $\text{C}_{10}\text{H}_{18}\text{Cu}_2\text{F}_{12}\text{N}_2\text{P}_2\text{S}_4$: C, 16.88; H, 2.54; N, 3.54; S, 18.03. Found: C, 61.75; H, 4.78. IR (ATR) : 2280 cm^{-1} w (weak) (CN), 835 cm^{-1} vs (very strong) (PF_6).

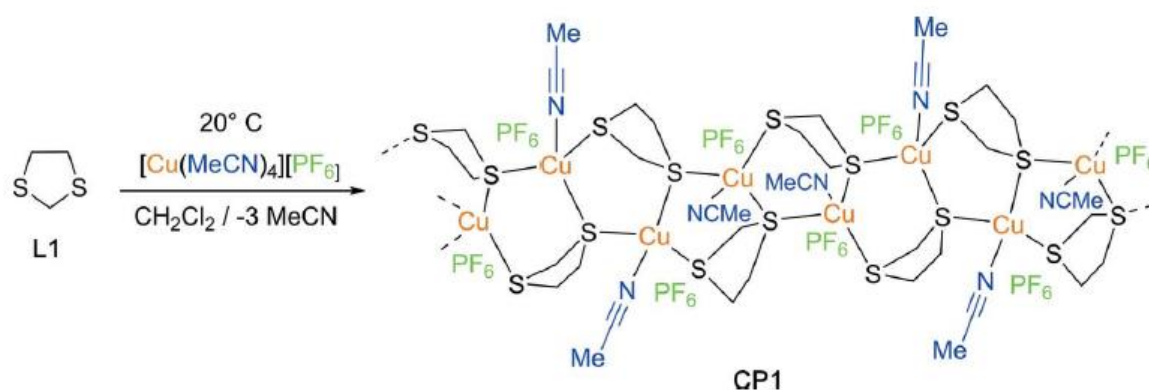


Figure 4. Reaction scheme for the synthesis of the title compound, **CP1**.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were included in calculated positions and treated as riding: C—H = 0.98–0.99 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms. The structure was refined as a two-component inversion twin $\text{BASF} = 0.121(12)$. In the final cycles of refinement three reflections were omitted; one was affected by the backstop and two were most disagreeable reflections

Table 3. Experimental details

Crystal data

Chemical formula	C ₁₀ H ₁₈ Cu ₂ N ₂ S ₄ ·2(F ₆ P)
<i>M_r</i>	711.52
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	105
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.8409 (9), 12.9273 (9), 15.2921 (11)
<i>V</i> (Å ³)	2340.8 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.41
Crystal size (mm)	0.33 × 0.32 × 0.27
Data collection	
Diffractometer	Bruker D8 VENTURE area detector
Absorption correction	Multi-scan TWINABS-2012/1 (Bruker,2012) was used for absorption correction.
<i>T_{min}</i> , <i>T_{max}</i>	0.608, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7731, 7136, 6518
<i>R_{int}</i>	0.100
(sin θ/λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.080, 1.05
No. of reflections	7136
No. of parameters	292
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.48, -0.44
Absolute structure	Flack <i>x</i> determined using 2796 quotients [(<i>I</i> ₊)-(<i>I</i> ₋)]/[(<i>I</i> ₊)+(<i>I</i> ₋)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.004 (9)

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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