

Received 10 October 2018

Accepted 29 October 2018

Edited by M. Weil, Vienna University of
Technology, Austria

Keywords: crystal structure; BEDT-TTF;
Cu(NCS)₂; superconductor; pseudo- κ arrange-
ment.

CCDC reference: 1876009

Supporting information: this article has
supporting information at journals.iucr.org/e

A new compound in the BEDT-TTF family [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] with a tetrathiocyanatocuprate(II) anion, (BEDT-TTF)₄[Cu(NCS)₄]

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A new phase combining BEDT-TTF and [Cu(NCS)₄]²⁻ as the counter-anion, namely bis[bis(ethylenedithio)tetrathiafulvalenium] tetrathiocyanatocuprate(II) bis[bis(ethylenedithio)tetrathiafulvalene], (C₁₀H₈S₈)₂[Cu(NCS)₄]₂·2C₁₀H₈S₈ or (BEDT-TTF)₄[Cu(NCS)₄] was obtained during a galvanostatic electrocrystallization process. As previously observed with BEDT-TTF-based compounds with oxalatometallate anions, the BEDT-TTF molecules in (BEDT-TTF)₄[Cu(NCS)₄] exhibit the so-called pseudo- κ arrangement, with two BEDT-TTF molecules being positively charged and two electronically neutral. The bond lengths and angles in the two unique BEDT-TTF molecules differ slightly. The crystal structure consists of layers of BEDT-TTF molecules extending parallel to (001). The width of this layer corresponds to the length of the *a* axis [16.9036 (17) Å]. The BEDT-TTF layers are separated by layers of centrosymmetric square-planar [Cu(NCS)₄]²⁻ dianions.

1. Chemical context

For several years, we have been interested in synthesizing molecular (super)conductors as nanoparticles (Chtioui-Gay *et al.*, 2016; Valade *et al.*, 2016; de Caro, Jacob *et al.*, 2013; de Caro, Souque *et al.*, 2013; de Caro *et al.*, 2014; Winter *et al.*, 2015) in order to study the effects of size reduction on the properties of this kind of material. As there are numerous structuring agents such as ionic liquids based, for instance, on imidazolium cations (Fig. 1), and long alkyl chains in ammonium salts or neutral amines, it is possible to obtain nanoparticles of these materials, either by electrochemical oxidation or by chemical reaction. Recently, we have focused on BEDT-TTF-based compounds [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene]. The BEDT-TTF family is one of the most studied in the field of molecular superconductors because it exhibits the largest number of superconductors with *T_c* above 10 K (Ishiguro *et al.*, 1998). During the planned electrosynthesis of (BEDT-TTF)₂[Cu(NCS)₂] as nanoparticles

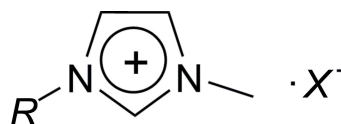
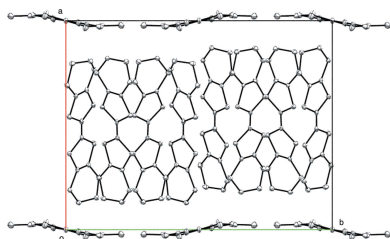
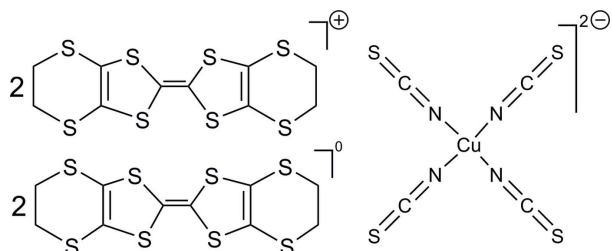


Figure 1

Examples of ionic liquids with the imidazolium fragment. For example, *R* = butyl: BMIM⁺; *R* = ethyl: EMIM⁺; *X* = PF₆⁻, BF₄⁻, SCN⁻.

from BEDT-TTF and Cu(SCN) in the presence of (EMIM)(SCN) (EMIM = 1-ethyl-3-methylimidazolium), a few crystals were formed as a minor product besides the desired powder as the main phase. A structure determination of these crystals revealed a new salt-like compound, based on the BEDT-TTF donor and the $[\text{Cu}(\text{NCS})_4]^{2-}$ dianion, namely pseudo- κ -(BEDT-TTF) $_4[\text{Cu}(\text{NCS})_4]$.



2. Structural commentary

The asymmetric unit of the title salt contains two well-ordered BEDT-TTF molecules and one $\text{Cu}(\text{NCS})_2$ entity with the Cu^{II} cation lying on an inversion centre (Fig. 2). This results in the composition $(\text{BEDT-TTF})_4[\text{Cu}(\text{NCS})_4]$, and thus is different from the well-known κ -phase $(\text{BEDT-TTF})_2[\text{Cu}(\text{NCS})_2]$ (Hiramatsu *et al.*, 2015; Schultz *et al.* 1991; Urayama *et al.*, 1988) and also from $(\text{BEDT-TTF})[\text{Cu}_2(\text{NCS})_3]$ (Geiser *et al.*, 1988). One of the two BEDT-TTF molecules (central bond C7–C8) forms a dimer that is related through an inversion centre, whereas the other BEDT-TTF molecules (central bond C17–C18) are farther away from each other. To our knowledge, this feature has not been observed within the $(\text{BEDT-TTF})[\text{Cu}(\text{NCS})_x]$ family, but it has been found in BEDT-TTF compounds with tris-(oxalato)metallate anions, such as $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\cdot\text{solv.}$ ($A = \text{K}, \text{NH}_4, \text{H}_3\text{O}$; $M = \text{Fe}, \text{Cr}, \text{Co}, \text{Ru}$; solv. = benzonitrile, 1,2-dichlorobenzene, bromobenzene) (Kurmoo *et al.*, 1995; Martin *et al.*, 2001; Prokhorova *et al.*, 2011, 2013). The latter compounds are representatives of

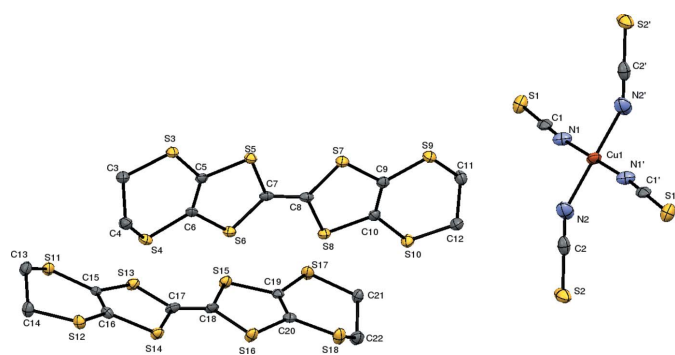


Figure 2

Molecular structure of $(\text{BEDT-TTF})_4[\text{Cu}(\text{NCS})_4]$, showing the BEDT-TTF molecule involved in the formation of a dimer (top), and the other BEDT-TTF molecule (bottom), as well as the centrosymmetric $[\text{Cu}(\text{NCS})_4]^{2-}$ dianion. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Primed atoms are generated by the symmetry operation $(-x, 1-y, 2-z)$.

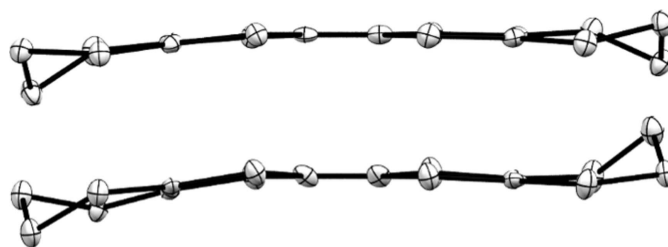


Figure 3

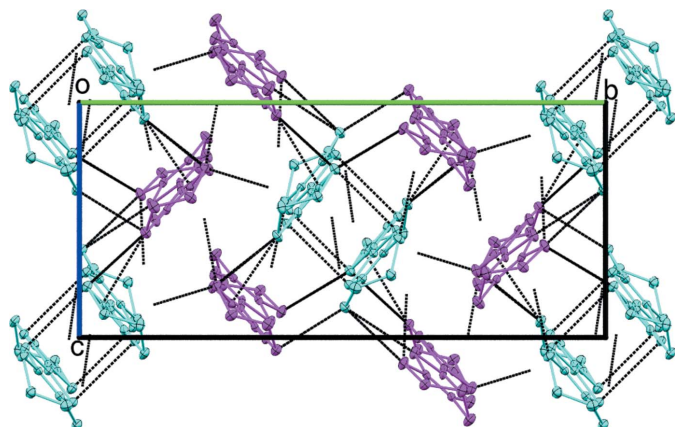
Side view of the BEDT-TTF molecules (top: in the dimer; bottom: the other molecule). Displacement ellipsoids are drawn at the 50% probability level.

the pseudo κ -phase where the two independent BEDT-TTF molecules show some slight structural differences. Similarly, the bond lengths within the central C_2S_4 core in the BEDT-TTF molecules of the title salt deviate by up to 0.035 Å. The bond lengths in the TTF core are indicative of the degree of charge in this family of BEDT-TTF compounds. According to Guionneau *et al.* (1997), this allows the charge Q of the two BEDT-TTF molecules in the title salt to be calculated. Whereas each BEDT-TTF molecule in the dimer carries a charge of +1 ($Q = 0.83$), the other BEDT-TTF molecule is neutral ($Q = 0.18$). Not only do the bond lengths of the BEDT-TTF molecules in the title salt show some differences, but the overall shape of the molecules also differs. The BEDT-TTF molecule in the dimer deviates less from planarity [r.m.s. deviation of 0.0853 Å neglecting the outer ethylene bridges, with the largest deviation being 0.1579 (19) Å for S5] than the other BEDT-TTF molecule [r.m.s. deviation of 0.1431 Å; highest deviation = 0.3273 (12) Å for S12]. Moreover, the outer ethylene groups tend to be more eclipsed in the molecule of the dimer whereas they tend to be more staggered in the other molecule (Fig. 3). All these features are similar to those reported for the $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\cdot\text{solv.}$ family.

Contrary to what is observed in other BEDT-TTF compounds associated with $[\text{Cu}(\text{NCS})_x]$ anions that are present as polymeric $[\text{Cu}(\text{NCS})_x]$ entities, in the title compound discrete $[\text{Cu}(\text{NCS})_4]^{2-}$ units are observed. The Cu^{II} cation (which lies on a centre of inversion) of the $[\text{Cu}(\text{NCS})_4]^{2-}$ dianion adopts an almost regular square-planar CuN_4 environment, with N–Cu–N angles close to 90 and 180°. Intramolecular bond lengths in the anion are in agreement with other tetrathiocyanatocuprates(II) (Wang *et al.*, 2008; Chekhlov, 2009). It should be noted that one Cu–NCS fragment is more bent than the other one [angle Cu–N2–C2 of 151.6 (4)° versus 175.2 (3)° for Cu–N1–C1; Fig. 2].

3. Supramolecular features

The BEDT-TTF molecules in the dimer stack face-to-face. The interplanar distance within the dimer is 3.62 (3) Å, considering the least-squares planes of the molecule except for the terminal ethylene groups. In addition, there are two pairs of short S···S contacts within the dimer [$\text{S5}\cdots\text{S8} = 3.461$ (1) and $\text{S6}\cdots\text{S7} = 3.515$ (1) Å]. Each dimer is surrounded by six

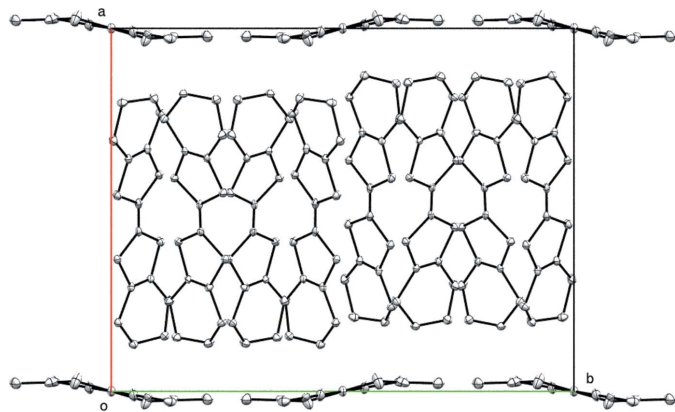

Figure 4

View along [100] of the packing of the molecular entities in the crystal structure of (BEDT-TTF)₄[Cu(NCS)₄]. The dimer of BEDT-TTF molecules (turquoise) is surrounded by other BEDT-TTF molecules (purple). Black dotted lines represent short S...S and S...H contacts shorter than the sum of the van der Waals radii (for numerical details, see: Table 1).

adjacent BEDT-TTF molecules (Fig. 4). Four of them lie nearly perpendicular to the dimer [angle of 86.16 (2)°] and are connected with the dimer through short S...S contacts (Table 1) and the two others are almost parallel to the dimer [angle of 7.09 (4)°] with short S...H contacts (Table 1). This arrangement leads to layers of BEDT-TTF donors, extending parallel to (001). The layers have a width that corresponds to the length of the *a* axis and are separated from each other by layers of [Cu(NCS)₄]²⁻ dianions (Fig. 5).

4. Synthesis and crystallization

(BEDT-TTF)₄[Cu(NCS)₄] was prepared by galvanostatic electrocrystallization in an H-shaped cell, equipped with Pt electrodes and with a glass frit between the anodic and cathodic compartments. To the cathodic compartment were added EMIM(SCN) (EMIM = 1-ethyl-3-methylimidazolium;


Figure 5

View of the structural arrangement of (BEDT-TTF)₄[Cu(NCS)₄], showing layers of BEDT-TTF molecules parallel to (001) separated by layers of [Cu(NCS)₄]²⁻ dianions.

Table 1

Table of contacts (Å) shorter than the sum of the van der Waals radii.

Atom 1...atom 2	Length	Symmetry operation on atom 2
S5...S8	3.461 (1)	1 - x, 1 - y, 1 - z
S6...S7	3.515 (1)	1 - x, 1 - y, 1 - z
S4...S12	3.463 (1)	x, y, z
S4...S14	3.586 (1)	x, y, z
S10...H21B	2.76	x, y, z
H12A...S17	2.81	x, y, 1 + z
S3...S11	3.511 (1)	x, y, 1 + z
S5...S11	3.508 (1)	x, y, 1 + z
S9...S15	3.571 (1)	x, y, 1 + z
S9...S17	3.574 (1)	x, y, 1 + z
S3...S17	3.470 (1)	1 - x, 1 - y, 1 - z
S5...S17	3.533 (1)	1 - x, 1 - y, 1 - z
S9...S11	3.522 (1)	1 - x, 1 - y, 1 - z
H4B...S12	2.74	x, $\frac{3}{2} - y, \frac{1}{2} + z$
S12...H14A	2.73	x, $\frac{3}{2} - y, \frac{1}{2} + z$

60 µl, 0.4 mmol) and freshly distilled 1,1,2-TCE (TCE = trichloroethylene; 10 ml). Cu(NCS) (8 mg, 0.07 mmol) and EMIM(SCN) (60 µL, 0.4 mmol) were added to the anodic compartment, which was immediately filled with BEDT-TTF (30 mg, 0.08 mmol), previously dissolved in 10 ml of 1,1,2-TCE at 343 K. The current was set at 100 µA (current density of 318 µA cm⁻²). After 12 h, a black powder corresponding to the desired compound (BEDT-TTF)₂[Cu(NCS)₂] was harvested by filtration, together with some crystals of (BEDT-TTF)₄[Cu(NCS)₄], which were washed with 1,1,2-TCE and dried under vacuum.

Table 2

Experimental details.

Crystal data	
Chemical formula	(C ₁₀ H ₈ S ₈) ₂ [Cu(CNS) ₄]·2C ₁₀ H ₈ S ₈
<i>M_r</i>	1834.43
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.9036 (17), 21.004 (2), 9.6205 (9)
β (°)	103.071 (3)
<i>V</i> (Å ³)	3327.1 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.50
Crystal size (mm)	0.18 × 0.16 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEXII Quazar CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.652, 0.745
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	48335, 5028, 3816
<i>R_{int}</i>	0.070
θ _{max} (°)	23.7
(sin θ/λ) _{max} (Å ⁻¹)	0.566
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.078, 1.02
No. of reflections	5028
No. of parameters	385
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.38, -0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *WinGX* (Farrugia, 2012).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal diffracted rather weakly ($2\theta_{\max} = 47.42^\circ$). The hydrogen atoms of the ethylene bridges were placed in idealized positions and were refined with C–H = 0.99 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Reflections (100) and (110) were obstructed by the beam stop and thus were excluded from the refinement.

Acknowledgements

Sonia Mallet-Ladeira is acknowledged for her help and discussions related with X-ray diffraction.

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supporting information

Acta Cryst. (2018). E74, 1755-1758 [https://doi.org/10.1107/S2056989018015293]

A new compound in the BEDT-TTF family [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] with a tetrathiocyanatocuprate(II) anion, (BEDT-TTF)₄[Cu(NCS)₄]

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bis[bis(ethylenedithio)tetrathiafulvalenium] tetrathiocyanatocuprate(II) bis[bis(ethylenedithio)tetrathiafulvalene]

Crystal data

(C₁₀H₈S₈)₂[Cu(CNS)₄]₂·2C₁₀H₈S₈
M_r = 1834.43
 Monoclinic, *P*2₁/*c*
a = 16.9036 (17) Å
b = 21.004 (2) Å
c = 9.6205 (9) Å
 β = 103.071 (3)°
V = 3327.1 (6) Å³
Z = 2

F(000) = 1858
D_x = 1.831 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 7249 reflections
 θ = 2.4–23.5°
 μ = 1.50 mm⁻¹
T = 100 K
 Plate, orange
 0.18 × 0.16 × 0.02 mm

Data collection

Bruker Kappa APEXII Quazar CCD
 diffractometer
 Radiation source: microfocus sealed tube
 Multilayer optics monochromator
 phi and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2012)
T_{min} = 0.652, *T_{max}* = 0.745

48335 measured reflections
 5028 independent reflections
 3816 reflections with *I* > 2σ(*I*)
R_{int} = 0.070
 θ_{\max} = 23.7°, θ_{\min} = 2.4°
h = -19→19
k = -23→23
l = -10→10

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.032
wR(*F*²) = 0.078
S = 1.02
 5028 reflections
 385 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 4.1709P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.0171 (2)	0.42002 (18)	0.7252 (4)	0.0213 (9)
C2	0.0246 (2)	0.6302 (2)	0.8878 (4)	0.0253 (10)
C3	0.8700 (2)	0.54753 (16)	0.5992 (4)	0.0187 (9)
H3A	0.928155	0.545997	0.647921	0.022*
H3B	0.862454	0.520423	0.512981	0.022*
C4	0.8478 (2)	0.61543 (17)	0.5535 (4)	0.0209 (9)
H4A	0.890091	0.632876	0.507824	0.025*
H4B	0.847851	0.641325	0.639476	0.025*
C5	0.7131 (2)	0.54291 (16)	0.6393 (4)	0.0149 (8)
C6	0.6896 (2)	0.58496 (16)	0.5308 (4)	0.0160 (8)
C7	0.5595 (2)	0.55932 (15)	0.6157 (4)	0.0149 (8)
C8	0.4827 (2)	0.55887 (16)	0.6416 (4)	0.0154 (8)
C9	0.3595 (2)	0.53724 (16)	0.7503 (4)	0.0154 (8)
C10	0.3323 (2)	0.57822 (16)	0.6408 (4)	0.0160 (8)
C11	0.2046 (2)	0.52444 (17)	0.7908 (4)	0.0209 (9)
H11A	0.184487	0.494450	0.711275	0.025*
H11B	0.171329	0.518267	0.862179	0.025*
C12	0.1924 (2)	0.59208 (17)	0.7337 (4)	0.0209 (9)
H12A	0.217762	0.621861	0.810709	0.025*
H12B	0.133437	0.601329	0.708352	0.025*
C13	0.8509 (2)	0.64170 (17)	0.0556 (4)	0.0215 (9)
H13A	0.858052	0.616445	0.144492	0.026*
H13B	0.892041	0.626958	0.004150	0.026*
C14	0.8670 (2)	0.71118 (17)	0.0950 (4)	0.0203 (9)
H14A	0.852389	0.737338	0.007359	0.024*
H14B	0.925749	0.716993	0.136028	0.024*
C15	0.6912 (2)	0.66642 (16)	0.0439 (4)	0.0132 (8)
C16	0.7133 (2)	0.71147 (16)	0.1441 (4)	0.0156 (8)
C17	0.5605 (2)	0.69326 (16)	0.1286 (4)	0.0169 (9)
C18	0.4857 (2)	0.69108 (16)	0.1551 (4)	0.0165 (9)
C19	0.3385 (2)	0.65929 (16)	0.1588 (4)	0.0141 (8)
C20	0.3569 (2)	0.70712 (16)	0.2528 (4)	0.0149 (8)
C21	0.1796 (2)	0.65689 (16)	0.2003 (4)	0.0168 (9)
H21A	0.123433	0.652063	0.142740	0.020*
H21B	0.182206	0.635883	0.293364	0.020*
C22	0.1970 (2)	0.72687 (17)	0.2261 (4)	0.0229 (9)
H22A	0.152515	0.746340	0.263158	0.028*
H22B	0.197940	0.747725	0.134226	0.028*
S1	−0.02733 (6)	0.37420 (5)	0.58614 (11)	0.0285 (3)

S2	0.02204 (7)	0.70695 (5)	0.86453 (12)	0.0331 (3)
S3	0.81075 (6)	0.51479 (4)	0.71701 (10)	0.0169 (2)
S4	0.75024 (6)	0.62342 (4)	0.43121 (10)	0.0210 (2)
S5	0.63665 (5)	0.51340 (4)	0.71623 (10)	0.0158 (2)
S6	0.58730 (6)	0.60578 (4)	0.48575 (10)	0.0173 (2)
S7	0.46026 (6)	0.51311 (4)	0.77698 (10)	0.0178 (2)
S8	0.40302 (6)	0.60313 (4)	0.54464 (10)	0.0167 (2)
S9	0.30860 (6)	0.50474 (4)	0.87210 (10)	0.0198 (2)
S10	0.23390 (6)	0.60719 (4)	0.57979 (10)	0.0198 (2)
S11	0.75135 (6)	0.62589 (4)	−0.05352 (10)	0.0183 (2)
S12	0.81090 (6)	0.73927 (4)	0.22123 (10)	0.0178 (2)
S13	0.58828 (6)	0.64487 (4)	−0.00163 (10)	0.0180 (2)
S14	0.63616 (6)	0.74608 (4)	0.21522 (10)	0.0183 (2)
S15	0.41224 (6)	0.63676 (4)	0.06567 (10)	0.0180 (2)
S16	0.45292 (6)	0.74247 (4)	0.27426 (11)	0.0212 (2)
S17	0.24819 (6)	0.61583 (4)	0.10988 (11)	0.0208 (2)
S18	0.29242 (6)	0.74148 (5)	0.35111 (10)	0.0232 (2)
Cu1	0.000000	0.500000	1.000000	0.02233 (18)
N1	−0.0100 (2)	0.45238 (15)	0.8251 (4)	0.0282 (8)
N2	0.0279 (2)	0.57616 (18)	0.9071 (4)	0.0379 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.015 (2)	0.017 (2)	0.030 (2)	0.0038 (17)	0.0001 (19)	0.0093 (19)
C2	0.019 (2)	0.037 (3)	0.021 (2)	−0.0072 (19)	0.0067 (19)	−0.005 (2)
C3	0.019 (2)	0.017 (2)	0.021 (2)	0.0019 (16)	0.0063 (18)	0.0027 (16)
C4	0.016 (2)	0.016 (2)	0.030 (2)	−0.0010 (16)	0.0057 (18)	0.0024 (17)
C5	0.019 (2)	0.0108 (19)	0.016 (2)	0.0001 (16)	0.0054 (17)	−0.0015 (16)
C6	0.018 (2)	0.0103 (19)	0.020 (2)	−0.0008 (16)	0.0063 (17)	−0.0007 (16)
C7	0.020 (2)	0.0085 (18)	0.014 (2)	0.0001 (16)	0.0009 (17)	−0.0022 (15)
C8	0.021 (2)	0.0120 (19)	0.0123 (19)	0.0009 (16)	0.0007 (17)	0.0001 (15)
C9	0.018 (2)	0.0137 (19)	0.015 (2)	−0.0001 (16)	0.0038 (17)	−0.0028 (16)
C10	0.022 (2)	0.0123 (19)	0.014 (2)	0.0002 (16)	0.0058 (17)	−0.0027 (16)
C11	0.018 (2)	0.024 (2)	0.022 (2)	−0.0023 (17)	0.0077 (18)	0.0015 (17)
C12	0.022 (2)	0.019 (2)	0.023 (2)	0.0047 (17)	0.0083 (18)	0.0018 (17)
C13	0.016 (2)	0.023 (2)	0.026 (2)	0.0008 (17)	0.0075 (18)	−0.0040 (18)
C14	0.017 (2)	0.024 (2)	0.021 (2)	−0.0037 (17)	0.0063 (18)	−0.0055 (17)
C15	0.014 (2)	0.0102 (19)	0.017 (2)	0.0009 (15)	0.0056 (16)	0.0041 (16)
C16	0.016 (2)	0.016 (2)	0.016 (2)	−0.0024 (16)	0.0046 (17)	0.0025 (16)
C17	0.017 (2)	0.0100 (19)	0.021 (2)	0.0014 (16)	−0.0003 (18)	−0.0036 (16)
C18	0.018 (2)	0.0079 (19)	0.022 (2)	−0.0009 (16)	0.0029 (18)	−0.0031 (16)
C19	0.014 (2)	0.0114 (19)	0.016 (2)	0.0010 (15)	0.0025 (17)	0.0051 (16)
C20	0.018 (2)	0.0107 (19)	0.015 (2)	−0.0001 (15)	0.0014 (17)	0.0026 (15)
C21	0.013 (2)	0.020 (2)	0.019 (2)	−0.0009 (16)	0.0042 (17)	−0.0043 (16)
C22	0.019 (2)	0.019 (2)	0.031 (2)	−0.0010 (17)	0.0078 (19)	−0.0043 (18)
S1	0.0236 (6)	0.0350 (6)	0.0274 (6)	0.0033 (5)	0.0066 (5)	−0.0062 (5)
S2	0.0253 (6)	0.0306 (6)	0.0430 (7)	0.0026 (5)	0.0070 (5)	0.0175 (5)

S3	0.0160 (5)	0.0153 (5)	0.0196 (5)	0.0019 (4)	0.0045 (4)	0.0046 (4)
S4	0.0236 (6)	0.0184 (5)	0.0222 (6)	0.0021 (4)	0.0079 (5)	0.0087 (4)
S5	0.0155 (5)	0.0143 (5)	0.0170 (5)	0.0004 (4)	0.0027 (4)	0.0033 (4)
S6	0.0195 (6)	0.0141 (5)	0.0183 (5)	0.0024 (4)	0.0041 (4)	0.0033 (4)
S7	0.0188 (5)	0.0169 (5)	0.0175 (5)	0.0019 (4)	0.0037 (4)	0.0032 (4)
S8	0.0173 (5)	0.0146 (5)	0.0180 (5)	0.0018 (4)	0.0034 (4)	0.0031 (4)
S9	0.0217 (6)	0.0186 (5)	0.0199 (5)	0.0014 (4)	0.0065 (4)	0.0051 (4)
S10	0.0189 (6)	0.0222 (5)	0.0185 (5)	0.0052 (4)	0.0046 (4)	0.0044 (4)
S11	0.0172 (5)	0.0180 (5)	0.0209 (5)	-0.0026 (4)	0.0067 (4)	-0.0048 (4)
S12	0.0160 (5)	0.0194 (5)	0.0180 (5)	-0.0045 (4)	0.0041 (4)	-0.0033 (4)
S13	0.0139 (5)	0.0148 (5)	0.0243 (6)	-0.0003 (4)	0.0024 (4)	-0.0042 (4)
S14	0.0151 (5)	0.0135 (5)	0.0259 (5)	-0.0006 (4)	0.0038 (4)	-0.0049 (4)
S15	0.0142 (5)	0.0156 (5)	0.0242 (5)	-0.0017 (4)	0.0045 (4)	-0.0062 (4)
S16	0.0163 (5)	0.0179 (5)	0.0300 (6)	-0.0027 (4)	0.0066 (5)	-0.0093 (4)
S17	0.0200 (6)	0.0175 (5)	0.0272 (6)	-0.0061 (4)	0.0099 (5)	-0.0074 (4)
S18	0.0221 (6)	0.0239 (5)	0.0260 (6)	-0.0060 (4)	0.0102 (5)	-0.0116 (4)
Cu1	0.0214 (4)	0.0135 (3)	0.0321 (4)	-0.0006 (3)	0.0061 (3)	-0.0034 (3)
N1	0.033 (2)	0.0178 (18)	0.032 (2)	0.0032 (16)	0.0023 (17)	0.0016 (17)
N2	0.053 (3)	0.026 (2)	0.041 (2)	-0.0139 (19)	0.024 (2)	-0.0099 (18)

Geometric parameters (Å, °)

C1—N1	1.161 (5)	C14—H14A	0.9900
C1—S1	1.625 (4)	C14—H14B	0.9900
C2—N2	1.149 (5)	C15—C16	1.342 (5)
C2—S2	1.627 (5)	C15—S11	1.752 (4)
C3—C4	1.514 (5)	C15—S13	1.755 (4)
C3—S3	1.809 (4)	C16—S12	1.749 (4)
C3—H3A	0.9900	C16—S14	1.761 (4)
C3—H3B	0.9900	C17—C18	1.346 (5)
C4—S4	1.804 (4)	C17—S14	1.755 (4)
C4—H4A	0.9900	C17—S13	1.758 (4)
C4—H4B	0.9900	C18—S16	1.753 (4)
C5—C6	1.357 (5)	C18—S15	1.761 (4)
C5—S5	1.742 (4)	C19—C20	1.340 (5)
C5—S3	1.753 (4)	C19—S17	1.749 (4)
C6—S6	1.740 (4)	C19—S15	1.757 (4)
C6—S4	1.751 (4)	C20—S18	1.752 (4)
C7—C8	1.377 (5)	C20—S16	1.755 (4)
C7—S5	1.731 (4)	C21—C22	1.508 (5)
C7—S6	1.732 (4)	C21—S17	1.817 (4)
C8—S8	1.726 (4)	C21—H21A	0.9900
C8—S7	1.728 (4)	C21—H21B	0.9900
C9—C10	1.358 (5)	C22—S18	1.807 (4)
C9—S7	1.740 (4)	C22—H22A	0.9900
C9—S9	1.742 (4)	C22—H22B	0.9900
C10—S10	1.743 (4)	S3—S17 ⁱ	3.4702 (13)
C10—S8	1.749 (4)	S3—S11 ⁱⁱ	3.5113 (13)

C11—C12	1.520 (5)	S4—S12	3.4627 (13)
C11—S9	1.803 (4)	S4—S14	3.5862 (13)
C11—H11A	0.9900	S5—S11 ⁱⁱ	3.5079 (13)
C11—H11B	0.9900	S5—S17 ⁱ	3.5330 (13)
C12—S10	1.805 (4)	S6—S7 ⁱ	3.5146 (13)
C12—H12A	0.9900	S9—S11 ⁱ	3.5216 (13)
C12—H12B	0.9900	S9—S15 ⁱⁱ	3.5707 (13)
C13—C14	1.517 (5)	S9—S17 ⁱⁱ	3.5743 (14)
C13—S11	1.802 (4)	Cu1—N1	1.932 (4)
C13—H13A	0.9900	Cu1—N1 ⁱⁱⁱ	1.932 (4)
C13—H13B	0.9900	Cu1—N2 ⁱⁱⁱ	1.942 (4)
C14—S12	1.800 (4)	Cu1—N2	1.942 (4)
N1—C1—S1	179.5 (4)	C19—C20—S18	126.5 (3)
N2—C2—S2	178.3 (4)	C19—C20—S16	117.6 (3)
C4—C3—S3	113.8 (3)	S18—C20—S16	115.7 (2)
C4—C3—H3A	108.8	C22—C21—S17	114.8 (3)
S3—C3—H3A	108.8	C22—C21—H21A	108.6
C4—C3—H3B	108.8	S17—C21—H21A	108.6
S3—C3—H3B	108.8	C22—C21—H21B	108.6
H3A—C3—H3B	107.7	S17—C21—H21B	108.6
C3—C4—S4	114.0 (3)	H21A—C21—H21B	107.5
C3—C4—H4A	108.8	C21—C22—S18	112.7 (3)
S4—C4—H4A	108.8	C21—C22—H22A	109.0
C3—C4—H4B	108.8	S18—C22—H22A	109.0
S4—C4—H4B	108.8	C21—C22—H22B	109.0
H4A—C4—H4B	107.7	S18—C22—H22B	109.0
C6—C5—S5	116.2 (3)	H22A—C22—H22B	107.8
C6—C5—S3	129.2 (3)	C5—S3—C3	101.87 (17)
S5—C5—S3	114.62 (19)	C5—S3—S17 ⁱ	97.25 (12)
C5—C6—S6	117.2 (3)	C3—S3—S17 ⁱ	149.40 (12)
C5—C6—S4	128.0 (3)	C5—S3—S11 ⁱⁱ	70.65 (12)
S6—C6—S4	114.8 (2)	C3—S3—S11 ⁱⁱ	114.76 (12)
C8—C7—S5	121.2 (3)	S17 ⁱ —S3—S11 ⁱⁱ	94.00 (3)
C8—C7—S6	123.7 (3)	C6—S4—C4	99.35 (18)
S5—C7—S6	115.1 (2)	C6—S4—S12	158.54 (12)
C7—C8—S8	123.5 (3)	C4—S4—S12	95.63 (13)
C7—C8—S7	121.1 (3)	C6—S4—S14	110.11 (12)
S8—C8—S7	115.4 (2)	C4—S4—S14	137.49 (12)
C10—C9—S7	116.6 (3)	S12—S4—S14	49.34 (3)
C10—C9—S9	129.6 (3)	C7—S5—C5	95.85 (17)
S7—C9—S9	113.8 (2)	C7—S5—S11 ⁱⁱ	102.50 (12)
C9—C10—S10	127.8 (3)	C5—S5—S11 ⁱⁱ	70.81 (12)
C9—C10—S8	116.6 (3)	C7—S5—S17 ⁱ	163.25 (12)
S10—C10—S8	115.6 (2)	C5—S5—S17 ⁱ	95.28 (12)
C12—C11—S9	114.3 (3)	S11 ⁱⁱ —S5—S17 ⁱ	92.97 (3)
C12—C11—H11A	108.7	C7—S6—C6	95.43 (17)
S9—C11—H11A	108.7	C7—S6—S7 ⁱ	93.63 (12)

C12—C11—H11B	108.7	C6—S6—S7 ⁱ	93.06 (12)
S9—C11—H11B	108.7	C8—S7—C9	95.80 (17)
H11A—C11—H11B	107.6	C8—S8—C10	95.53 (17)
C11—C12—S10	114.5 (3)	C8—S8—S5 ⁱ	90.59 (12)
C11—C12—H12A	108.6	C10—S8—S5 ⁱ	97.38 (12)
S10—C12—H12A	108.6	C9—S9—C11	101.52 (17)
C11—C12—H12B	108.6	C9—S9—S11 ⁱ	151.62 (12)
S10—C12—H12B	108.6	C11—S9—S11 ⁱ	91.85 (12)
H12A—C12—H12B	107.6	C9—S9—S15 ⁱⁱ	77.75 (12)
C14—C13—S11	114.4 (3)	C11—S9—S15 ⁱⁱ	111.30 (13)
C14—C13—H13A	108.6	S11 ⁱ —S9—S15 ⁱⁱ	120.58 (3)
S11—C13—H13A	108.6	C9—S9—S17 ⁱⁱ	115.51 (12)
C14—C13—H13B	108.6	C11—S9—S17 ⁱⁱ	74.71 (13)
S11—C13—H13B	108.6	S11 ⁱ —S9—S17 ⁱⁱ	92.03 (3)
H13A—C13—H13B	107.6	S15 ⁱⁱ —S9—S17 ⁱⁱ	48.46 (3)
C13—C14—S12	113.1 (3)	C10—S10—C12	100.41 (17)
C13—C14—H14A	109.0	C15—S11—C13	100.20 (17)
S12—C14—H14A	109.0	C16—S12—C14	101.22 (17)
C13—C14—H14B	109.0	C16—S12—S4	68.74 (12)
S12—C14—H14B	109.0	C14—S12—S4	115.70 (13)
H14A—C14—H14B	107.8	C15—S13—C17	94.73 (17)
C16—C15—S11	128.8 (3)	C17—S14—C16	94.53 (17)
C16—C15—S13	117.4 (3)	C17—S14—S4	93.43 (12)
S11—C15—S13	113.79 (19)	C16—S14—S4	65.17 (11)
C15—C16—S12	128.5 (3)	C19—S15—C18	94.55 (17)
C15—C16—S14	117.4 (3)	C18—S16—C20	94.76 (17)
S12—C16—S14	114.1 (2)	C19—S17—C21	103.65 (17)
C18—C17—S14	123.1 (3)	C20—S18—C22	98.12 (17)
C18—C17—S13	122.0 (3)	N1—Cu1—N1 ⁱⁱⁱ	180.0
S14—C17—S13	114.9 (2)	N1—Cu1—N2 ⁱⁱⁱ	89.53 (14)
C17—C18—S16	123.5 (3)	N1 ⁱⁱⁱ —Cu1—N2 ⁱⁱⁱ	90.47 (14)
C17—C18—S15	121.2 (3)	N1—Cu1—N2	90.46 (14)
S16—C18—S15	115.2 (2)	N1 ⁱⁱⁱ —Cu1—N2	89.53 (14)
C20—C19—S17	128.9 (3)	N2 ⁱⁱⁱ —Cu1—N2	180.0
C20—C19—S15	117.6 (3)	C1—N1—Cu1	175.2 (3)
S17—C19—S15	113.5 (2)	C2—N2—Cu1	151.6 (4)

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