

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# (Acetato- $\kappa$ O)(2-bromo-6-[[3-(dimethylazanumyl)propylimino- $\kappa$ N]methyl]-phenolato- $\kappa$ O)(thiocyanato- $\kappa$ N)zinc

Cheng-Li Han

College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, People's Republic of China

Correspondence e-mail: chengli\_han@126.com

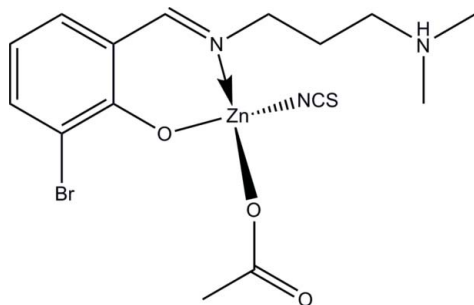
Received 10 April 2012; accepted 20 April 2012

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.010$  Å;  $R$  factor = 0.072;  $wR$  factor = 0.201; data-to-parameter ratio = 16.9.

In the title compound,  $[\text{Zn}(\text{CH}_3\text{COO})(\text{NCS})(\text{C}_{12}\text{H}_{17}\text{BrN}_2\text{O})]$ , the  $\text{Zn}^{\text{II}}$  atom is four-coordinated in a distorted tetrahedral geometry, binding to a phenolate O and an imine N atom of the Schiff base ligand, the O atom of an acetate ligand and one thiocyanate N atom. In the crystal, molecules are linked *via* pairs of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, forming inversion dimers.

## Related literature

For a zinc Schiff base complex reported previously by the author, see: Han (2009). For related zinc complexes, see: Ali *et al.* (2008); You (2005); Zhu & Yang (2008).



## Experimental

## Crystal data

 $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)(\text{NCS})\cdot(\text{C}_{12}\text{H}_{17}\text{BrN}_2\text{O})]$ 
 $M_r = 467.68$   
Triclinic,  $P\bar{1}$ 
 $a = 9.3091$  (6) Å  
 $b = 10.2687$  (6) Å  
 $c = 11.8353$  (7) Å  
 $\alpha = 66.299$  (2)°  
 $\beta = 79.891$  (2)°  
 $\gamma = 88.122$  (2)°

 $V = 1018.96$  (11) Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 3.28$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.17 \times 0.15 \times 0.15$  mm

## Data collection

 Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.605$ ,  $T_{\text{max}} = 0.639$ 

 9684 measured reflections  
3720 independent reflections  
3021 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.129$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.072$   
 $wR(F^2) = 0.201$   
 $S = 1.07$   
3720 reflections

 220 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.61$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O3}^{\text{i}}$	0.91	1.81	2.703 (6)	168

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); 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 and PLATON (Spek, 2009).

The author acknowledges Qiqihar University for a research grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2407).

## References

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## supplementary materials

*Acta Cryst.* (2012). E68, m677 [doi:10.1107/S1600536812017564]

**(Acetato- $\kappa$ O)(2-bromo-6-[3-(dimethylazaniumyl)propylimino- $\kappa$ N]methyl)-phenolato- $\kappa$ O)(thiocyanato- $\kappa$ N)zinc**

**Cheng-Li Han**

**Comment**

Continuing our research into the synthesis of Schiff base zinc(II) complexes (Han, 2009), we report herein on the crystal structure of the title complex. It was synthesized by the reaction of equimolar quantities of 3-bromosalicylaldehyde, N,N-dimethylpropane-1,3-diamine, ammonium thiocyanate, and zinc acetate in methanol.

In the title complex (Fig. 1), the Zn<sup>II</sup> atom is four-coordinate in a tetrahedral geometry, with one O and one imine N atoms of the Schiff base ligand, one O atom of an acetate ligand, and one thiocyanate N atom. The tetrahedral geometry is severely distorted, as evidenced by the coordinate bond lengths [1.931 (4) - 1.994 (5) Å] and bond angles [96.3 (2) - 124.1 (2)°]. They are however comparable to those in similar zinc(II) complexes (Ali *et al.*, 2008; You, 2005; Zhu & Yang, 2008).

In the crystal, molecules are linked through N–H...O hydrogen bonds to form inversion dimers (Table 1 and Fig. 2).

**Experimental**

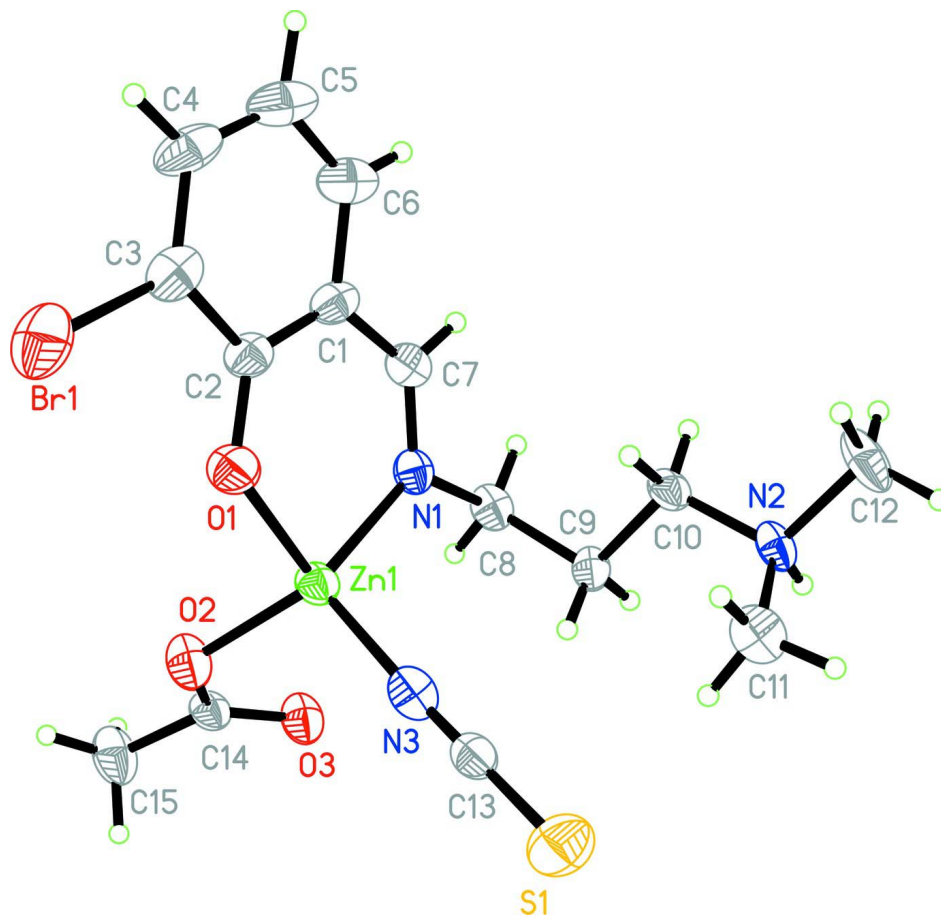
Equimolar quantities (1.0 mmol each) of 3-bromosalicylaldehyde, N,N-dimethylpropane-1,3-diamine, ammonium thiocyanate, and zinc acetate were mixed in methanol. The mixture was stirred at reflux for 30 min and filtered. The filtrate was left to evaporate slowly for a few days, yielding colourless block-like crystals.

**Refinement**

The NH and C-bound H-atoms were included in calculated positions and treated as riding atoms: N–H = 0.91 Å, C–H = 0.93, 0.97 and 0.96 Å for CH, CH<sub>2</sub>, and CH<sub>3</sub> H-atoms, respectively, with  $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$ , where  $k = 1.5$  for CH<sub>3</sub> H-atoms, and  $= 1.2$  for other H-atoms. A region of disordered electron density (ca. 1.3 Å<sup>3</sup>) was located at position 0,0,0.5 but it could not be identified and was not taken into consideration during refinement; it corresponds to the position of a small void in the unit cell of ca. 83 Å<sup>3</sup>, as detected by checkcif (PLATON; Spek, 2009).

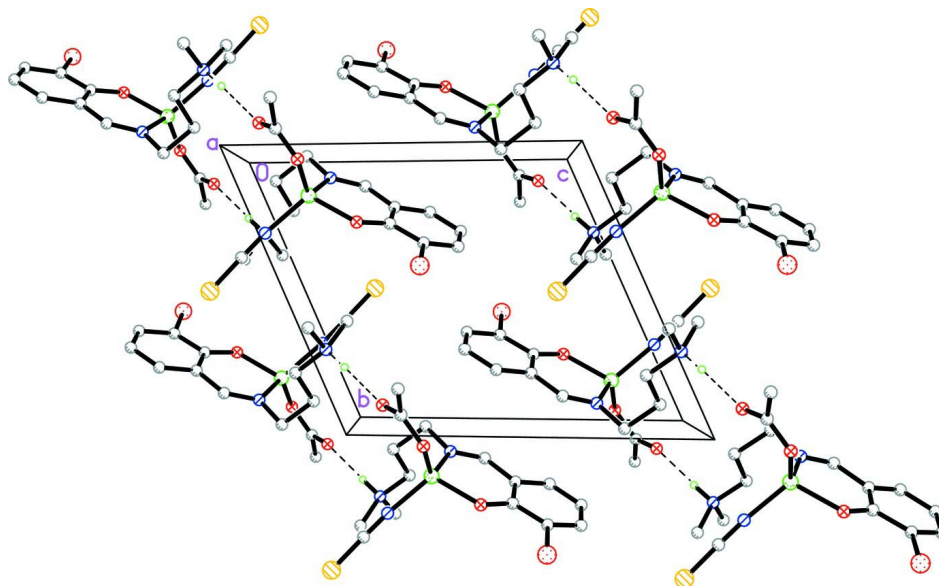
**Computing details**

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE* (Bruker, 1998); 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* (Sheldrick, 2008) and *PLATON* (Spek, 2009).



**Figure 1**

The molecular structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering.

**Figure 2**

The crystal packing of the title complex viewed along the *a* axis, showing the formation of the inversion dimers. The N···O hydrogen bonds are shown as dashed lines.

**(Acetato- $\kappa$ O)(2-bromo-6-[[3-(dimethylazaniumyl)propylimino- $\kappa$ N]methyl]phenolato- $\kappa$ O)(thiocyanato- $\kappa$ N)zinc**

*Crystal data*

[Zn(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)(NCS)(C<sub>12</sub>H<sub>17</sub>BrN<sub>2</sub>O)]

*M<sub>r</sub>* = 467.68

Triclinic, *P* $\bar{1}$

Hall symbol: -*P* 1

*a* = 9.3091 (6) Å

*b* = 10.2687 (6) Å

*c* = 11.8353 (7) Å

$\alpha$  = 66.299 (2)°

$\beta$  = 79.891 (2)°

$\gamma$  = 88.122 (2)°

*V* = 1018.96 (11) Å<sup>3</sup>

*Z* = 2

*F*(000) = 472

*D<sub>x</sub>* = 1.524 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 5991 reflections

$\theta$  = 2.2–27.9°

$\mu$  = 3.28 mm<sup>-1</sup>

*T* = 298 K

Block, colourless

0.17 × 0.15 × 0.15 mm

*Data collection*

Bruker SMART CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

*T<sub>min</sub>* = 0.605, *T<sub>max</sub>* = 0.639

9684 measured reflections

3720 independent reflections

3021 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.129

$\theta_{\max}$  = 25.5°,  $\theta_{\min}$  = 2.2°

*h* = -11→11

*k* = -12→12

*l* = -14→14

*Refinement*

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.072

*wR*(*F*<sup>2</sup>) = 0.201

*S* = 1.07

3720 reflections

220 parameters

0 restraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2 + 2.5468P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.32 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{Å}^{-3}$

*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  $F^2 > 2\text{sigma}(F^2)$  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 ( $\text{Å}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.71920 (7)	0.16314 (7)	0.17582 (7)	0.0445 (3)
Br1	0.86805 (11)	0.41595 (10)	0.41002 (10)	0.0872 (4)
N1	0.5145 (5)	0.0900 (5)	0.2551 (5)	0.0429 (11)
N2	0.2396 (5)	0.2871 (5)	-0.0322 (5)	0.0436 (11)
H2	0.2172	0.2258	-0.0653	0.052*
N3	0.7308 (6)	0.2974 (7)	0.0016 (6)	0.0642 (15)
O1	0.7416 (5)	0.2599 (5)	0.2823 (5)	0.0599 (12)
O2	0.8893 (5)	0.0442 (5)	0.1972 (5)	0.0598 (12)
O3	0.7888 (5)	-0.0922 (5)	0.1276 (5)	0.0565 (11)
S1	0.7396 (3)	0.5055 (2)	-0.2352 (2)	0.0807 (6)
C1	0.5007 (7)	0.1983 (6)	0.4068 (5)	0.0478 (14)
C2	0.6446 (7)	0.2621 (6)	0.3737 (6)	0.0475 (14)
C3	0.6772 (9)	0.3331 (6)	0.4473 (7)	0.0589 (17)
C4	0.5794 (11)	0.3442 (7)	0.5422 (7)	0.070 (2)
H4	0.6069	0.3901	0.5891	0.084*
C5	0.4342 (11)	0.2853 (8)	0.5701 (7)	0.075 (2)
H5	0.3646	0.2963	0.6320	0.090*
C6	0.4007 (9)	0.2134 (7)	0.5044 (6)	0.0640 (19)
H6	0.3073	0.1718	0.5243	0.077*
C7	0.4463 (7)	0.1182 (6)	0.3462 (6)	0.0473 (14)
H7	0.3503	0.0826	0.3767	0.057*
C8	0.4325 (7)	0.0049 (6)	0.2105 (6)	0.0486 (14)
H8A	0.3428	-0.0341	0.2699	0.058*
H8B	0.4903	-0.0740	0.2065	0.058*
C9	0.3960 (6)	0.0940 (6)	0.0817 (6)	0.0430 (13)
H9A	0.4839	0.1438	0.0248	0.052*
H9B	0.3587	0.0321	0.0485	0.052*
C10	0.2827 (6)	0.2011 (7)	0.0899 (6)	0.0468 (14)
H10A	0.1967	0.1508	0.1495	0.056*
H10B	0.3217	0.2641	0.1210	0.056*
C11	0.3592 (8)	0.3865 (8)	-0.1235 (8)	0.0659 (19)
H11A	0.3239	0.4437	-0.1991	0.099*

H11B	0.4392	0.3329	-0.1423	0.099*
H11C	0.3916	0.4470	-0.0879	0.099*
C12	0.1071 (7)	0.3664 (8)	-0.0167 (9)	0.074 (2)
H12A	0.0287	0.3006	0.0379	0.110*
H12B	0.0797	0.4187	-0.0969	0.110*
H12C	0.1269	0.4314	0.0192	0.110*
C13	0.7343 (6)	0.3843 (7)	-0.0990 (6)	0.0471 (14)
C14	0.8872 (6)	-0.0647 (6)	0.1725 (6)	0.0418 (13)
C15	1.0122 (8)	-0.1603 (8)	0.2014 (8)	0.068 (2)
H15A	0.9755	-0.2559	0.2535	0.102*
H15B	1.0720	-0.1286	0.2445	0.102*
H15C	1.0694	-0.1579	0.1247	0.102*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0424 (4)	0.0461 (4)	0.0530 (5)	0.0063 (3)	-0.0081 (3)	-0.0288 (3)
Br1	0.1033 (7)	0.0773 (6)	0.1037 (7)	-0.0066 (5)	-0.0388 (6)	-0.0506 (5)
N1	0.041 (2)	0.038 (2)	0.050 (3)	0.0034 (19)	-0.012 (2)	-0.017 (2)
N2	0.036 (2)	0.036 (2)	0.073 (3)	0.0091 (18)	-0.018 (2)	-0.034 (2)
N3	0.047 (3)	0.075 (4)	0.072 (4)	0.007 (3)	-0.010 (3)	-0.031 (3)
O1	0.056 (2)	0.069 (3)	0.072 (3)	-0.001 (2)	-0.008 (2)	-0.047 (3)
O2	0.053 (2)	0.057 (3)	0.095 (4)	0.016 (2)	-0.027 (2)	-0.052 (3)
O3	0.052 (2)	0.055 (2)	0.082 (3)	0.0154 (19)	-0.024 (2)	-0.044 (2)
S1	0.0938 (15)	0.0725 (13)	0.0613 (12)	-0.0063 (11)	-0.0086 (11)	-0.0134 (10)
C1	0.067 (4)	0.038 (3)	0.039 (3)	0.013 (3)	-0.012 (3)	-0.017 (2)
C2	0.062 (4)	0.039 (3)	0.049 (3)	0.013 (3)	-0.014 (3)	-0.024 (3)
C3	0.088 (5)	0.037 (3)	0.057 (4)	0.013 (3)	-0.023 (4)	-0.020 (3)
C4	0.127 (7)	0.044 (3)	0.049 (4)	0.018 (4)	-0.021 (4)	-0.027 (3)
C5	0.112 (7)	0.058 (4)	0.051 (4)	0.016 (4)	0.001 (4)	-0.025 (3)
C6	0.084 (5)	0.047 (3)	0.051 (4)	0.011 (3)	0.001 (3)	-0.015 (3)
C7	0.047 (3)	0.040 (3)	0.048 (3)	0.002 (2)	-0.004 (3)	-0.012 (3)
C8	0.046 (3)	0.040 (3)	0.062 (4)	0.003 (2)	-0.011 (3)	-0.022 (3)
C9	0.046 (3)	0.041 (3)	0.057 (3)	0.012 (2)	-0.020 (3)	-0.032 (3)
C10	0.042 (3)	0.051 (3)	0.061 (4)	0.012 (2)	-0.010 (3)	-0.035 (3)
C11	0.061 (4)	0.051 (4)	0.079 (5)	-0.003 (3)	-0.008 (4)	-0.021 (4)
C12	0.048 (3)	0.063 (4)	0.130 (7)	0.027 (3)	-0.028 (4)	-0.057 (5)
C13	0.038 (3)	0.053 (3)	0.055 (4)	0.002 (2)	-0.005 (3)	-0.027 (3)
C14	0.040 (3)	0.040 (3)	0.052 (3)	0.010 (2)	-0.007 (2)	-0.026 (3)
C15	0.058 (4)	0.059 (4)	0.104 (6)	0.023 (3)	-0.031 (4)	-0.045 (4)

*Geometric parameters (Å, °)*

Zn1—O1	1.931 (4)	C5—C6	1.345 (11)
Zn1—N3	1.952 (7)	C5—H5	0.9300
Zn1—O2	1.957 (4)	C6—H6	0.9300
Zn1—N1	1.994 (5)	C7—H7	0.9300
Br1—C3	1.897 (8)	C8—C9	1.523 (9)
N1—C7	1.284 (8)	C8—H8A	0.9700
N1—C8	1.476 (8)	C8—H8B	0.9700

N2—C10	1.477 (8)	C9—C10	1.518 (7)
N2—C12	1.482 (7)	C9—H9A	0.9700
N2—C11	1.488 (8)	C9—H9B	0.9700
N2—H2	0.9100	C10—H10A	0.9700
N3—C13	1.161 (9)	C10—H10B	0.9700
O1—C2	1.289 (7)	C11—H11A	0.9600
O2—C14	1.265 (7)	C11—H11B	0.9600
O3—C14	1.229 (7)	C11—H11C	0.9600
S1—C13	1.586 (7)	C12—H12A	0.9600
C1—C6	1.407 (9)	C12—H12B	0.9600
C1—C2	1.430 (9)	C12—H12C	0.9600
C1—C7	1.442 (9)	C14—C15	1.493 (8)
C2—C3	1.414 (9)	C15—H15A	0.9600
C3—C4	1.356 (11)	C15—H15B	0.9600
C4—C5	1.428 (13)	C15—H15C	0.9600
C4—H4	0.9300		
O1—Zn1—N3	111.3 (2)	N1—C8—H8A	109.3
O1—Zn1—O2	100.4 (2)	C9—C8—H8A	109.3
N3—Zn1—O2	111.2 (2)	N1—C8—H8B	109.3
O1—Zn1—N1	96.3 (2)	C9—C8—H8B	109.3
N3—Zn1—N1	111.3 (2)	H8A—C8—H8B	108.0
O2—Zn1—N1	124.1 (2)	C10—C9—C8	110.5 (5)
C7—N1—C8	116.7 (5)	C10—C9—H9A	109.5
C7—N1—Zn1	121.0 (4)	C8—C9—H9A	109.5
C8—N1—Zn1	122.2 (4)	C10—C9—H9B	109.5
C10—N2—C12	111.3 (5)	C8—C9—H9B	109.5
C10—N2—C11	112.8 (5)	H9A—C9—H9B	108.1
C12—N2—C11	110.2 (5)	N2—C10—C9	112.7 (5)
C10—N2—H2	107.4	N2—C10—H10A	109.1
C12—N2—H2	107.4	C9—C10—H10A	109.1
C11—N2—H2	107.4	N2—C10—H10B	109.1
C13—N3—Zn1	175.3 (6)	C9—C10—H10B	109.1
C2—O1—Zn1	125.7 (4)	H10A—C10—H10B	107.8
C14—O2—Zn1	117.7 (4)	N2—C11—H11A	109.5
C6—C1—C2	119.7 (6)	N2—C11—H11B	109.5
C6—C1—C7	115.5 (6)	H11A—C11—H11B	109.5
C2—C1—C7	124.8 (5)	N2—C11—H11C	109.5
O1—C2—C3	119.9 (6)	H11A—C11—H11C	109.5
O1—C2—C1	124.3 (5)	H11B—C11—H11C	109.5
C3—C2—C1	115.8 (6)	N2—C12—H12A	109.5
C4—C3—C2	123.3 (7)	N2—C12—H12B	109.5
C4—C3—Br1	119.1 (6)	H12A—C12—H12B	109.5
C2—C3—Br1	117.6 (5)	N2—C12—H12C	109.5
C3—C4—C5	120.0 (7)	H12A—C12—H12C	109.5
C3—C4—H4	120.0	H12B—C12—H12C	109.5
C5—C4—H4	120.0	N3—C13—S1	178.7 (6)
C6—C5—C4	118.3 (7)	O3—C14—O2	122.9 (5)
C6—C5—H5	120.9	O3—C14—C15	120.9 (5)

C4—C5—H5	120.9	O2—C14—C15	116.2 (6)
C5—C6—C1	122.9 (8)	C14—C15—H15A	109.5
C5—C6—H6	118.6	C14—C15—H15B	109.5
C1—C6—H6	118.6	H15A—C15—H15B	109.5
N1—C7—C1	127.8 (6)	C14—C15—H15C	109.5
N1—C7—H7	116.1	H15A—C15—H15C	109.5
C1—C7—H7	116.1	H15B—C15—H15C	109.5
N1—C8—C9	111.6 (5)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2 $\cdots$ O3 <sup>i</sup>	0.91	1.81	2.703 (6)	168

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