Crystal structure of the coordination polymer *catena*-poly[[[(acetonitrile-κN)copper(I)]-μ_3-1,3-dithiolane-$\kappa^3 S$:S:S'] hexafluoridophosphate]

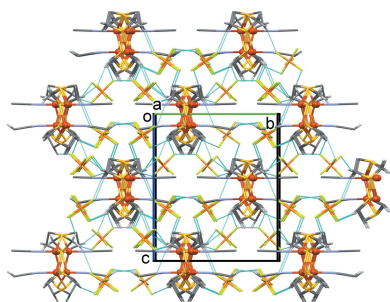## Lena Knauer,[a] Michael Knorr,[b]* Lydie Viau[b] and Carsten Strohmann[a]*

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The polymeric title compound, [Cu$_2$(C$_2$H$_3$N)$_2$(C$_3$H$_6$S$_2$)$_2$](PF$_6$)$_2$, represents an example of a one-dimensional coordination polymer resulting from the reaction of [Cu(MeCN)$_4$][PF$_6$] 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.
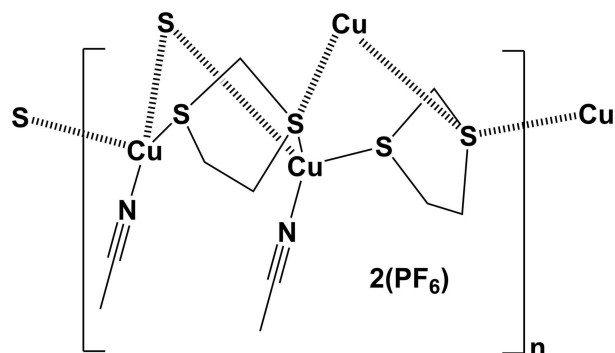
1. Chemical context

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 copper(I), silver(I) and gold(I), numerous structurally characterized examples coordinated by terminal or bridging THT ligands have been documented (Ahrland *et al.*, 1993; Dembo *et al.*, 2010; Norén & Oskarsson, 1985; Mälger *et al.*, 1992; Usón *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 CH$_2$ unit is replaced by a second sulfur atom, there is one report on its coordination to Hg$_2$(NO$_3$)$_2$ yielding the Hg^I adduct 1,2-dithiolane·Hg$_2$(NO$_3$)$_2$ (Brodersen & Rölz, 1977). Furthermore, the dinuclear organometallic species [η^5-CpMn(CO)$_2$(μ_2-1,2-dithiolane)]$_2$ has been characterized crystallographically (Braunwarth *et al.*, 1991). The fluxional complexes [M(CO)$_5$(1,3-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-CH$_2$-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). However, surprisingly, a survey of the Cambridge Structural Database (Groom *et al.*, 2016), 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 [Cu(MeCN)$_4$][PF$_6$] as reactant to obtain the title polymeric ionic salt-like material, which could be interesting for electrochemical investigations.

2. Structural commentary

We have previously described (Raghuvanshi *et al.*, 2017), the structural features of the ribbon-like structures of compounds [{Cu(μ_2-Br)}(μ_2-**L1**)]$_n$ and [{Cu(μ_2-Cl)}(μ_2-**L1**)]$_n$, formed upon treatment of CuBr and CuCl with 1,3-dithiolane (**L1**). The title complex salt, a ribbon of composition [Cu(1,3-di-thiane)(MeCN)]$_n$$^+$ (**CP1**) also results from the reaction of
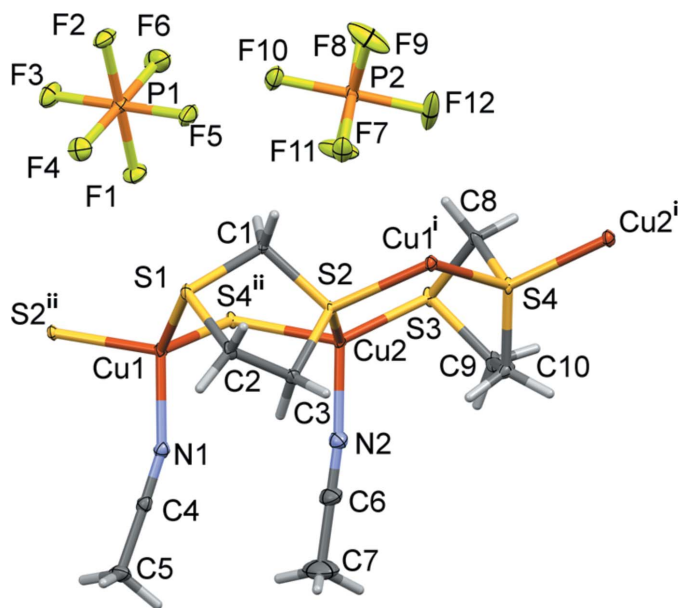
Figure 1
A view of the asymmetric unit of the title compound, with atom labelling [symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$]. Displacement ellipsoids are drawn at the 30% probability level.

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) $x - \frac{1}{2}, -y + \frac{3}{2}, z$.

[Cu(MeCN)$_4$][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 tetrafluoridoborate salt [Cu(1,3-dithiane)-(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 CuNS$_3$ 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 four-fold 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

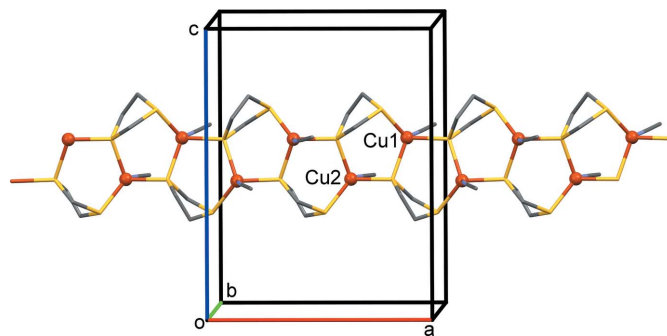**Figure 2**
A partial view along the *b* axis of the crystal packing of the title compound. For clarity, the H atoms and the PF$_6$$^-$ anions have been omitted.

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

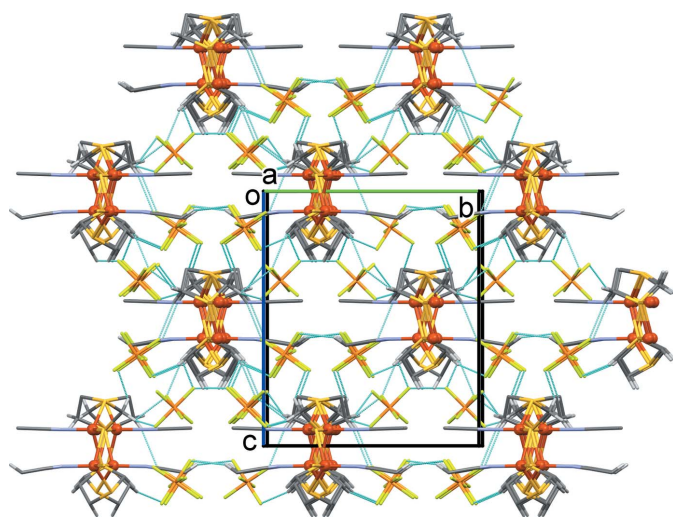| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$A\cdots$F9^{iii}	0.99	2.55	3.264 (4)	129
C1—H1$A\cdots$F12^{iii}	0.99	2.40	3.277 (5)	147
C2—H2$A\cdots$F9^{iii}	0.99	2.50	3.287 (5)	136
C3—H3$B\cdots$F4^{ii}	0.99	2.42	3.376 (5)	161
C5—H5$C\cdots$F6^{iv}	0.98	2.54	3.426 (6)	151
C8—H8$A\cdots$F11	0.99	2.34	3.186 (5)	143
C8—H8$B\cdots$F2^{v}	0.99	2.46	3.323 (5)	145
C10—H10$A\cdots$F7^{ii}	0.99	2.31	3.221 (5)	152
C10—H10$B\cdots$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) $-x + 1, -y + 1, z - \frac{1}{2}$.

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$\cdots$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).

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).

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

4. Database survey

Other examples of crystallographically characterized 1,3-dithiolane complexes substituted at the 2-position found in the Cambridge Structural Database (CSD, version 5.40, update August 2019; Groom *et al.*, 2016) include *catena*-[(μ_5-1,3-dithiolane-2-carboxylato)(μ_4-1,3-dithiolane-2-carboxylato)(μ_2-trifluoromethanesulfonato-O,O')trisilver(I)] (CSD refcode FAQIPY; Gondi *et al.*, 2011), *catena*-[(μ_3-1,3-dithiolane-2-methanol-S,S,S')(nitrato-O)silver(I)] (HESLUN; Zhang *et al.*, 2006), chlorotriphenylphosphine[2,5-bis(1,3-dithiolan-2-yl)-phenyl-S]palladium(II) (IVUFEK; Vicente *et al.*, 2004), *rac-trans*-dichlorobis{[2-(1,3-dithiolan-2-yl)phenyl](diphenyl)-phosphine}ruthenium(II) chloroform solvate (TUMKOC; 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 [Cu(MeCN)$_4$][PF$_6$] (372 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 ml) was added an equimolar amount of 1,3-dithiolane (**L1**) *via* a syringe. The solution was stirred at 293 K for 2 h, then layered with Et$_2$O (10 ml) and stored in a refrigerator for 2 days. Colourless block-like crystals formed progressively (245 mg, 68% yield).

Elemental analysis calculated for C$_{10}$H$_{18}$Cu$_2$F$_{12}$N$_2$P$_2$S$_4$: C, 16.88; H, 2.54; N, 3.94; S, 18.03%. Found: C, 16.44; H, 2.28; N, 3.44; S, 17.81%. IR (ATR; cm^{-1}): 2280 *w* (weak) (CN), 835 *vs* (very strong) (PF$_6$).

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_{iso}(H) = 1.5U_{eq}(C-methyl) and 1.2U_{eq}(C) for other H atoms. The structure was refined as a two-component inversion twin; 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.

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

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_2H_3N)_2(C_3H_6S_2)_2]$ $(PF_6)_2$
M_r	711.52
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	105
a, b, c (Å)	11.8409 (9), 12.9273 (9), 15.2921 (11)
V (Å³)	2340.8 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	2.41
Crystal size (mm)	$0.33 \times 0.32 \times 0.27$
Data collection	
Diffractometer	Bruker D8 VENTURE area detector
Absorption correction	Multi-scan (*TWINABS*; Bruker, 2016)
T_{min}, T_{max}	0.608, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40393, 8122, 7092
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.769
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.080, 1.03
No. of reflections	8122
No. of parameters	293
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.93, −0.73

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).

References

Abel, E. W., Orrell, K. G., Qureshi, K. B. & Šik, V. (1990). *Polyhedron*, **9**, 703–711.

Ahrland, S., Dreisch, K., Norén, B. & Oskarsson, A. (1993). *Mater. Chem. Phys.* **35**, 281–289.

Ainscough, E. W., Brodie, A. M., Husbands, J. M., Gainsford, G. J., Gabe, E. J. & Curtis, N. F. (1985). *J. Chem. Soc. Dalton Trans.* pp. 151–158.

Bayly, S. R., Cowley, A. R., Dilworth, J. R. & Ward, C. V. (2009). *Eur. J. Inorg. Chem.* pp. 3807–3813.

Braunwarth, H., Lau, P., Huttner, V., Minelli, M., Günauer, D., Zsolnai, V., Jibril, I. & Evertz, V. (1991). *J. Organomet. Chem.* **411**, 383–394.

Brodersen, K. & Rölz, W. (1977). *Chem. Ber.* **110**, 1042–1046.

Bruker (2016). *APEX2, SAINT* and *TWINABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chaabéne, M., Khatyr, A., Knorr, M., Askri, M., Rousselin, Y. & Kubicki, M. M. (2016). *Inorg. Chim. Acta*, **451**, 177–186.

Dembo, M. D., Dunaway, L. E., Jones, J. S., Lepekhina, E. A., McCullough, S. M., Ming, J. L., Li, X., Baril-Robert, F., Patterson, H. H., Bayse, C. A. & Pike, R. D. (2010). *Inorg. Chim. Acta*, **364**, 102–114.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Gondi, S. R., Zhang, H. & Son, D. Y. (2011). *J. Sulfur Chem.* **32**, 17–21.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Knaust, J. M. & Keller, S. W. (2003). *CrystEngComm*, **5**, 459–465.

Knorr, M., Khatyr, A., Dini Aleo, A., El Yaagoubi, A., Strohmann, C., Kubicki, M. M., Rousselin, Y., Aly, S. M., Fortin, D., Lapprand, A. & Harvey, P. D. (2014). *Cryst. Growth Des.* **14**, 5373–5387.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Mälger, H., Olbrich, F., Kopf, J., Abeln, D. & Weiss, E. (1992). *Z. Naturforsch. B*, **47**, 1276–1280.

Norén, B. & Oskarsson, Å. (1985). *Acta Chem. Scand.* **39a**, 701–709.

Peindy, H. N., Guyon, F., Khatyr, A., Knorr, M. & Strohmann, C. (2007). *Eur. J. Inorg. Chem.* pp. 1823–1828.

Raghuvanshi, A., Dargallay, N. J., Knorr, M., Viau, L., Knauer, L. & Strohmann, C. (2017). *J. Inorg. Organomet. Polym.* **27**, 1501–1513.

Raghuvanshi, A., Knorr, M., Knauer, L., Strohmann, C., Boullanger, S., Moutarlier, V. & Viau, L. (2019). *Inorg. Chem.* **58**, 5753–5775.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Usón, R., Laguna, A., Laguna, M., Manzano, B. R., Jones, P. G. & Sheldrick, G. M. (1984). *J. Chem. Soc. Dalton Trans.* pp. 285–292.

Vicente, J., Abad, J.-A., Hernández-Mata, F. S., Rink, B., Jones, P. G. & Ramírez de Arellano, M. C. (2004). *Organometallics*, **23**, 1292–1304.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Yang, L., Powell, D. R. & Houser, R. P. (2007). *Dalton Trans.* pp. 955–964.

Zhang, H., Gondi, S. R. & Son, D. Y. (2006). *Acta Cryst.* E**62**, m3086–m3088.

supporting information

Crystal structure of the coordination polymer *catena*-poly[[[(acetonitrile-*κN*)copper(I)]-*μ₃*-1,3-dithiolane-*κ³S:S:S′*] hexafluoridophosphate]

Lena Knauer, Michael Knorr, Lydie Viau and Carsten Strohmann

Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2*(Dolomanov *et al.*, 2009), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

catena-**Poly[[[(acetonitrile-*κN*)copper(I)]-*μ₃*-1,3-dithiolane-*κ³S:S:S′*] hexafluoridophosphate]**

Crystal data

$[Cu_2(C_2H_3N)_2(C_3H_6S_2)_2](PF_6)_2$	$D_x = 2.019$ Mg m^{-3}
$M_r = 711.52$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pna2_1$	Cell parameters from 9565 reflections
$a = 11.8409$ (9) Å	$\theta = 2.7–31.8°$
$b = 12.9273$ (9) Å	$\mu = 2.41$ mm^{-1}
$c = 15.2921$ (11) Å	$T = 105$ K
$V = 2340.8$ (3) Å^3	Block, colourless
$Z = 4$	$0.33 \times 0.32 \times 0.27$ mm
$F(000) = 1408$	

Data collection

Bruker D8 VENTURE area detector diffractometer	$T_{min} = 0.608$, $T_{max} = 0.746$
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs	40393 measured reflections
HELIOS mirror optics monochromator	8122 independent reflections
Detector resolution: 10.4167 pixels mm^{-1}	7092 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.040$
Absorption correction: multi-scan (*TWINABS*; Bruker, 2016)	$\theta_{max} = 33.1°$, $\theta_{min} = 2.3°$
	$h = -17 \rightarrow 17$
	$k = -19 \rightarrow 18$
	$l = -21 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.080$	
$S = 1.03$	H-atom parameters constrained
8122 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 1.7169P]$ where $P = (F_o^2 + 2F_c^2)/3$
293 parameters	
1 restraint	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: dual	$\Delta\rho_{max} = 0.93$ e Å^{-3}
	$\Delta\rho_{min} = -0.73$ e Å^{-3}

Extinction correction: (SHELXL-2018/3;
   Sheldrick, 2015b),
   $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0012 (3)

Absolute structure: Refined as an inversion
   twin.
Absolute structure parameter: 0.115 (11)

Special details

Geometry. 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.

Refinement. Refined as a two-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.84315 (3)	0.78973 (3)	0.57850 (3)	0.01740 (10)
Cu2	0.59217 (4)	0.80128 (3)	0.43586 (3)	0.01907 (10)
S1	0.73437 (7)	0.71169 (7)	0.68074 (6)	0.01758 (17)
S2	0.53256 (7)	0.75921 (6)	0.57705 (6)	0.01552 (15)
S3	0.47858 (7)	0.74560 (8)	0.32430 (7)	0.02113 (18)
S4	0.28017 (7)	0.75139 (6)	0.43792 (6)	0.01688 (16)
N1	0.8599 (3)	0.9416 (2)	0.5802 (3)	0.0218 (6)
N2	0.6146 (3)	0.9531 (3)	0.4352 (3)	0.0271 (7)
C1	0.6181 (3)	0.6541 (3)	0.6216 (3)	0.0176 (6)
H1A	0.572111	0.610665	0.661277	0.021*
H1B	0.646981	0.609859	0.573648	0.021*
C2	0.6454 (3)	0.8120 (3)	0.7273 (3)	0.0216 (7)
H2A	0.595280	0.781936	0.772430	0.026*
H2B	0.692894	0.865649	0.755319	0.026*
C3	0.5748 (3)	0.8604 (3)	0.6548 (3)	0.0229 (8)
H3A	0.619383	0.914115	0.624196	0.027*
H3B	0.506878	0.893506	0.680033	0.027*
C4	0.8973 (3)	1.0220 (3)	0.5899 (3)	0.0233 (7)
C5	0.9471 (4)	1.1236 (3)	0.6047 (3)	0.0337 (10)
H5A	1.026569	1.122572	0.586966	0.051*
H5B	0.941772	1.141126	0.666932	0.051*
H5C	0.906273	1.175400	0.570202	0.051*
C6	0.6404 (4)	1.0373 (4)	0.4332 (4)	0.0384 (10)
C7	0.6757 (8)	1.1462 (5)	0.4299 (6)	0.081 (3)
H7A	0.631809	1.182650	0.385163	0.122*
H7B	0.756221	1.150048	0.415362	0.122*
H7C	0.662709	1.178524	0.486982	0.122*
C8	0.3636 (3)	0.6684 (3)	0.3662 (3)	0.0212 (7)
H8A	0.393246	0.608356	0.399149	0.025*
H8B	0.316389	0.642406	0.317440	0.025*
C9	0.3864 (3)	0.8562 (3)	0.3071 (3)	0.0250 (8)
H9A	0.431480	0.917698	0.290743	0.030*
H9B	0.332220	0.841488	0.259437	0.030*
C10	0.3233 (3)	0.8761 (3)	0.3924 (3)	0.0241 (8)

H10A	0.256090	0.919716	0.381185	0.029*
H10B	0.372927	0.912903	0.434195	0.029*
P1	0.83561 (9)	0.41114 (8)	0.64167 (8)	0.0243 (2)
F1	0.8514 (2)	0.5141 (2)	0.5834 (2)	0.0352 (6)
F2	0.8195 (2)	0.3098 (2)	0.7025 (2)	0.0381 (7)
F3	0.9652 (2)	0.3807 (2)	0.6263 (2)	0.0400 (6)
F4	0.8733 (3)	0.4757 (2)	0.72667 (18)	0.0373 (6)
F5	0.7068 (2)	0.4413 (2)	0.6591 (3)	0.0478 (8)
F6	0.8011 (3)	0.3459 (3)	0.5585 (2)	0.0564 (10)
P2	0.56386 (9)	0.42170 (8)	0.34899 (7)	0.0242 (2)
F7	0.6297 (4)	0.5004 (3)	0.2875 (2)	0.0639 (11)
F8	0.4947 (4)	0.3435 (3)	0.4073 (2)	0.0765 (14)
F9	0.5737 (2)	0.3338 (2)	0.27453 (18)	0.0295 (5)
F10	0.6798 (2)	0.3850 (2)	0.3895 (2)	0.0402 (7)
F11	0.5557 (2)	0.5097 (2)	0.4233 (2)	0.0394 (7)
F12	0.4494 (3)	0.4601 (3)	0.3056 (3)	0.0836 (17)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01103 (17)	0.02016 (19)	0.0210 (2)	−0.00064 (14)	0.00107 (16)	−0.00060 (19)
Cu2	0.01171 (18)	0.0229 (2)	0.0226 (2)	−0.00045 (15)	0.00019 (17)	0.00155 (19)
S1	0.0107 (3)	0.0221 (4)	0.0200 (4)	0.0000 (3)	−0.0009 (3)	0.0023 (3)
S2	0.0092 (3)	0.0186 (3)	0.0188 (4)	0.0002 (3)	0.0004 (3)	0.0008 (4)
S3	0.0130 (4)	0.0303 (4)	0.0201 (4)	0.0001 (3)	0.0025 (3)	−0.0025 (4)
S4	0.0098 (3)	0.0221 (4)	0.0187 (4)	0.0007 (3)	0.0008 (3)	0.0005 (4)
N1	0.0211 (14)	0.0210 (13)	0.0232 (15)	0.0036 (11)	0.0000 (14)	−0.0005 (14)
N2	0.0294 (17)	0.0244 (14)	0.0275 (16)	−0.0013 (13)	−0.0028 (17)	0.0032 (16)
C1	0.0109 (13)	0.0188 (15)	0.0232 (17)	0.0004 (12)	−0.0012 (13)	0.0041 (13)
C2	0.0162 (16)	0.0276 (17)	0.0210 (18)	−0.0007 (13)	0.0018 (13)	−0.0030 (15)
C3	0.0167 (16)	0.0221 (16)	0.030 (2)	0.0020 (13)	−0.0030 (14)	−0.0058 (15)
C4	0.0253 (18)	0.0239 (17)	0.0208 (18)	0.0042 (14)	−0.0024 (15)	−0.0012 (15)
C5	0.044 (3)	0.0210 (18)	0.036 (2)	−0.0023 (17)	−0.010 (2)	−0.0038 (17)
C6	0.050 (3)	0.030 (2)	0.036 (2)	−0.0020 (19)	−0.009 (2)	0.006 (2)
C7	0.115 (7)	0.031 (3)	0.097 (6)	−0.017 (3)	−0.028 (6)	0.022 (4)
C8	0.0131 (15)	0.0248 (17)	0.026 (2)	−0.0002 (13)	0.0027 (13)	−0.0048 (15)
C9	0.0189 (17)	0.032 (2)	0.0241 (19)	−0.0009 (14)	−0.0017 (14)	0.0094 (16)
C10	0.0189 (17)	0.0233 (17)	0.030 (2)	0.0052 (14)	0.0044 (15)	0.0058 (15)
P1	0.0237 (5)	0.0215 (4)	0.0276 (5)	0.0015 (4)	−0.0041 (4)	0.0034 (4)
F1	0.0441 (15)	0.0313 (12)	0.0302 (13)	0.0015 (11)	−0.0016 (13)	0.0093 (12)
F2	0.0352 (14)	0.0288 (13)	0.0505 (18)	0.0056 (11)	0.0069 (13)	0.0147 (12)
F3	0.0305 (13)	0.0460 (15)	0.0434 (16)	0.0103 (12)	0.0071 (12)	0.0068 (14)
F4	0.0461 (16)	0.0389 (14)	0.0269 (13)	−0.0004 (13)	−0.0021 (13)	−0.0024 (11)
F5	0.0238 (13)	0.0352 (14)	0.084 (3)	0.0063 (11)	−0.0003 (14)	0.0167 (16)
F6	0.080 (3)	0.0400 (16)	0.049 (2)	0.0039 (16)	−0.0306 (18)	−0.0073 (14)
P2	0.0207 (4)	0.0254 (5)	0.0267 (5)	0.0014 (4)	−0.0027 (4)	−0.0060 (4)
F7	0.125 (3)	0.0390 (17)	0.0273 (15)	−0.034 (2)	−0.010 (2)	0.0043 (13)
F8	0.089 (3)	0.086 (3)	0.054 (2)	−0.059 (2)	0.040 (2)	−0.024 (2)

F9	0.0261 (12)	0.0282 (11)	0.0341 (14)	0.0008 (10)	−0.0020 (10)	−0.0097 (11)
F10	0.0383 (15)	0.0422 (15)	0.0400 (16)	0.0129 (13)	−0.0168 (13)	−0.0089 (13)
F11	0.0354 (14)	0.0431 (14)	0.0397 (17)	0.0112 (12)	−0.0089 (12)	−0.0241 (13)
F12	0.061 (2)	0.093 (3)	0.097 (3)	0.052 (2)	−0.053 (2)	−0.069 (3)

Geometric parameters (Å, º)

Cu1—N1	1.973 (3)	C5—H5A	0.9800
Cu1—S1	2.2630 (10)	C5—H5B	0.9800
Cu1—S2[i]	2.3305 (9)	C5—H5C	0.9800
Cu1—S4[i]	2.3367 (11)	C6—C7	1.469 (7)
Cu2—N2	1.980 (3)	C7—H7A	0.9800
Cu2—S3	2.2886 (11)	C7—H7B	0.9800
Cu2—S4[i]	2.3281 (9)	C7—H7C	0.9800
Cu2—S2	2.3357 (11)	C8—H8A	0.9900
S1—C1	1.808 (4)	C8—H8B	0.9900
S1—C2	1.817 (4)	C9—C10	1.524 (6)
S2—C1	1.827 (4)	C9—H9A	0.9900
S2—C3	1.836 (4)	C9—H9B	0.9900
S3—C8	1.806 (4)	C10—H10A	0.9900
S3—C9	1.817 (4)	C10—H10B	0.9900
S4—C8	1.825 (4)	P1—F6	1.579 (3)
S4—C10	1.830 (4)	P1—F5	1.597 (3)
N1—C4	1.140 (5)	P1—F3	1.602 (3)
N2—C6	1.132 (6)	P1—F4	1.608 (3)
C1—H1A	0.9900	P1—F1	1.613 (3)
C1—H1B	0.9900	P1—F2	1.617 (3)
C2—C3	1.523 (6)	P2—F8	1.577 (4)
C2—H2A	0.9900	P2—F10	1.579 (3)
C2—H2B	0.9900	P2—F12	1.588 (3)
C3—H3A	0.9900	P2—F7	1.590 (4)
C3—H3B	0.9900	P2—F11	1.611 (3)
C4—C5	1.456 (6)	P2—F9	1.613 (3)
N1—Cu1—S1	119.47 (11)	H5B—C5—H5C	109.5
N1—Cu1—S2[i]	99.97 (9)	N2—C6—C7	179.0 (7)
S1—Cu1—S2[i]	115.68 (4)	C6—C7—H7A	109.5
N1—Cu1—S4[i]	105.68 (12)	C6—C7—H7B	109.5
S1—Cu1—S4[i]	110.65 (4)	H7A—C7—H7B	109.5
S2[i]—Cu1—S4[i]	103.69 (4)	C6—C7—H7C	109.5
N2—Cu2—S3	112.75 (12)	H7A—C7—H7C	109.5
N2—Cu2—S4[i]	99.29 (11)	H7B—C7—H7C	109.5
S3—Cu2—S4[i]	118.69 (4)	S3—C8—S4	107.2 (2)
N2—Cu2—S2	106.03 (13)	S3—C8—H8A	110.3
S3—Cu2—S2	115.99 (4)	S4—C8—H8A	110.3
S4[i]—Cu2—S2	102.03 (4)	S3—C8—H8B	110.3
C1—S1—C2	92.80 (17)	S4—C8—H8B	110.3
C1—S1—Cu1	105.74 (13)	H8A—C8—H8B	108.5

C2—S1—Cu1	106.41 (13)	C10—C9—S3	107.7 (3)
C1—S2—C3	97.91 (17)	C10—C9—H9A	110.2
C1—S2—Cu1ii	109.15 (11)	S3—C9—H9A	110.2
C3—S2—Cu1ii	116.70 (13)	C10—C9—H9B	110.2
C1—S2—Cu2	110.50 (13)	S3—C9—H9B	110.2
C3—S2—Cu2	110.50 (14)	H9A—C9—H9B	108.5
Cu1ii—S2—Cu2	111.28 (4)	C9—C10—S4	108.2 (3)
C8—S3—C9	91.90 (18)	C9—C10—H10A	110.0
C8—S3—Cu2	110.66 (14)	S4—C10—H10A	110.0
C9—S3—Cu2	102.31 (14)	C9—C10—H10B	110.0
C8—S4—C10	97.95 (18)	S4—C10—H10B	110.0
C8—S4—Cu2ii	109.72 (13)	H10A—C10—H10B	108.4
C10—S4—Cu2ii	121.31 (13)	F6—P1—F5	91.0 (2)
C8—S4—Cu1ii	104.29 (13)	F6—P1—F3	89.9 (2)
C10—S4—Cu1ii	117.50 (15)	F5—P1—F3	178.8 (2)
Cu2ii—S4—Cu1ii	104.54 (4)	F6—P1—F4	178.58 (19)
C4—N1—Cu1	161.5 (3)	F5—P1—F4	90.19 (18)
C6—N2—Cu2	172.0 (4)	F3—P1—F4	88.87 (17)
S1—C1—S2	107.58 (19)	F6—P1—F1	91.48 (18)
S1—C1—H1A	110.2	F5—P1—F1	90.12 (16)
S2—C1—H1A	110.2	F3—P1—F1	90.55 (16)
S1—C1—H1B	110.2	F4—P1—F1	89.24 (16)
S2—C1—H1B	110.2	F6—P1—F2	89.98 (19)
H1A—C1—H1B	108.5	F5—P1—F2	89.37 (16)
C3—C2—S1	109.0 (3)	F3—P1—F2	89.94 (15)
C3—C2—H2A	109.9	F4—P1—F2	89.31 (17)
S1—C2—H2A	109.9	F1—P1—F2	178.46 (18)
C3—C2—H2B	109.9	F8—P2—F10	92.1 (2)
S1—C2—H2B	109.9	F8—P2—F12	89.6 (3)
H2A—C2—H2B	108.3	F10—P2—F12	178.1 (3)
C2—C3—S2	109.2 (3)	F8—P2—F7	177.8 (2)
C2—C3—H3A	109.8	F10—P2—F7	89.9 (2)
S2—C3—H3A	109.8	F12—P2—F7	88.4 (3)
C2—C3—H3B	109.8	F8—P2—F11	91.27 (19)
S2—C3—H3B	109.8	F10—P2—F11	89.26 (15)
H3A—C3—H3B	108.3	F12—P2—F11	91.32 (16)
N1—C4—C5	178.2 (5)	F7—P2—F11	89.70 (18)
C4—C5—H5A	109.5	F8—P2—F9	89.15 (17)
C4—C5—H5B	109.5	F10—P2—F9	90.17 (15)
H5A—C5—H5B	109.5	F12—P2—F9	89.25 (16)
C4—C5—H5C	109.5	F7—P2—F9	89.90 (17)
H5A—C5—H5C	109.5	F11—P2—F9	179.30 (16)
C2—S1—C1—S2	40.7 (2)	C9—S3—C8—S4	−41.9 (2)
Cu1—S1—C1—S2	−67.21 (18)	Cu2—S3—C8—S4	62.0 (2)
C3—S2—C1—S1	−23.4 (2)	C10—S4—C8—S3	22.5 (2)
Cu1ii—S2—C1—S1	−145.34 (13)	Cu2ii—S4—C8—S3	149.92 (14)
Cu2—S2—C1—S1	91.98 (18)	Cu1ii—S4—C8—S3	−98.58 (18)

C1—S1—C2—C3	−48.2 (3)	C8—S3—C9—C10	51.8 (3)
Cu1—S1—C2—C3	59.1 (3)	Cu2—S3—C9—C10	−59.9 (3)
S1—C2—C3—S2	37.2 (3)	S3—C9—C10—S4	−41.7 (3)
C1—S2—C3—C2	−8.0 (3)	C8—S4—C10—C9	11.4 (3)
Cu1ii—S2—C3—C2	108.1 (2)	Cu2ii—S4—C10—C9	−107.6 (2)
Cu2—S2—C3—C2	−123.5 (2)	Cu1ii—S4—C10—C9	122.1 (3)

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

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1A⋯F9iii	0.99	2.55	3.264 (4)	129
C1—H1A⋯F12iii	0.99	2.40	3.277 (5)	147
C2—H2A⋯F9iii	0.99	2.50	3.287 (5)	136
C3—H3B⋯F4ii	0.99	2.42	3.376 (5)	161
C5—H5C⋯F6iv	0.98	2.54	3.426 (6)	151
C8—H8A⋯F11	0.99	2.34	3.186 (5)	143
C8—H8B⋯F2v	0.99	2.46	3.323 (5)	145
C10—H10A⋯F7ii	0.99	2.31	3.221 (5)	152
C10—H10B⋯F1ii	0.99	2.48	3.264 (5)	136

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