Bromido{N-methyl-N'-[1-(2-pyridyl)-ethylidene]ethane-1,2-diamine-$\kappa^3 N,N',N''$}(thiocyanato-κN)copper(II)

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In the title mononuclear copper(II) compound, [CuBr(NCS)-($C_{10}H_{15}N_3$)], the Cu^{II} atom is five-coordinated by three N atoms of the Schiff base ligand, the N atom of a thiocyanate ligand and by one bromide ion forming a distorted square-pyramidal geometry. In the crystal structure, molecules are linked through intermolecular N—H···Br hydrogen bonds into chains propagating along [101].

Related literature

For general background to Schiff base–copper(II) complexes, see: Adhikary *et al.* (2009); Al-Karawi (2009); Xiao & Zhang (2009); Rajasekar *et al.* (2010); Sang & Lin (2010); Qin *et al.* (2010). For related copper complexes with square-pyramidal coordination, see: Wang *et al.* (2010); Zhang *et al.* (2009); Wei *et al.* (2007).
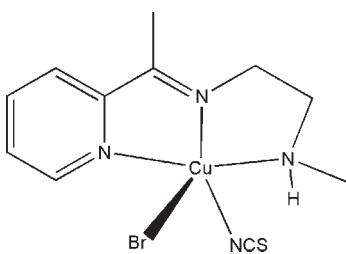
Experimental

Crystal data

[CuBr(NCS)($C_{10}H_{15}N_3$)]
M_r = 378.78
Monoclinic, $P2_1/n$
a = 10.979 (2) Å
b = 11.407 (2) Å
c = 12.001 (3) Å
β = 109.033 (2)°

V = 1420.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.48 mm^{-1}
T = 298 K
0.30 × 0.27 × 0.27 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.347, T_{max} = 0.377

8078 measured reflections
3022 independent reflections
1892 reflections with $I > 2\sigma(I)$
R_{int} = 0.070

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.137
S = 0.97
3022 reflections
168 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.86 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N4	1.949 (5)	Cu1—N3	2.044 (5)
Cu1—N2	1.965 (5)	Cu1—Br1	2.7228 (10)
Cu1—N1	2.019 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···Br1^i	0.90 (1)	2.69 (4)	3.494 (5)	150 (6)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5132).

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supporting information

Bromido{*N*-methyl-*N*′-[1-(2-pyridyl)ethylidene]ethane-1,2-diamine-*κ*³*N*,*N*′,*N*′′} (thiocyanato-*κN*)copper(II)

Li-Jun Liu

S1. Comment

Copper(II) complexes with Schiff bases have been widely investigated in coordination chemistry and biological chemistry (Adhikary *et al.*, 2009; Al-Karawi, 2009; Xiao & Zhang, 2009; Rajasekar *et al.*, 2010; Sang & Lin, 2010; Qin *et al.*, 2010). In the present paper, the title new copper complex with the Schiff base ligand *N*methyl-*N*′-(1-pyridin-2-yl-ethylidene)ethane-1,2-diamine, is reported.

The Cu$^{\mathrm{II}}$ atom in the title complex (Fig. 1) is five-coordinated by one pyridine N, one imine N, and one amine N atoms of a Schiff base ligand, by one bromide atom, and by one N atom of a thiocyanate ligand, forming a square-pyramidal geometry. The bond lengths (Table 1) related to the Cu atom are comparable with those observed in similar copper complexes with square-pyramidal geometry (Wang *et al.*, 2010; Zhang *et al.*, 2009; Wei *et al.*, 2007).

In the crystal structure, molecules are linked through intermolecular N—H···Br hydrogen bonds (Table 2) to form chains running along the *a* axis (Fig. 2).

S2. Experimental

2-Acetylpyridine (0.1 mmol, 12.1 mg), ammonium thiocyanate (0.1 mmol, 7.6 mg), and copper bromide (0.1 mmol, 22.3 mg) were mixed and stirred in methanol (20 ml) at reflux for 2 h, to give a blue solution. The solution was cooled to room temperature, and blue block-shaped single crystals were formed by slow evaporation of the solution in air.

S3. Refinement

Atom H3A attached to N3 was located in a difference Fourier map and refined isotropically, with the N–H distance restrained to 0.90 (1) Å. The remaining H atoms were positioned geometrically (C–H = 0.93-0.97 Å) and refined using a riding model, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $1.5U_{\mathrm{eq}}(\mathrm{C}_{\mathrm{methyl}})$.
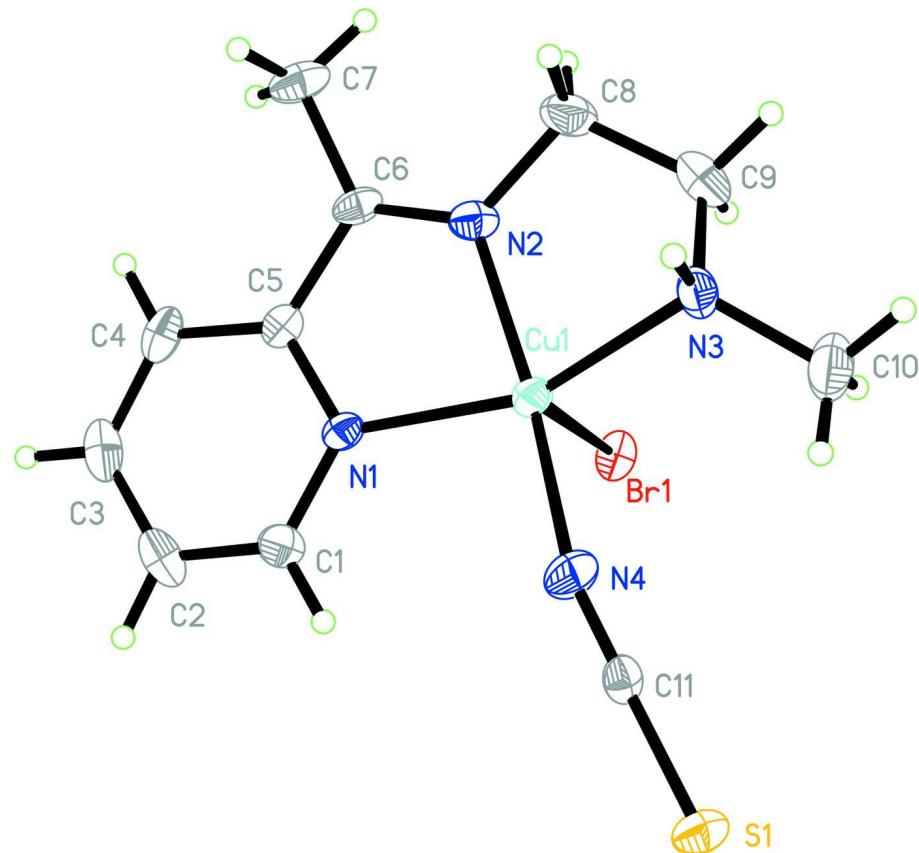
Figure 1

The molecular structure of the title complex with 30% probability displacement ellipsoids.
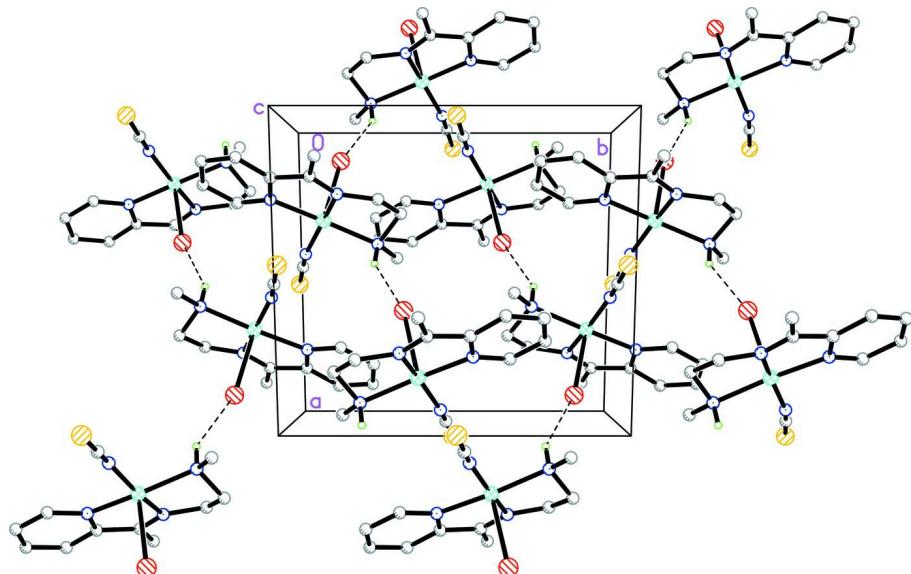
Figure 2

The crystal packing of the title complex, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

Bromido{*N*-methyl-*N′*-[1-(2-pyridyl)ethylidene]ethane-1,2-diamine- $\kappa^3 N,N′,N′′$}(thiocyanato-κN)copper(II)

Crystal data

$[CuBr(NCS)(C_{10}H_{15}N_3)]$	$F(000) = 756$
$M_r = 378.78$	$D_x = 1.771$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2570 reflections
$a = 10.979$ (2) Å	$\theta = 2.5–26.5°$
$b = 11.407$ (2) Å	$\mu = 4.48$ mm^{-1}
$c = 12.001$ (3) Å	$T = 298$ K
$\beta = 109.033$ (2)°	Block, blue
$V = 1420.8$ (5) Å^3	$0.30 \times 0.27 \times 0.27$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD area-detector diffractometer	8078 measured reflections
Radiation source: fine-focus sealed tube	3022 independent reflections
Graphite monochromator	1892 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.070$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$\theta_{max} = 27.0°$, $\theta_{min} = 2.2°$
	$h = -13\rightarrow14$
$T_{min} = 0.347$, $T_{max} = 0.377$	$k = -14\rightarrow12$
	$l = -15\rightarrow8$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.053$	
$wR(F^2) = 0.137$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.97$	
3022 reflections	$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
168 parameters	
1 restraint	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.86$ e Å^{-3}
	$\Delta\rho_{min} = -1.01$ e Å^{-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.

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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	0.18062 (6)	0.60367 (6)	0.05737 (6)	0.0319 (2)
Br1	0.38736 (6)	0.64845 (6)	0.25208 (5)	0.0412 (2)
N1	0.2487 (4)	0.4486 (4)	0.0218 (4)	0.0292 (11)

N2	0.2631 (5)	0.6533 (5)	−0.0577 (4)	0.0356 (12)
N3	0.1033 (5)	0.7682 (4)	0.0253 (4)	0.0405 (13)
N4	0.0715 (5)	0.5412 (5)	0.1429 (5)	0.0451 (14)
S1	−0.03147 (18)	0.50606 (17)	0.32203 (16)	0.0522 (5)
C1	0.2396 (6)	0.3440 (5)	0.0690 (5)	0.0390 (15)
H1	0.1917	0.3382	0.1200	0.047*
C2	0.2974 (7)	0.2460 (6)	0.0456 (7)	0.0527 (19)
H2	0.2893	0.1748	0.0803	0.063*
C3	0.3683 (7)	0.2534 (6)	−0.0307 (6)	0.0528 (19)
H3	0.4090	0.1874	−0.0474	0.063*
C4	0.3778 (6)	0.3601 (6)	−0.0815 (6)	0.0454 (17)
H4	0.4249	0.3672	−0.1330	0.054*
C5	0.3152 (5)	0.4572 (5)	−0.0541 (5)	0.0314 (13)
C6	0.3174 (5)	0.5760 (5)	−0.1021 (5)	0.0331 (14)
C7	0.3743 (7)	0.5979 (6)	−0.1975 (6)	0.0519 (18)
H7A	0.3179	0.5672	−0.2706	0.078*
H7B	0.4566	0.5597	−0.1780	0.078*
H7C	0.3851	0.6806	−0.2052	0.078*
C8	0.2442 (7)	0.7750 (6)	−0.0943 (6)	0.0518 (18)
H8A	0.1787	0.7814	−0.1712	0.062*
H8B	0.3238	0.8082	−0.0987	0.062*
C9	0.2019 (7)	0.8386 (6)	−0.0024 (6)	0.0535 (19)
H9A	0.2752	0.8504	0.0683	0.064*
H9B	0.1669	0.9148	−0.0322	0.064*
C10	0.0578 (8)	0.8231 (6)	0.1167 (6)	0.064 (2)
H10A	0.1306	0.8425	0.1842	0.096*
H10B	0.0030	0.7692	0.1395	0.096*
H10C	0.0104	0.8931	0.0855	0.096*
C11	0.0286 (5)	0.5262 (5)	0.2159 (5)	0.0312 (14)
H3A	0.038 (5)	0.760 (6)	−0.043 (3)	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0334 (4)	0.0328 (4)	0.0350 (4)	0.0035 (3)	0.0184 (3)	0.0024 (3)
Br1	0.0369 (4)	0.0467 (4)	0.0389 (4)	0.0031 (3)	0.0108 (3)	−0.0090 (3)
N1	0.028 (3)	0.034 (3)	0.029 (3)	−0.001 (2)	0.014 (2)	0.000 (2)
N2	0.030 (3)	0.042 (3)	0.036 (3)	0.004 (2)	0.013 (2)	0.011 (2)
N3	0.049 (3)	0.030 (3)	0.043 (3)	0.007 (2)	0.014 (3)	−0.003 (2)
N4	0.039 (3)	0.056 (4)	0.050 (3)	0.000 (3)	0.028 (3)	0.000 (3)
S1	0.0599 (12)	0.0548 (11)	0.0570 (11)	−0.0083 (9)	0.0397 (10)	−0.0003 (9)
C1	0.041 (4)	0.036 (4)	0.040 (4)	−0.001 (3)	0.015 (3)	0.003 (3)
C2	0.052 (5)	0.029 (4)	0.071 (5)	0.001 (3)	0.012 (4)	−0.003 (3)
C3	0.055 (5)	0.040 (5)	0.057 (5)	0.006 (3)	0.009 (4)	−0.016 (4)
C4	0.039 (4)	0.058 (5)	0.042 (4)	0.006 (3)	0.017 (3)	−0.016 (3)
C5	0.026 (3)	0.039 (4)	0.028 (3)	0.001 (3)	0.008 (3)	−0.002 (3)
C6	0.023 (3)	0.050 (4)	0.029 (3)	0.002 (3)	0.013 (2)	0.007 (3)
C7	0.046 (4)	0.077 (5)	0.041 (4)	0.002 (4)	0.026 (3)	0.013 (4)

C8	0.056 (5)	0.046 (5)	0.066 (5)	0.006 (3)	0.036 (4)	0.020 (4)
C9	0.055 (5)	0.033 (4)	0.065 (5)	0.002 (3)	0.008 (4)	0.008 (3)
C10	0.079 (6)	0.060 (5)	0.054 (5)	0.026 (4)	0.022 (4)	−0.008 (4)
C11	0.022 (3)	0.029 (3)	0.044 (4)	0.000 (2)	0.012 (3)	−0.006 (3)

Geometric parameters (Å, º)

Cu1—N4	1.949 (5)	C3—C4	1.380 (9)
Cu1—N2	1.965 (5)	C3—H3	0.93
Cu1—N1	2.019 (5)	C4—C5	1.398 (8)
Cu1—N3	2.044 (5)	C4—H4	0.93
Cu1—Br1	2.7228 (10)	C5—C6	1.476 (8)
N1—C1	1.338 (7)	C6—C7	1.494 (8)
N1—C5	1.343 (7)	C7—H7A	0.96
N2—C6	1.274 (7)	C7—H7B	0.96
N2—C8	1.451 (8)	C7—H7C	0.96
N3—C9	1.470 (9)	C8—C9	1.514 (9)
N3—C10	1.484 (8)	C8—H8A	0.97
N3—H3A	0.899 (10)	C8—H8B	0.97
N4—C11	1.135 (7)	C9—H9A	0.97
S1—C11	1.630 (7)	C9—H9B	0.97
C1—C2	1.359 (9)	C10—H10A	0.96
C1—H1	0.93	C10—H10B	0.96
C2—C3	1.384 (10)	C10—H10C	0.96
C2—H2	0.93		
N4—Cu1—N2	168.1 (2)	C3—C4—H4	120.6
N4—Cu1—N1	97.2 (2)	C5—C4—H4	120.6
N2—Cu1—N1	79.4 (2)	N1—C5—C4	121.3 (6)
N4—Cu1—N3	98.4 (2)	N1—C5—C6	114.4 (5)
N2—Cu1—N3	82.0 (2)	C4—C5—C6	124.3 (6)
N1—Cu1—N3	157.5 (2)	N2—C6—C5	113.7 (5)
N4—Cu1—Br1	95.75 (16)	N2—C6—C7	125.1 (6)
N2—Cu1—Br1	95.90 (14)	C5—C6—C7	121.1 (6)
N1—Cu1—Br1	94.79 (12)	C6—C7—H7A	109.5
N3—Cu1—Br1	99.67 (15)	C6—C7—H7B	109.5
C1—N1—C5	118.9 (5)	H7A—C7—H7B	109.5
C1—N1—Cu1	127.4 (4)	C6—C7—H7C	109.5
C5—N1—Cu1	113.6 (4)	H7A—C7—H7C	109.5
C6—N2—C8	125.1 (5)	H7B—C7—H7C	109.5
C6—N2—Cu1	118.7 (4)	N2—C8—C9	106.6 (5)
C8—N2—Cu1	115.8 (4)	N2—C8—H8A	110.4
C9—N3—C10	112.8 (5)	C9—C8—H8A	110.4
C9—N3—Cu1	104.6 (4)	N2—C8—H8B	110.4
C10—N3—Cu1	117.9 (4)	C9—C8—H8B	110.4
C9—N3—H3A	106 (5)	H8A—C8—H8B	108.6
C10—N3—H3A	111 (5)	N3—C9—C8	109.1 (5)
Cu1—N3—H3A	104 (5)	N3—C9—H9A	109.9

C11—N4—Cu1	160.6 (5)	C8—C9—H9A	109.9
N1—C1—C2	122.8 (6)	N3—C9—H9B	109.9
N1—C1—H1	118.6	C8—C9—H9B	109.9
C2—C1—H1	118.6	H9A—C9—H9B	108.3
C1—C2—C3	119.2 (7)	N3—C10—H10A	109.5
C1—C2—H2	120.4	N3—C10—H10B	109.5
C3—C2—H2	120.4	H10A—C10—H10B	109.5
C4—C3—C2	119.1 (6)	N3—C10—H10C	109.5
C4—C3—H3	120.5	H10A—C10—H10C	109.5
C2—C3—H3	120.5	H10B—C10—H10C	109.5
C3—C4—C5	118.7 (6)	N4—C11—S1	179.1 (6)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···Br1[i]	0.90 (1)	2.69 (4)	3.494 (5)	150 (6)

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