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1,1′-(Ethane-1,2-diyl)dipyridinium bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')cuprate(II)

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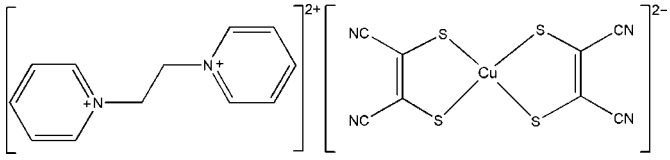
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.005 Å; R factor = 0.036; wR factor = 0.083; data-to-parameter ratio = 14.0.

In the title ion-pair complex, $(C_{12}H_{14}N_2)[Cu(C_4N_2S_2)_2]$, the complex anion exhibits a highly twisted coordination environment around the tetracoordinated Cu^{II} atom. The dihedral angles between the 1,2-dicyanoethene-1,2-dithiolato ligands and between the two pyridine rings in the cation are 37.49 (3) and 29.18 (10)°, respectively. Weak C—H···N and C—H···S hydrogen bonds link the cations and anions into a three-dimensional network.

Related literature

For background to crystalline molecular materials and coordination polymer networks, see: Brammer (2004); Robin & Fromm (2006). For 1,2-dithiolene–metal complexes, see: Duan *et al.* (2010); Ni *et al.* (2005). For related structures, see: Ren *et al.* (2006); Wang *et al.* (2012).



Experimental

Crystal data

$(C_{12}H_{14}N_2)[Cu(C_4N_2S_2)_2]$
M_r = 530.20
Triclinic, $P\overline{1}$
a = 7.7598 (10) Å
b = 12.3811 (15) Å
c = 12.6572 (16) Å
α = 77.676 (2)°
β = 72.791 (2)°
γ = 84.122 (2)°
V = 1133.8 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.35 mm^{-1}
T = 291 K
0.25 × 0.20 × 0.15 mm

Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.730, T_{max} = 0.815
5682 measured reflections
3921 independent reflections
3217 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.083
S = 1.00
3921 reflections
280 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11A···N2^{i}	0.93	2.61	3.356 (4)	137
C14—H14A···N4^{ii}	0.97	2.60	3.341 (4)	133
C14—H14B···N1^{iii}	0.97	2.60	3.479 (4)	151
C15—H15B···S1	0.97	2.83	3.769 (3)	163
C16—H16A···N2^{iv}	0.93	2.56	3.368 (4)	146
C17—H17A···S2^{iv}	0.93	2.82	3.743 (3)	171
C19—H19A···N3^{v}	0.93	2.56	3.235 (4)	129
C20—H20A···N1^{iii}	0.93	2.52	3.422 (4)	164

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2624).

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Wang, F.-M., Chen, L.-Z., Liu, Y.-M., Lu, C.-S., Duan, X.-Y. & Meng, Q.-J. (2012). *J. Coord. Chem.* **65**, 87–103.

supplementary materials

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1,1′-(Ethane-1,2-diyl)dipyridinium bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')cuprate(II)

Bing-Xiang Hu, Chang-Xiao Zhou, Yang-Mei Liu, Li-Zhuang Chen and Fang-Ming Wang

Comment

During the past few years, the molecular-based materials are widely studied due to their novel applications in the areas of materials science, medicines, biology and so on (Brammer, 2004; Robin & Fromm, 2006). Among these materials, maleonitriledithiolate (mnt) transition metal complexes are a typical kind of bis(1,2-dithiolene) complexes used as building blocks, because they possess an extended electronically delocalized core comprising a central metal, four S atoms and C═C units (Duan *et al.*, 2010; Ni *et al.*, 2005). Studies showed that weak inter- or intramolecular interactions in the complexes could influence on their properties (Ren *et al.*, 2006; Wang *et al.*, 2012).

In order to know how the cations affects the stacking mode of $[Cu(mnt)_2]^{2-}$ anion, herein, we present a new ion-pair complex. As shown in Fig. 1, it consists of one ethane-1,2-dipydinium $(PyEtPy)^{2+}$ cation and a $[Cu(mnt)_2]^{2-}$ dianion in the asymmetric unit. The $[Cu(mnt)_2]^{2-}$ anion exhibits highly twisted coordination environment around the tetracoordinated Cu^{II} atom. The dihedral angle between the two mnt ligands is 37.49 (3)°, which is the largest value in this kind complexes. The dihedral angle between two pyridyl planes in the organic cation is 29.18 (10)°. It is seen from Table 1 and Fig. 2 that the crystal structure is stabilized by weak C—H···N and C—H···S hydrogen bonds, which link the cations and anions into a three-dimensional network.

Experimental

The synthesis route of the title compound is similar to reference (Wang *et al.*, 2012). It was prepared by a direct reaction of $CuCl_2$ (0.171g, 1.0 mmol), Na_2(mnt) (0.372g, 2.0 mmol) and ethane-1,2-dipydinium bromide (0.344g, 1.0 mmol) in a mixed solution of ethanol and H_2O (v/v 1:1; 20 ml). After filtration, brown-red block-like single crystals were obtained by slow evaporation of the crude in an acetonitrile solution at room temperature in about two weeks.

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.97 (methylene) and 0.93 (pyridyl) Å and with U_{iso}(H) = 1.2U_{eq}(C).

Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

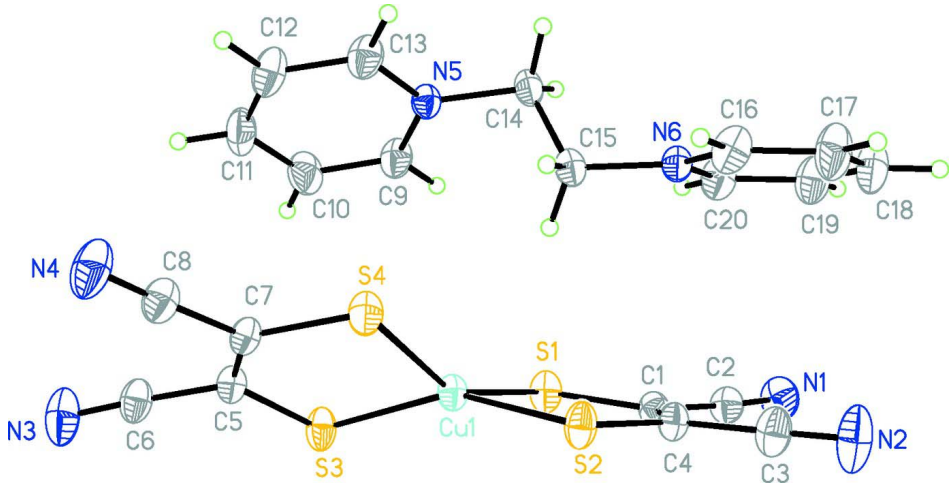

Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

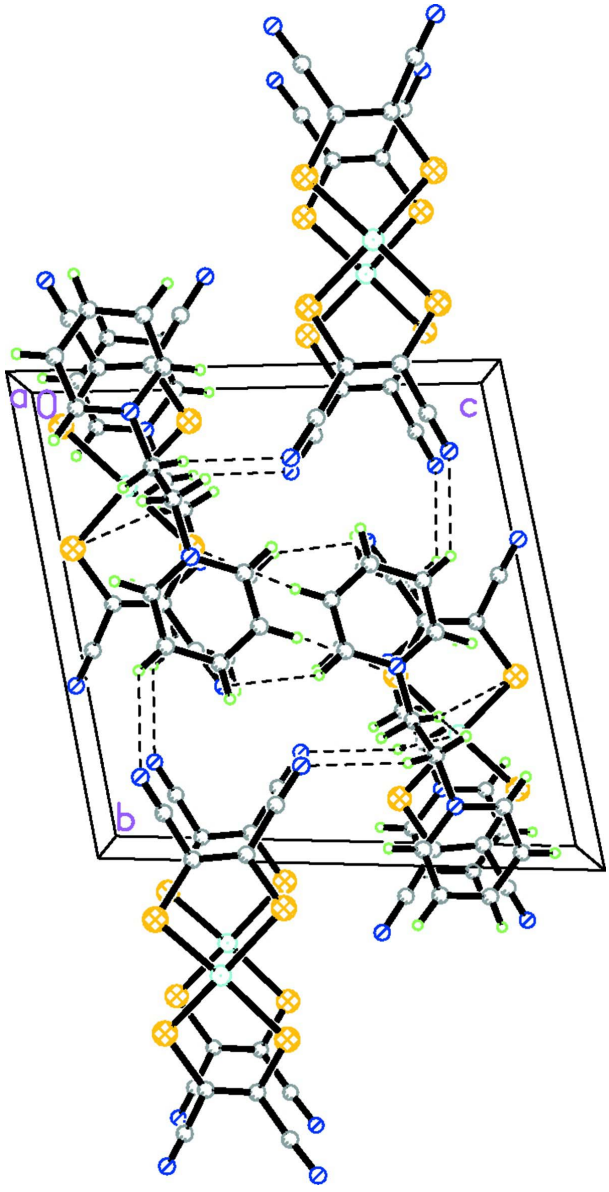

Figure 2

The packing diagram of the title compound as viewed along the *a* axis. Dashed lines denote hydrogen bonds.

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c = 12.6572 (16) Å
α = 77.676 (2)°
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γ = 84.122 (2)°
V = 1133.8 (2) Å^3
Z = 2
$F(000)$ = 538
D_x = 1.553 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2653 reflections
θ = 2.2–28.0°
μ = 1.35 mm^{-1}

T = 291 K
Block, brown-red

0.25 × 0.20 × 0.15 mm

Data collection

Bruker APEX CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.730, T_{max} = 0.815

5682 measured reflections
3921 independent reflections
3217 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25.0°, θ_{min} = 1.7°
h = −9→8
k = −14→12
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.083
S = 1.00
3921 reflections
280 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Experimental. Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
6.9701 (0.0047) x + 5.1850 (0.0148) y + 7.5933 (0.0151) z = 5.1170 (0.0027)
* -0.0036 (0.0020) N5 * 0.0025 (0.0022) C9 * 0.0020 (0.0024) C10 * -0.0053 (0.0025) C11 * 0.0043 (0.0025) C12 * 0.0001 (0.0022) C13
Rms deviation of fitted atoms = 0.0034
7.3331 (0.0038) x + 4.3436 (0.0161) y + 1.7102 (0.0200) z = 4.6388 (0.0108)
Angle to previous plane (with approximate e.s.d.) = 29.18 (10)
* 0.0013 (0.0022) N6 * -0.0036 (0.0025) C16 * 0.0015 (0.0028) C17 * 0.0027 (0.0028) C18 * -0.0049 (0.0027) C19 * 0.0029 (0.0024) C20
Rms deviation of fitted atoms = 0.0031
6.9588 (0.0022) x + 3.8087 (0.0081) y - 0.7118 (0.0088) z = 7.0678 (0.0051)
Angle to previous plane (with approximate e.s.d.) = 10.99 (12)
* -0.0330 (0.0015) S1 * -0.0111 (0.0015) S2 * 0.0353 (0.0026) C1 * 0.0220 (0.0028) C4 * 0.0292 (0.0027) C2 * 0.0074 (0.0032) C3 * -0.0259 (0.0020) N1 * -0.0239 (0.0024) N2
Rms deviation of fitted atoms = 0.0252
7.2222 (0.0021) x + 4.6573 (0.0073) y + 6.9013 (0.0071) z = 8.7279 (0.0018)
Angle to previous plane (with approximate e.s.d.) = 36.27 (4)
* 0.0321 (0.0014) S3 * 0.0067 (0.0014) S4 * -0.0293 (0.0025) C5 * -0.0251 (0.0025) C7 * 0.0012 (0.0029) C8 * -0.0242 (0.0028) C6 * 0.0188 (0.0021) N3 * 0.0197 (0.0021) N4
Rms deviation of fitted atoms = 0.0220

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7697 (4)	0.4815 (2)	0.1224 (2)	0.0391 (7)
C2	0.7087 (4)	0.5794 (2)	0.0580 (2)	0.0438 (7)
C3	0.7285 (5)	0.5782 (3)	0.2764 (3)	0.0534 (9)
C4	0.7788 (4)	0.4812 (2)	0.2281 (2)	0.0399 (7)
C5	1.0203 (4)	−0.0026 (2)	0.1945 (2)	0.0381 (7)
C6	1.1186 (5)	−0.0989 (2)	0.1573 (2)	0.0471 (8)
C7	0.9214 (4)	−0.0103 (2)	0.3037 (2)	0.0383 (7)
C8	0.9143 (5)	−0.1115 (2)	0.3834 (3)	0.0476 (8)
C9	0.4956 (4)	0.0999 (2)	0.1511 (2)	0.0473 (8)
H9A	0.5115	0.1626	0.0943	0.057*
C10	0.5896 (5)	0.0029 (3)	0.1309 (3)	0.0597 (10)
H10A	0.6695	−0.0002	0.0604	0.072*
C11	0.5661 (5)	−0.0882 (3)	0.2138 (3)	0.0638 (10)
H11A	0.6283	−0.1545	0.2005	0.077*
C12	0.4494 (5)	−0.0818 (3)	0.3178 (3)	0.0622 (10)
H12A	0.4333	−0.1435	0.3759	0.075*
C13	0.3573 (5)	0.0154 (2)	0.3354 (3)	0.0511 (8)
H13A	0.2774	0.0200	0.4056	0.061*
C14	0.2858 (4)	0.2108 (2)	0.2732 (3)	0.0413 (7)
H14A	0.1753	0.1975	0.3341	0.050*
H14B	0.2547	0.2506	0.2061	0.050*
C15	0.4079 (4)	0.2779 (2)	0.3040 (3)	0.0453 (8)
H15A	0.4296	0.2404	0.3747	0.054*
H15B	0.5232	0.2838	0.2464	0.054*
C16	0.2857 (5)	0.4217 (2)	0.4142 (3)	0.0525 (9)
H16A	0.2996	0.3717	0.4776	0.063*
C17	0.2222 (5)	0.5267 (3)	0.4229 (3)	0.0678 (11)
H17A	0.1934	0.5488	0.4921	0.081*
C18	0.2010 (5)	0.5992 (3)	0.3304 (3)	0.0662 (11)
H18A	0.1578	0.6712	0.3359	0.079*
C19	0.2430 (5)	0.5663 (3)	0.2295 (3)	0.0593 (10)
H19A	0.2276	0.6150	0.1657	0.071*
C20	0.3078 (4)	0.4609 (2)	0.2238 (3)	0.0506 (8)
H20A	0.3384	0.4378	0.1551	0.061*
Cu1	0.88151 (5)	0.23822 (3)	0.20268 (3)	0.03682 (13)
N1	0.6543 (4)	0.6544 (2)	0.0053 (2)	0.0597 (8)
N2	0.6877 (5)	0.6526 (2)	0.3190 (3)	0.0809 (11)
N3	1.2014 (5)	−0.1729 (2)	0.1268 (2)	0.0733 (10)
N4	0.9043 (5)	−0.1908 (2)	0.4499 (2)	0.0708 (9)
N5	0.3814 (3)	0.10412 (17)	0.25224 (19)	0.0362 (6)
N6	0.3283 (3)	0.39007 (18)	0.31502 (19)	0.0375 (6)
S1	0.81723 (12)	0.36536 (6)	0.06140 (6)	0.0456 (2)
S2	0.84617 (12)	0.36517 (6)	0.31245 (6)	0.0456 (2)
S3	1.04488 (12)	0.11853 (6)	0.09586 (6)	0.0457 (2)
S4	0.80239 (11)	0.10227 (6)	0.35693 (6)	0.0459 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0419 (18)	0.0328 (15)	0.0380 (17)	0.0020 (13)	−0.0092 (14)	−0.0017 (13)
C2	0.051 (2)	0.0408 (17)	0.0368 (17)	−0.0010 (15)	−0.0112 (15)	−0.0036 (14)
C3	0.079 (3)	0.0398 (18)	0.049 (2)	0.0081 (17)	−0.0337 (19)	−0.0061 (16)
C4	0.0478 (19)	0.0299 (15)	0.0422 (18)	0.0034 (13)	−0.0154 (15)	−0.0060 (13)
C5	0.0471 (19)	0.0306 (15)	0.0361 (17)	0.0025 (13)	−0.0127 (14)	−0.0060 (12)
C6	0.067 (2)	0.0352 (17)	0.0350 (17)	0.0019 (15)	−0.0125 (16)	−0.0032 (14)
C7	0.0486 (19)	0.0275 (14)	0.0375 (17)	−0.0017 (13)	−0.0135 (14)	−0.0018 (12)
C8	0.063 (2)	0.0393 (18)	0.0370 (18)	−0.0026 (15)	−0.0067 (16)	−0.0102 (15)
C9	0.063 (2)	0.0375 (17)	0.0339 (17)	0.0012 (15)	−0.0050 (16)	−0.0033 (13)
C10	0.065 (2)	0.054 (2)	0.050 (2)	0.0092 (18)	0.0008 (18)	−0.0185 (18)
C11	0.076 (3)	0.0374 (19)	0.082 (3)	0.0137 (18)	−0.026 (2)	−0.0213 (19)
C12	0.090 (3)	0.0356 (18)	0.059 (2)	0.0010 (18)	−0.027 (2)	0.0027 (16)
C13	0.069 (2)	0.0411 (18)	0.0373 (18)	−0.0007 (16)	−0.0114 (17)	−0.0022 (14)
C14	0.0418 (18)	0.0342 (15)	0.0461 (18)	0.0081 (13)	−0.0112 (15)	−0.0103 (13)
C15	0.0436 (19)	0.0362 (16)	0.056 (2)	0.0069 (14)	−0.0153 (16)	−0.0110 (14)
C16	0.079 (3)	0.0449 (19)	0.0355 (18)	−0.0065 (17)	−0.0199 (17)	−0.0051 (14)
C17	0.108 (3)	0.050 (2)	0.042 (2)	0.002 (2)	−0.010 (2)	−0.0206 (17)
C18	0.093 (3)	0.0376 (19)	0.065 (3)	0.0082 (19)	−0.017 (2)	−0.0171 (18)
C19	0.086 (3)	0.0396 (19)	0.052 (2)	0.0044 (18)	−0.026 (2)	−0.0020 (16)
C20	0.071 (2)	0.0458 (18)	0.0339 (18)	−0.0015 (16)	−0.0114 (16)	−0.0099 (14)
Cu1	0.0427 (2)	0.0313 (2)	0.0346 (2)	0.00331 (15)	−0.01034 (17)	−0.00546 (15)
N1	0.071 (2)	0.0499 (17)	0.0505 (18)	0.0040 (15)	−0.0195 (16)	0.0059 (14)
N2	0.139 (3)	0.0435 (18)	0.074 (2)	0.0230 (19)	−0.053 (2)	−0.0209 (17)
N3	0.108 (3)	0.0440 (17)	0.058 (2)	0.0173 (17)	−0.0132 (19)	−0.0122 (15)
N4	0.108 (3)	0.0420 (17)	0.0482 (18)	−0.0037 (17)	−0.0094 (18)	0.0032 (15)
N5	0.0413 (15)	0.0309 (12)	0.0347 (14)	0.0027 (11)	−0.0111 (12)	−0.0043 (10)
N6	0.0417 (15)	0.0319 (13)	0.0377 (14)	0.0017 (11)	−0.0096 (12)	−0.0075 (11)
S1	0.0638 (6)	0.0395 (4)	0.0309 (4)	0.0057 (4)	−0.0127 (4)	−0.0057 (3)
S2	0.0669 (6)	0.0341 (4)	0.0418 (5)	0.0090 (4)	−0.0272 (4)	−0.0091 (3)
S3	0.0639 (6)	0.0335 (4)	0.0312 (4)	0.0070 (4)	−0.0053 (4)	−0.0034 (3)
S4	0.0571 (5)	0.0370 (4)	0.0342 (4)	0.0031 (4)	−0.0018 (4)	−0.0046 (3)

Geometric parameters (Å, º)

C1—C4	1.360 (4)	C13—H13A	0.9300
C1—C2	1.431 (4)	C14—N5	1.482 (3)
C1—S1	1.730 (3)	C14—C15	1.503 (4)
C2—N1	1.143 (3)	C14—H14A	0.9700
C3—N2	1.136 (4)	C14—H14B	0.9700
C3—C4	1.430 (4)	C15—N6	1.479 (3)
C4—S2	1.732 (3)	C15—H15A	0.9700
C5—C7	1.357 (4)	C15—H15B	0.9700
C5—C6	1.437 (4)	C16—N6	1.333 (3)
C5—S3	1.721 (3)	C16—C17	1.357 (4)
C6—N3	1.134 (3)	C16—H16A	0.9300
C7—C8	1.425 (4)	C17—C18	1.356 (4)
C7—S4	1.738 (3)	C17—H17A	0.9300

C8—N4	1.141 (4)	C18—C19	1.361 (4)
C9—N5	1.332 (4)	C18—H18A	0.9300
C9—C10	1.371 (4)	C19—C20	1.358 (4)
C9—H9A	0.9300	C19—H19A	0.9300
C10—C11	1.353 (5)	C20—N6	1.332 (4)
C10—H10A	0.9300	C20—H20A	0.9300
C11—C12	1.373 (5)	Cu1—S3	2.2554 (8)
C11—H11A	0.9300	Cu1—S1	2.2561 (8)
C12—C13	1.361 (4)	Cu1—S2	2.2571 (8)
C12—H12A	0.9300	Cu1—S4	2.2630 (8)
C13—N5	1.335 (4)		

C4—C1—C2	120.1 (2)	N6—C15—C14	111.5 (2)
C4—C1—S1	123.3 (2)	N6—C15—H15A	109.3
C2—C1—S1	116.5 (2)	C14—C15—H15A	109.3
N1—C2—C1	176.5 (3)	N6—C15—H15B	109.3
N2—C3—C4	177.2 (3)	C14—C15—H15B	109.3
C1—C4—C3	120.8 (2)	H15A—C15—H15B	108.0
C1—C4—S2	122.9 (2)	N6—C16—C17	120.2 (3)
C3—C4—S2	116.3 (2)	N6—C16—H16A	119.9
C7—C5—C6	119.5 (2)	C17—C16—H16A	119.9
C7—C5—S3	124.0 (2)	C18—C17—C16	119.7 (3)
C6—C5—S3	116.5 (2)	C18—C17—H17A	120.1
N3—C6—C5	177.7 (4)	C16—C17—H17A	120.1
C5—C7—C8	121.6 (2)	C17—C18—C19	119.9 (3)
C5—C7—S4	122.7 (2)	C17—C18—H18A	120.1
C8—C7—S4	115.7 (2)	C19—C18—H18A	120.1
N4—C8—C7	177.6 (3)	C20—C19—C18	118.7 (3)
N5—C9—C10	119.9 (3)	C20—C19—H19A	120.6
N5—C9—H9A	120.0	C18—C19—H19A	120.6
C10—C9—H9A	120.0	N6—C20—C19	121.1 (3)
C11—C10—C9	119.9 (3)	N6—C20—H20A	119.4
C11—C10—H10A	120.1	C19—C20—H20A	119.4
C9—C10—H10A	120.1	S3—Cu1—S1	97.08 (3)
C10—C11—C12	119.3 (3)	S3—Cu1—S2	153.90 (4)
C10—C11—H11A	120.4	S1—Cu1—S2	92.15 (3)
C12—C11—H11A	120.4	S3—Cu1—S4	92.28 (3)
C13—C12—C11	119.6 (3)	S1—Cu1—S4	152.11 (4)
C13—C12—H12A	120.2	S2—Cu1—S4	90.80 (3)
C11—C12—H12A	120.2	C9—N5—C13	121.1 (2)
N5—C13—C12	120.2 (3)	C9—N5—C14	119.0 (2)
N5—C13—H13A	119.9	C13—N5—C14	119.9 (2)
C12—C13—H13A	119.9	C20—N6—C16	120.3 (2)
N5—C14—C15	108.6 (2)	C20—N6—C15	119.3 (2)
N5—C14—H14A	110.0	C16—N6—C15	120.2 (2)
C15—C14—H14A	110.0	C1—S1—Cu1	100.72 (10)
N5—C14—H14B	110.0	C4—S2—Cu1	100.81 (9)
C15—C14—H14B	110.0	C5—S3—Cu1	100.54 (9)
H14A—C14—H14B	108.4	C7—S4—Cu1	100.40 (10)

C2—C1—C4—C3	−0.3 (5)	C17—C16—N6—C20	−0.4 (5)
S1—C1—C4—C3	−176.6 (3)	C17—C16—N6—C15	176.2 (3)
C2—C1—C4—S2	178.5 (2)	C14—C15—N6—C20	−67.1 (4)
S1—C1—C4—S2	2.1 (4)	C14—C15—N6—C16	116.2 (3)
C6—C5—C7—C8	0.8 (5)	C4—C1—S1—Cu1	1.0 (3)
S3—C5—C7—C8	−176.3 (2)	C2—C1—S1—Cu1	−175.5 (2)
C6—C5—C7—S4	178.5 (2)	S3—Cu1—S1—C1	−158.09 (11)
S3—C5—C7—S4	1.4 (4)	S2—Cu1—S1—C1	−2.55 (11)
N5—C9—C10—C11	0.0 (5)	S4—Cu1—S1—C1	93.23 (12)
C9—C10—C11—C12	−0.8 (5)	C1—C4—S2—Cu1	−3.9 (3)
C10—C11—C12—C13	1.0 (6)	C3—C4—S2—Cu1	174.9 (2)
C11—C12—C13—N5	−0.5 (5)	S3—Cu1—S2—C4	114.23 (12)
N5—C14—C15—N6	174.3 (2)	S1—Cu1—S2—C4	3.32 (11)
N6—C16—C17—C18	0.4 (6)	S4—Cu1—S2—C4	−148.94 (11)
C16—C17—C18—C19	0.2 (6)	C7—C5—S3—Cu1	1.0 (3)
C17—C18—C19—C20	−0.8 (6)	C6—C5—S3—Cu1	−176.2 (2)
C18—C19—C20—N6	0.8 (6)	S1—Cu1—S3—C5	−155.81 (11)
C10—C9—N5—C13	0.5 (5)	S2—Cu1—S3—C5	94.35 (12)
C10—C9—N5—C14	178.0 (3)	S4—Cu1—S3—C5	−2.14 (11)
C12—C13—N5—C9	−0.3 (5)	C5—C7—S4—Cu1	−2.9 (3)
C12—C13—N5—C14	−177.7 (3)	C8—C7—S4—Cu1	174.9 (2)
C15—C14—N5—C9	−83.5 (3)	S3—Cu1—S4—C7	2.65 (11)
C15—C14—N5—C13	94.0 (3)	S1—Cu1—S4—C7	112.46 (11)
C19—C20—N6—C16	−0.2 (5)	S2—Cu1—S4—C7	−151.43 (10)
C19—C20—N6—C15	−176.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···N2^{i}	0.93	2.61	3.356 (4)	137
C14—H14*A*···N4^{ii}	0.97	2.60	3.341 (4)	133
C14—H14*B*···N1^{iii}	0.97	2.60	3.479 (4)	151
C15—H15*B*···S1	0.97	2.83	3.769 (3)	163
C16—H16*A*···N2^{iv}	0.93	2.56	3.368 (4)	146
C17—H17*A*···S2^{iv}	0.93	2.82	3.743 (3)	171
C19—H19*A*···N3^{v}	0.93	2.56	3.235 (4)	129
C20—H20*A*···N1^{iii}	0.93	2.52	3.422 (4)	164

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*−1, *y*+1, *z*.