(3,3′-Diamino-2,2′-bipyridine-κ^2N,N')-bis(thiocyanato-κN)copper(II)

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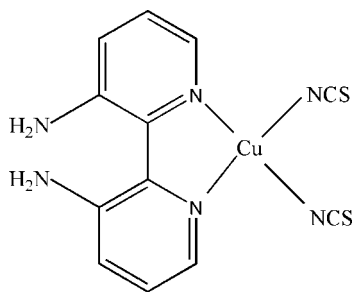
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The title mononuclear complex, $[Cu(NCS)_2(C_{10}H_{10}N_4)]$, is located on a twofold rotation axis. The Cu^{II} ion assumes a tetrahedrally distorted square-planar coordination geometry. Two thiocyanate (NCS) anions and two N atoms from pyridine (py) rings coordinate in a *cis* manner to the Cu^{II} ion with a dihedral angle of 26.29 (16) Å between the $Cu/N_{py}/N_{py}$ and $Cu/N_{NCS}/N_{NCS}$ planes. There is a π–π stacking interaction between neighbouring pyridine rings [with a centroid–centroid distance of 3.7302 (14) Å and an interplanar distance of 3.311 Å] and N—H···N, N—H···S and C—H···N hydrogen bonds.

Related literature

For the crystal structures of related complexes, see: Rice *et al.* (2002); Shi *et al.* (2006*a*,*b*).

Experimental

Crystal data

$[Cu(NCS)_2(C_{10}H_{10}N_4)]$	b = 14.991 (3) Å
M_r = 365.92	c = 10.627 (2) Å
Monoclinic, $C2/c$	β = 90.738 (3)°
a = 8.8127 (18) Å	V = 1403.8 (5) Å³

Z = 4	T = 298 (2) K
Mo $K\alpha$ radiation	$0.38 \times 0.36 \times 0.30$ mm
μ = 1.85 mm^{-1}	

Data collection

Bruker SMART APEX CCD diffractometer	3905 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1450 independent reflections
T_{min} = 0.539, T_{max} = 0.606 (expected range = 0.510–0.573)	1285 reflections with $I > 2\sigma(I)$
	R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033	96 parameters
$wR(F^2)$ = 0.088	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
1450 reflections	$\Delta\rho_{min}$ = -0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.947 (2)	Cu1—N1	1.9728 (19)
N2—Cu1—N2^i	92.80 (13)	N2—Cu1—N1	95.61 (9)
N2—Cu1—N1^i	161.13 (9)	N1^i—Cu1—N1	81.60 (11)

Symmetry code: (i) $-x, y, -z + \frac{3}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···S1^{ii}	0.86	2.69	3.550 (2)	174
N3—H3B···N3^i	0.86	2.23	2.775 (4)	121
C1—H1···N2	0.93	2.58	3.044 (4)	112

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2392).

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supplementary materials

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Comment

As a derivative of 2,2'-bipyridine 3,3'-diamino-2,'2-bipyridine may function as a useful chelating multi-dentate ligand, and a few complexes dealing with this ligand have been published (Rice *et al.*, 2002; Shi *et al.*, 2006*a*; Shi *et al.*, 2006*b*), in which there are two mono-nuclear Cu^{II} complexes. Here we report another Cu^{II} mono-nuclear complex (Fig. 1).

Fig. 1 shows the asymmetric unit with the Cu^{II} atom in a four-coordinate geometry. The Cu/N1/N1^i plane is tilted with respect to the CuN2N2^i plane by a dihedral angle of 26.29 (16)°. The bond angles at the Cu atom (Table 1) also show the extent of the distortion of the coordinated geometry from square planar. In the uncoordinated 3,3'-diamino-2,'2-bipyridine all non-hydrogen atoms are located in a plane and two amino groups are in *trans*-configuration, whereas in the title compound the dihedral angle between the two pyridine ring planes is 22.15 (7)°. There is a π-π stacking interaction between adjacent pyridine rings, with a centroid⋯centroid distance of 3.7302 (14)Å and an interplanar distance of 3.311 Å [symmetry code: 1/2 - *X*, 1/2 - Y, 2 - *Z*]. In addition, there are intra- and intermolecular hydrogen bonds.

Experimental

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.0637 g, 0.172 mmol) and NaSCN (0.0139 g, 0.172 mmol) were dissoved in 5 ml H_2O, respectively, and stirred for a few minutes. The solution was poured into 5 ml acetonitrile solution containing 3,3'-diamino-2,2'-bipyridine (0.0160 g, 0.0860 mmol), and the mixed solution was stirred for a few minutes. The green single crystals were obtained after the solution had been allowed to stand at room temperature for two weeks. The IR peaks at 1640 cm^{-1}, 1566 cm^{-1}, 1465 cm^{-1} and 1383 cm^{-1} may be attributed to the stretching vibrations of the C=C, C=N and NH_2 groups, whereas strong and sharp peak at 2090 cm^{-1} obviously is from the stretching vibration of thiocyanate group.

Refinement

All H atoms were placed in calculated positions, and refined as riding, with C—H = 0.93 Å, $U_{iso}(H) = 1.2_{eq}(C)$ for pyridine ring; N—H = 0.86 Å, $U_{iso}(H) = 1.2$ (N) for amino group.
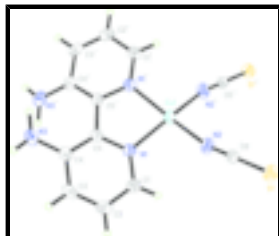
supplementary materials

Figures

Fig. 1. Complex structure of (I) showing the atom numbering scheme with thermal ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x, y, -z + 3/2$].
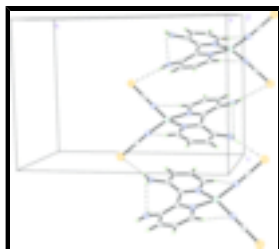

Fig. 2. Packing diagram with hydrogen bonds shown as dashed lines.

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Crystal data

[Cu(NCS)$_2$(C$_{10}$H$_{10}$N$_4$)]	$F_{000} = 740$
$M_r = 365.92$	$D_x = 1.731$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1907 reflections
$a = 8.8127$ (18) Å	$\theta = 2.7–27.3°$
$b = 14.991$ (3) Å	$\mu = 1.85$ mm^{-1}
$c = 10.627$ (2) Å	$T = 298$ (2) K
$\beta = 90.738$ (3)°	Block, green
$V = 1403.8$ (5) Å^3	$0.38 \times 0.36 \times 0.30$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	1450 independent reflections
Radiation source: fine-focus sealed tube	1285 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.019$
$T = 298(2)$ K	$\theta_{max} = 26.5°$
φ and ω scans	$\theta_{min} = 2.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 8$
$T_{min} = 0.539$, $T_{max} = 0.606$	$k = -17 \rightarrow 18$
3905 measured reflections	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.0653P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
1450 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
96 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cu1	0.0000	0.39730 (3)	0.7500	0.04805 (18)
S1	0.21601 (8)	0.62017 (5)	1.00428 (7)	0.0497 (2)
N1	0.1402 (2)	0.29769 (13)	0.78613 (17)	0.0366 (4)
C2	0.3693 (3)	0.2373 (2)	0.8676 (2)	0.0464 (6)
H2	0.4711	0.2450	0.8893	0.056*
N2	0.1172 (3)	0.48687 (15)	0.8415 (2)	0.0509 (5)
C6	0.1577 (3)	0.54235 (16)	0.9084 (2)	0.0381 (5)
N3	0.0829 (3)	0.06250 (16)	0.8619 (3)	0.0636 (7)
H3A	0.1330	0.0207	0.8992	0.076*
H3B	−0.0101	0.0539	0.8395	0.076*
C5	0.0762 (2)	0.21557 (15)	0.78060 (19)	0.0339 (5)
C1	0.2826 (3)	0.30898 (18)	0.8271 (2)	0.0443 (6)
H1	0.3243	0.3660	0.8284	0.053*
C4	0.1515 (3)	0.14310 (16)	0.8380 (2)	0.0418 (5)
C3	0.3032 (3)	0.15565 (18)	0.8753 (2)	0.0462 (6)
H3	0.3593	0.1075	0.9056	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0534 (3)	0.0320 (2)	0.0580 (3)	0.000	−0.0273 (2)	0.000
S1	0.0562 (4)	0.0435 (4)	0.0492 (4)	−0.0030 (3)	−0.0126 (3)	−0.0086 (3)
N1	0.0383 (10)	0.0386 (10)	0.0328 (9)	0.0013 (8)	−0.0093 (8)	0.0003 (8)
C2	0.0357 (13)	0.0640 (18)	0.0394 (14)	0.0077 (11)	−0.0046 (10)	−0.0025 (12)
N2	0.0589 (13)	0.0373 (11)	0.0560 (13)	−0.0041 (10)	−0.0179 (10)	−0.0018 (10)
C6	0.0373 (12)	0.0350 (12)	0.0419 (13)	0.0011 (9)	−0.0067 (10)	0.0059 (10)
N3	0.0594 (15)	0.0423 (13)	0.0888 (19)	0.0083 (11)	−0.0059 (13)	0.0216 (12)
C5	0.0377 (12)	0.0354 (12)	0.0283 (10)	0.0011 (9)	−0.0031 (9)	−0.0015 (9)
C1	0.0416 (13)	0.0500 (15)	0.0410 (13)	−0.0047 (10)	−0.0076 (10)	−0.0001 (11)
C4	0.0469 (13)	0.0386 (13)	0.0399 (12)	0.0074 (10)	0.0011 (10)	−0.0002 (10)
C3	0.0451 (14)	0.0535 (15)	0.0401 (13)	0.0184 (12)	0.0009 (10)	0.0017 (11)

Geometric parameters (Å, °)

Cu1—N2	1.947 (2)	N2—C6	1.147 (3)
Cu1—N2^i	1.947 (2)	N3—C4	1.376 (3)
Cu1—N1^i	1.9728 (19)	N3—H3A	0.8600
Cu1—N1	1.9728 (19)	N3—H3B	0.8600
S1—C6	1.628 (3)	C5—C4	1.408 (3)
N1—C1	1.333 (3)	C5—C5^i	1.484 (4)
N1—C5	1.355 (3)	C1—H1	0.9300
C2—C3	1.359 (4)	C4—C3	1.402 (3)
C2—C1	1.384 (4)	C3—H3	0.9300
C2—H2	0.9300		
N2—Cu1—N2^i	92.80 (13)	C4—N3—H3B	120.0
N2—Cu1—N1^i	161.13 (9)	H3A—N3—H3B	120.0
N2^i—Cu1—N1^i	95.61 (9)	N1—C5—C4	119.24 (19)
N2—Cu1—N1	95.61 (9)	N1—C5—C5^i	113.13 (12)
N2^i—Cu1—N1	161.13 (9)	C4—C5—C5^i	127.48 (14)
N1^i—Cu1—N1	81.60 (11)	N1—C1—C2	121.1 (2)
C1—N1—C5	121.3 (2)	N1—C1—H1	119.4
C1—N1—Cu1	123.49 (17)	C2—C1—H1	119.4
C5—N1—Cu1	114.82 (14)	N3—C4—C3	119.0 (2)
C3—C2—C1	118.8 (2)	N3—C4—C5	123.5 (2)
C3—C2—H2	120.6	C3—C4—C5	117.5 (2)
C1—C2—H2	120.6	C2—C3—C4	120.8 (2)
C6—N2—Cu1	165.4 (2)	C2—C3—H3	119.6
N2—C6—S1	179.3 (2)	C4—C3—H3	119.6
C4—N3—H3A	120.0		
N2—Cu1—N1—C1	−16.6 (2)	Cu1—N1—C5—C5^i	13.7 (3)
N2^i—Cu1—N1—C1	99.5 (3)	C5—N1—C1—C2	−1.2 (3)
N1^i—Cu1—N1—C1	−177.8 (2)	Cu1—N1—C1—C2	170.89 (18)

N2—Cu1—N1—C5	155.98 (16)	C3—C2—C1—N1	−5.5 (4)
N2ⁱ—Cu1—N1—C5	−88.0 (3)	N1—C5—C4—N3	165.2 (2)
N1ⁱ—Cu1—N1—C5	−5.21 (11)	C5ⁱ—C5—C4—N3	−10.0 (4)
N2ⁱ—Cu1—N2—C6	71.6 (8)	N1—C5—C4—C3	−13.0 (3)
N1ⁱ—Cu1—N2—C6	−44.8 (10)	C5ⁱ—C5—C4—C3	171.8 (3)
N1—Cu1—N2—C6	−125.3 (8)	C1—C2—C3—C4	2.6 (4)
C1—N1—C5—C4	10.6 (3)	N3—C4—C3—C2	−171.8 (2)
Cu1—N1—C5—C4	−162.18 (16)	C5—C4—C3—C2	6.5 (3)
C1—N1—C5—C5ⁱ	−173.6 (2)		

Symmetry codes: (i) −*x*, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···S1ⁱⁱ	0.86	2.69	3.550 (2)	174
N3—H3B···N3ⁱ	0.86	2.23	2.775 (4)	121
C1—H1···N2	0.93	2.58	3.044 (4)	112

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

Fig. 1

Fig. 2