Di-μ-thocyanato-bis{2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]-phenolatocopper(II)}

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The title compound, $[Cu_2(C_{10}H_{11}BrClN_2O)_2(NCS)_2]$, is a centrosymmetric dithiocyanate-bridged binuclear copper(II) complex. The Cu^{II} atoms are pentacoordinated by the N,N',O-donor atoms of the Schiff base ligand 2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]phenol (HBCP), and by one N and one S atom from two symmetry-related thiocyanate anions, so forming a slightly distorted square-pyramidal coordination configuration. The Cu···Cu distance is 5.480 (2) Å.

Related literature

For related literature, see: Zhang (2004).
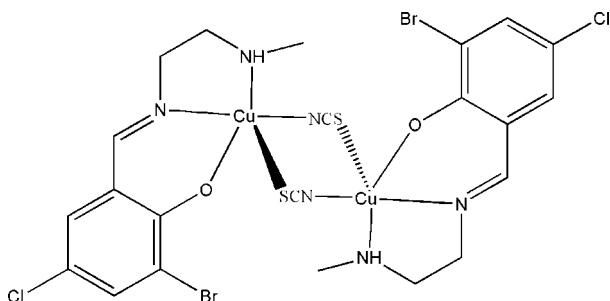
Experimental

Crystal data

$[Cu_2(C_{10}H_{11}BrClN_2O)_2(NCS)_2]$
M_r = 824.38
Monoclinic, $C2/c$
a = 7.2440 (14) Å
b = 19.693 (4) Å
c = 21.128 (4) Å
β = 90.98 (3)°

V = 3013.6 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.41 mm^{-1}
T = 298 (2) K
$0.23 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.430, T_{max} = 0.472
(expected range = 0.377–0.414)

12868 measured reflections
3443 independent reflections
2187 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.115
S = 0.99
3443 reflections
176 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.914 (3)	Cu1—N1	1.936 (4)
Cu1—N3	1.935 (4)	Cu1—N2	2.028 (4)
O1—Cu1—N3	89.25 (14)	O1—Cu1—N2	167.94 (16)
O1—Cu1—N1	92.72 (14)	N3—Cu1—N2	92.91 (17)
N3—Cu1—N1	176.34 (16)	N1—Cu1—N2	84.53 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Br1^i	0.899 (10)	3.09 (4)	3.777 (4)	135 (4)
N2—H2···O1^i	0.899 (10)	2.27 (3)	3.031 (5)	142 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2019).

References

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supplementary materials

Di-*μ*-thocyanato-bis{2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]phenolatocopper(II)}

P. Zhang

Comment

Recently, we has reported the crystal structure of a mononuclear copper(II) complex derived from the Schiff base ligand 1-[3-(cyclohexylamino)propyliminomethyl]-2-naphthol (Zhang, 2004). As an extension of this work on the structural characterization of Schiff base copper(II) compounds, we report on the crystal structure of the new title binuclear complex.

The title compound is a centrosymmetric dithiocyanato-bridged binuclear copper(II) complex, as shown in Fig. 1. The Cu^{II} atoms are pentacoordinated by the NNO donor atoms of the Schiff base ligand, 2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]phenol (HBCP), and by one N and one S atom, from symmetry related thiocyanate anions, forming a slightly distorted square pyramidal coordination configuration. The Cu···Cu distance is 5.480 (2) Å. The bond lengths and angles (Table 1) are within normal ranges and comparable to the values found in the complex mentioned above.

Experimental

N-Methyl-1,2-diaminoethane (0.1 mmol, 7.4 mg) and 3-bromo-5-chlorosalicylaldehyde (0.1 mmol, 23.5 mg) were dissolved in ethanol (10 cm^3). The mixture was stirred for 10 min to give a clear yellow solution. To the solution was added an aqueous solution (2 cm^3) of ammonium thiocyanate (0.1 mmol, 7.6 mg) and $CuCl_2 \cdot 2H_2O$ (0.1 mmol, 17.1 mg), with stirring. The mixture was stirred at room temperature for 1 h and then filtered. After keeping the brown filtrate in air for seven days, blue block-shaped crystals were formed with high yield (73% based on 3-bromo-5-chlorosalicylaldehyde).

Refinement

The H2 atom was located in a difference Fourier map and refined isotropically, with the N—H distance restrained to 0.90 (1) Å. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}$(methyl C).

Figures

Fig. 1. The structure of the complex, showing the atom-numbering scheme with displacement ellipsoids drawn at the 30% probability level.

supplementary materials

Di-µ-thocyanato-bis{2-bromo-4-chloro-6-[(2- methylaminoethylimino)methyl]phenolatocopper(II)}

Crystal data

$[Cu_2(C_{10}H_{11}Br_1Cl_1N_2O_1)_2(NCS)_2]$	$F_{000} = 1624$
$M_r = 824.38$	$D_x = 1.817$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.2440$ (14) Å	Cell parameters from 1694 reflections
$b = 19.693$ (4) Å	$\theta = 2.4$–24.5º
$c = 21.128$ (4) Å	$\mu = 4.41$ mm^{-1}
$\beta = 90.98$ (3)º	$T = 298$ (2) K
$V = 3013.6$ (10) Å^3	Block, blue
$Z = 4$	$0.23 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	3443 independent reflections
Radiation source: fine-focus sealed tube	2187 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.064$
$T = 298(2)$ K	$\theta_{max} = 27.5$º
ω scans	$\theta_{min} = 1.9$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.430$, $T_{max} = 0.472$	$k = -25 \rightarrow 25$
12868 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
3443 reflections	$\Delta\rho_{max} = 0.51$ e Å^{-3}
176 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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	0.08641 (8)	0.23561 (3)	0.44417 (3)	0.03910 (18)
Br1	0.10518 (8)	0.48082 (3)	0.42831 (3)	0.0597 (2)
Cl1	0.30665 (19)	0.45169 (8)	0.17930 (7)	0.0700 (4)
S1	−0.2341 (2)	0.28910 (9)	0.62831 (7)	0.0673 (4)
O1	0.1260 (4)	0.32908 (14)	0.42352 (13)	0.0400 (8)
N1	0.1986 (5)	0.20430 (18)	0.36694 (17)	0.0404 (9)
N2	0.1020 (6)	0.13676 (19)	0.4707 (2)	0.0489 (10)
N3	−0.0142 (6)	0.2635 (2)	0.52432 (18)	0.0475 (10)
C1	0.2193 (6)	0.3142 (2)	0.3153 (2)	0.0374 (10)
C2	0.1652 (6)	0.3537 (2)	0.3687 (2)	0.0363 (10)
C3	0.1652 (6)	0.4246 (2)	0.3588 (2)	0.0410 (11)
C4	0.2047 (6)	0.4542 (3)	0.3019 (2)	0.0505 (13)
H4	0.1992	0.5011	0.2972	0.061*
C5	0.2524 (6)	0.4136 (3)	0.2519 (2)	0.0495 (13)
C6	0.2593 (7)	0.3449 (3)	0.2576 (2)	0.0479 (12)
H6	0.2906	0.3183	0.2230	0.057*
C7	0.2399 (6)	0.2413 (2)	0.3195 (2)	0.0430 (12)
H7	0.2877	0.2193	0.2845	0.052*
C8	0.2424 (8)	0.1311 (2)	0.3683 (3)	0.0628 (15)
H8A	0.3704	0.1247	0.3812	0.075*
H8B	0.2255	0.1120	0.3263	0.075*
C9	0.1205 (8)	0.0960 (2)	0.4131 (2)	0.0623 (15)
H9A	−0.0002	0.0891	0.3936	0.075*
H9B	0.1719	0.0519	0.4238	0.075*
C10	−0.0439 (8)	0.1095 (3)	0.5115 (3)	0.0659 (16)
H10A	−0.1620	0.1155	0.4910	0.099*
H10B	−0.0421	0.1333	0.5511	0.099*
H10C	−0.0224	0.0620	0.5189	0.099*
C11	−0.1063 (6)	0.2737 (2)	0.5673 (2)	0.0447 (12)
H2	0.211 (4)	0.132 (3)	0.491 (2)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0502 (4)	0.0315 (3)	0.0357 (3)	−0.0015 (3)	0.0049 (2)	0.0000 (2)
Br1	0.0834 (4)	0.0382 (3)	0.0574 (4)	0.0070 (3)	−0.0037 (3)	−0.0075 (2)
Cl1	0.0670 (9)	0.0903 (11)	0.0529 (8)	0.0032 (8)	0.0099 (7)	0.0358 (8)
S1	0.0625 (9)	0.0938 (12)	0.0463 (8)	0.0121 (8)	0.0181 (7)	0.0091 (8)
O1	0.059 (2)	0.0303 (17)	0.0310 (17)	−0.0028 (15)	0.0085 (15)	0.0012 (13)
N1	0.047 (2)	0.032 (2)	0.043 (2)	−0.0035 (17)	0.0084 (19)	−0.0033 (18)
N2	0.062 (3)	0.037 (2)	0.047 (3)	−0.002 (2)	0.000 (2)	0.0011 (19)
N3	0.059 (3)	0.045 (2)	0.038 (2)	−0.003 (2)	0.009 (2)	0.0016 (19)
C1	0.037 (3)	0.040 (3)	0.036 (3)	0.000 (2)	0.006 (2)	0.002 (2)
C2	0.031 (2)	0.039 (3)	0.039 (3)	−0.003 (2)	−0.004 (2)	−0.002 (2)
C3	0.042 (3)	0.039 (3)	0.042 (3)	0.002 (2)	−0.002 (2)	−0.003 (2)
C4	0.043 (3)	0.047 (3)	0.061 (4)	−0.001 (2)	−0.003 (3)	0.015 (3)
C5	0.043 (3)	0.068 (4)	0.037 (3)	0.001 (3)	0.006 (2)	0.018 (3)
C6	0.044 (3)	0.061 (4)	0.039 (3)	0.000 (2)	0.008 (2)	0.000 (2)
C7	0.042 (3)	0.043 (3)	0.043 (3)	−0.001 (2)	0.008 (2)	−0.015 (2)
C8	0.080 (4)	0.033 (3)	0.076 (4)	0.002 (3)	0.020 (3)	−0.007 (3)
C9	0.093 (4)	0.036 (3)	0.058 (4)	0.003 (3)	−0.001 (3)	−0.003 (3)
C10	0.083 (4)	0.041 (3)	0.074 (4)	−0.013 (3)	0.003 (3)	0.010 (3)
C11	0.047 (3)	0.045 (3)	0.043 (3)	−0.004 (2)	−0.002 (2)	0.008 (2)

Geometric parameters (Å, °)

Cu1—O1	1.914 (3)	C1—C7	1.445 (6)
Cu1—N3	1.935 (4)	C2—C3	1.412 (6)
Cu1—N1	1.936 (4)	C3—C4	1.370 (6)
Cu1—N2	2.028 (4)	C4—C5	1.374 (7)
Br1—C3	1.896 (4)	C4—H4	0.9300
Cl1—C5	1.758 (5)	C5—C6	1.359 (6)
S1—C11	1.628 (5)	C6—H6	0.9300
O1—C2	1.291 (5)	C7—H7	0.9300
N1—C7	1.278 (6)	C8—C9	1.478 (7)
N1—C8	1.475 (6)	C8—H8A	0.9700
N2—C9	1.464 (6)	C8—H8B	0.9700
N2—C10	1.476 (6)	C9—H9A	0.9700
N2—H2	0.899 (10)	C9—H9B	0.9700
N3—C11	1.154 (6)	C10—H10A	0.9600
C1—C6	1.397 (6)	C10—H10B	0.9600
C1—C2	1.430 (6)	C10—H10C	0.9600
O1—Cu1—N3	89.25 (14)	C6—C5—C4	121.4 (4)
O1—Cu1—N1	92.72 (14)	C6—C5—Cl1	119.6 (4)
N3—Cu1—N1	176.34 (16)	C4—C5—Cl1	119.0 (4)
O1—Cu1—N2	167.94 (16)	C5—C6—C1	120.1 (5)
N3—Cu1—N2	92.91 (17)	C5—C6—H6	120.0
N1—Cu1—N2	84.53 (16)	C1—C6—H6	120.0

C2—O1—Cu1	126.9 (3)	N1—C7—C1	126.1 (4)
C7—N1—C8	121.3 (4)	N1—C7—H7	117.0
C7—N1—Cu1	125.9 (3)	C1—C7—H7	117.0
C8—N1—Cu1	112.8 (3)	N1—C8—C9	109.8 (4)
C9—N2—C10	111.2 (4)	N1—C8—H8A	109.7
C9—N2—Cu1	107.6 (3)	C9—C8—H8A	109.7
C10—N2—Cu1	118.2 (3)	N1—C8—H8B	109.7
C9—N2—H2	104 (3)	C9—C8—H8B	109.7
C10—N2—H2	108 (3)	H8A—C8—H8B	108.2
Cu1—N2—H2	106 (3)	N2—C9—C8	109.9 (4)
C11—N3—Cu1	166.0 (4)	N2—C9—H9A	109.7
C6—C1—C2	121.1 (4)	C8—C9—H9A	109.7
C6—C1—C7	117.4 (4)	N2—C9—H9B	109.7
C2—C1—C7	121.4 (4)	C8—C9—H9B	109.7
O1—C2—C3	120.3 (4)	H9A—C9—H9B	108.2
O1—C2—C1	124.8 (4)	N2—C10—H10A	109.5
C3—C2—C1	114.9 (4)	N2—C10—H10B	109.5
C4—C3—C2	123.5 (4)	H10A—C10—H10B	109.5
C4—C3—Br1	119.0 (4)	N2—C10—H10C	109.5
C2—C3—Br1	117.5 (3)	H10A—C10—H10C	109.5
C3—C4—C5	119.1 (5)	H10B—C10—H10C	109.5
C3—C4—H4	120.5	N3—C11—S1	179.1 (5)
C5—C4—H4	120.5		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Br1[i]	0.899 (10)	3.09 (4)	3.777 (4)	135 (4)
N2—H2···O1[i]	0.899 (10)	2.27 (3)	3.031 (5)	142 (4)

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

Fig. 1