



Crystal structure of bis(isonicotinamide- κN^1)-bis(thiocyanato- κN)zinc

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Received 29 May 2016

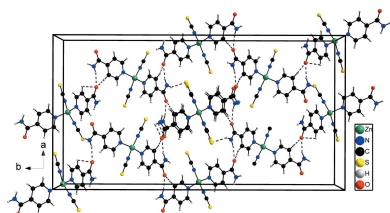
Accepted 3 June 2016

Edited by M. Weil, Vienna University of
Technology, Austria**Keywords:** crystal structure; discrete complex;
zinc thiocyanate; isonicotinamide; hydrogen
bonding.**CCDC reference:** 1483379**Supporting information:** this article has
supporting information at journals.iucr.org/e

The asymmetric unit of the title complex, $[\text{Zn}(\text{SCN})_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2]$, consists of one Zn^{2+} cation located on a twofold rotation axis, as well as of one thiocyanate anion and one neutral isonicotinamide ligand, both occupying general positions. The Zn^{2+} cation is tetrahedrally coordinated into a discrete complex by the N atoms of two symmetry-related thiocyanate anions and by the pyridine N atoms of two isonicotinamide ligands. The complexes are linked by intermolecular C—H \cdots O and N—H \cdots O, and weak intermolecular N—H \cdots S hydrogen-bonding interactions into a three-dimensional network.

1. Chemical context

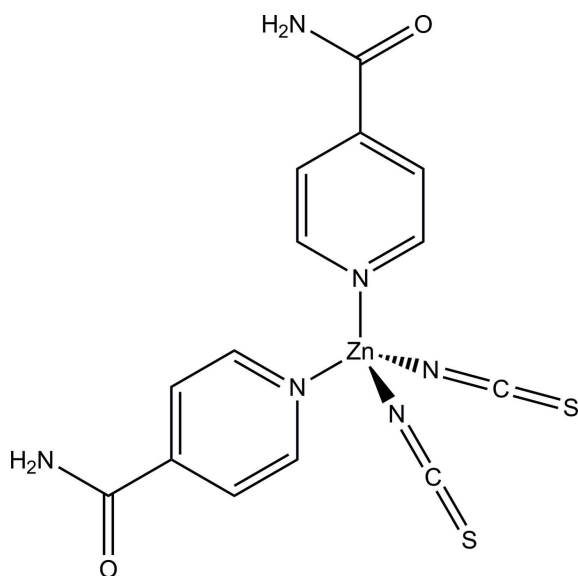
The synthesis of magnetic materials is still a major field in coordination chemistry (Liu *et al.*, 2006). For their construction, paramagnetic cations can be linked by small anionic ligands such as thiocyanate anions to enable a magnetic exchange between the cations (Palion-Gazda *et al.*, 2015; Banerjee *et al.*, 2005). In this context we have reported on a number of coordination polymers with thiocyanato ligands that show different magnetic phenomena, including a slow relaxation of the magnetization which is indicative of single-chain magnetism (Werner *et al.*, 2014; 2015*a,b,c*). In several cases, such phases can only be prepared by thermal decomposition of suitable precursor compounds (Näther *et al.*, 2013), leading to microcrystalline powders for which a straightforward crystal structure determination is difficult. In order to avoid this scenario, compounds of the same composition based on cadmium or zinc can be prepared in the form of single crystals. In many cases, such zinc and cadmium compounds are isotopic to the paramagnetic analogues, and the structure of the latter can then easily be refined by the Rietveld method (Wöhlert *et al.*, 2013). It should be mentioned that the structures of cadmium compounds are useful as prototypes for transition metal compounds with octahedral coordination spheres, whereas the structures of zinc compounds are useful prototypes for compounds with tetrahedral coordination spheres for the transition metal. The thermal decomposition of cobalt complexes is an example of the latter. In the course of our systematic investigation in this regard, we became interested in isonicotinamide as a co-ligand to be reacted with $\text{Zn}(\text{SCN})_2$. The synthesis and crystal structure of the resulting compound, $[\text{Zn}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2]$, are reported here.



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2. Structural commentary

The asymmetric unit of the title compound consists of one Zn^{2+} cation, one thiocyanate anion and one neutral isonicotinamide ligand. The thiocyanate anion and the isonicotinamide ligand are located on general positions whereas the Zn^{2+} cation is located on a twofold rotation axis. The Zn^{2+} cation is tetrahedrally coordinated by two terminal N-bonded thiocyanato ligands and by two isonicotinamide ligands through their pyridine N atoms into a discrete complex (Fig. 1). As expected, the $\text{Zn}-\text{N}$ bond length involving the thiocyanate anion (N1) is significantly shorter than that to the pyridine N atom (N11) of the neutral ligand (Table 1). The angular distortion of the ZnN_4 tetrahedron is noticeable, with $\text{N}-\text{Zn}-\text{N}$ angles ranging from $104.32(13)$ to $123.6(2)^\circ$.



3. Supramolecular features

In the crystal structure, the discrete complexes are stacked along the c axis and are linked by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding between one of the two amide H atoms and the amide O atom of a neighboring complex (Fig. 2 and Table 2). There is a further weak contact between one aromatic H atom of the pyridine ring and the carbonyl O atom of a neighboring complex (Table 2). The second H atom of the NH_2 group is involved in intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonding to the S atoms of the anionic ligand. In this way a three-dimensional hydrogen-bonded network is formed.

4. Database survey

To the best of our knowledge, there are only five coordination polymers with isonicotinamide and thiocyanate anions deposited in the Cambridge Structure Database (Version 5.37, last update 2015; Groom *et al.*, 2016). This includes two clathrate-structures of Ni compounds with μ -1,3-bridging thiocyanate anions and with 9,10-anthraquinone and pyrene as solvate molecules (Sekiya *et al.*, 2009). Furthermore, a one-

Table 1
Selected bond lengths (\AA).

Zn1–N1	1.921 (3)	Zn1–N11	2.033 (3)
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Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C14–H14 \cdots O11 ⁱ	0.95	2.54	3.365 (6)	145
N12–H12A \cdots S1 ⁱⁱ	0.88	2.62	3.407 (3)	150
N12–H12B \cdots O11 ⁱ	0.88	1.97	2.821 (4)	162

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{5}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{7}{2}$.

dimensional μ -1,3-thiocyanate-bridged cadmium compound with 9,10-dichloroanthracene as clathrate molecule (Sekiya & Nishikiori, 2005) as well as a three-dimensional network of Cd with μ -1,3-bridging thiocyanate anions (Yang *et al.*, 2001) are known. Finally, a compound consisting of Cu^{II} -NCS sheets has been reported (Đaković *et al.*, 2010).

5. Synthesis and crystallization

$\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and isonicotinamide were purchased from Alfa Aesar. $\text{Zn}(\text{NCS})_2$ was synthesized by stirring 3.076 g $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ (10 mmol) with 1.795 g

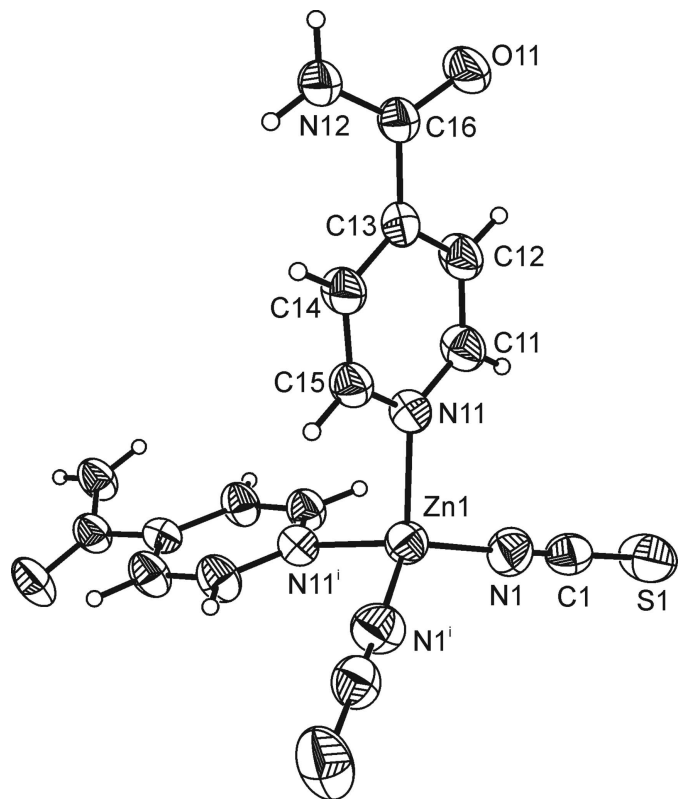


Figure 1
View of the discrete complex with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, z$.]

Table 3
Experimental details.

Crystal data	
Chemical formula	[Zn(NCS) ₂ (C ₆ H ₆ N ₂ O) ₂]
<i>M_r</i>	425.79
Crystal system, space group	Orthorhombic, <i>Fdd2</i>
Temperature (K)	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.1926 (9), 36.3044 (12), 5.2930 (2)
<i>V</i> (Å ³)	3688.0 (3)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	1.58
Crystal size (mm)	0.20 × 0.16 × 0.11
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (<i>X-SHAPE</i> and <i>X-RED32</i> ; Stoe, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.595, 0.742
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	15338, 2132, 2012
<i>R_{int}</i>	0.035
(sin θ/λ) _{max} (Å ⁻¹)	0.662
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.067, 1.13
No. of reflections	2132
No. of parameters	114
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.24, -0.27
Absolute structure	Flack <i>x</i> determined using 819 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013).
Absolute structure parameter	-0.005 (8)

Computer programs: *X-AREA* (Stoe, 2008), *SHELXS97* and *XP* in *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

ZnSO₄·H₂O (10 mmol) in 350 ml water. The white residue was filtered off and the filtrate was dried using a rotary evaporator. The homogeneity was checked by X-ray powder diffraction and elemental analysis. Crystals of the title compound suitable for single crystal X-Ray diffraction were obtained by the reaction of 27.2 mg Zn(NCS)₂ (0.15 mmol) with 36.64 mg isonicotinamide (0.3 mmol) in methylocyanide (1.5 ml) within a few days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C- and N-bound H atoms were located in a difference Fourier map but were positioned with idealized geometry. They were refined with *U*_{iso}(H) = 1.2*U*_{eq}(C, N) using a riding model with C–H = 0.95 Å for aromatic and N–H = 0.88 Å for the amide H atoms. The absolute structure was determined and is in agreement with the selected setting [Flack *x* parameter: 0.005 (19) by classical fit to all intensities (Flack, 1983) and -0.005 (8) from 819 selected quotients (Parsons *et al.*, 2013)].

Acknowledgements

This project was supported by the Deutsche Forschungsgemeinschaft (Project No. NA 720/5-1) and the State of Schleswig-Holstein. We thank Professor Dr Wolfgang Bensch for access to his experimental facilities.

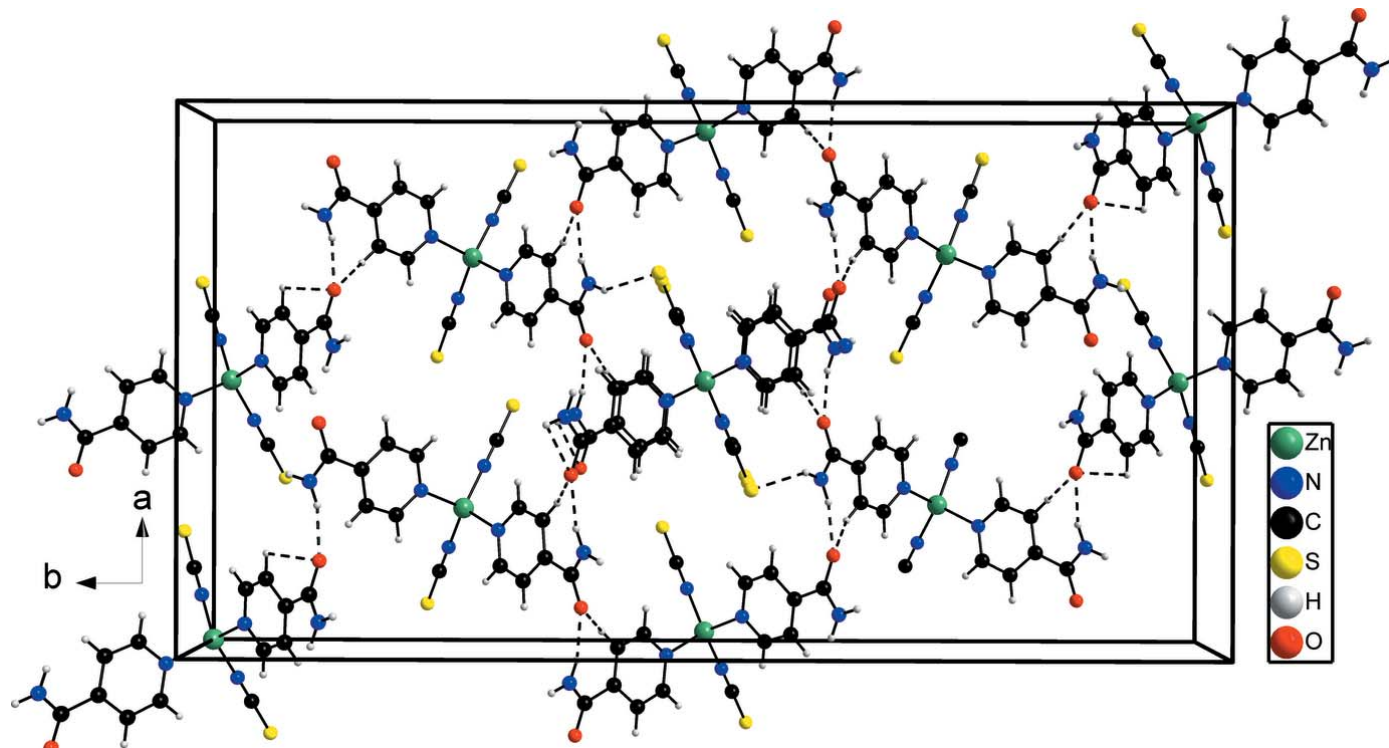


Figure 2
The packing of the complexes in the title compound, in a view along the *c* axis. Intermolecular hydrogen bonding is shown as dashed lines.

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supporting information

Acta Cryst. (2016). E72, 922-925 [https://doi.org/10.1107/S2056989016008963]

Crystal structure of bis(isonicotinamide- κN^1)bis(thiocyanato- κN)zinc

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Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(isonicotinamide- κN^1)bis(thiocyanato- κN)zinc

Crystal data

[Zn(NCS)₂(C₆H₆N₂O)₂]

$M_r = 425.79$

Orthorhombic, *Fdd2*

$a = 19.1926$ (9) Å

$b = 36.3044$ (12) Å

$c = 5.2930$ (2) Å

$V = 3688.0$ (3) Å³

$Z = 8$

$F(000) = 1728$

$D_x = 1.534$ Mg m⁻³

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

Cell parameters from 15683 reflections

$\theta = 4.2$ – 56.2°

$\mu = 1.58$ mm⁻¹

$T = 200$ K

Block, colorless

$0.20 \times 0.16 \times 0.11$ mm

Data collection

Stoe IPDS-2
diffractometer

ω scans

Absorption correction: numerical
(*X-SHAPE* and *X-RED32*; Stoe, 2008)

$T_{\min} = 0.595$, $T_{\max} = 0.742$

15338 measured reflections

2132 independent reflections

2012 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 28.1^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -25 \rightarrow 25$

$k = -47 \rightarrow 47$

$l = -6 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.067$

$S = 1.13$

2132 reflections

114 parameters

1 restraint

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 4.6943P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ e Å⁻³

Absolute structure: Flack x determined using

819 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*,
2013).

Absolute structure parameter: -0.005 (8)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.5000	0.00134 (10)	0.04197 (15)
N1	0.41911 (18)	0.48143 (9)	−0.1702 (7)	0.0562 (8)
C1	0.3688 (2)	0.46990 (10)	−0.2648 (9)	0.0514 (9)
S1	0.29987 (6)	0.45456 (4)	−0.4003 (3)	0.0802 (4)
N11	0.46205 (13)	0.53943 (7)	0.2367 (6)	0.0399 (6)
C11	0.39419 (17)	0.54254 (10)	0.2958 (8)	0.0465 (9)
H11	0.3616	0.5266	0.2164	0.056*
C12	0.37026 (17)	0.56804 (10)	0.4673 (8)	0.0466 (8)
H12	0.3219	0.5697	0.5036	0.056*
C13	0.41714 (16)	0.59132 (9)	0.5870 (7)	0.0373 (7)
C14	0.48690 (15)	0.58811 (9)	0.5240 (9)	0.0438 (8)
H14	0.5205	0.6037	0.6011	0.053*
C15	0.50720 (17)	0.56217 (10)	0.3489 (7)	0.0428 (8)
H15	0.5552	0.5604	0.3063	0.051*
C16	0.39066 (16)	0.61924 (9)	0.7711 (8)	0.0429 (7)
N12	0.43541 (15)	0.63295 (9)	0.9372 (6)	0.0486 (8)
H12A	0.4215	0.6495	1.0479	0.058*
H12B	0.4791	0.6255	0.9367	0.058*
O11	0.32905 (12)	0.62889 (8)	0.7653 (7)	0.0590 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0442 (3)	0.0394 (2)	0.0424 (3)	0.0020 (3)	0.000	0.000
N1	0.059 (2)	0.0546 (19)	0.055 (2)	0.0028 (16)	−0.0093 (16)	−0.0096 (15)
C1	0.056 (2)	0.0481 (18)	0.050 (2)	0.0044 (16)	0.0007 (19)	−0.011 (2)
S1	0.0496 (6)	0.0997 (10)	0.0914 (10)	−0.0051 (6)	−0.0034 (6)	−0.0432 (8)
N11	0.0374 (13)	0.0388 (13)	0.0434 (16)	0.0011 (10)	−0.0010 (13)	−0.0002 (13)
C11	0.0353 (16)	0.0455 (17)	0.059 (3)	−0.0030 (14)	−0.0043 (16)	−0.0088 (17)
C12	0.0311 (15)	0.0500 (17)	0.059 (2)	−0.0009 (13)	−0.0041 (15)	−0.0082 (18)
C13	0.0330 (15)	0.0381 (15)	0.0408 (17)	0.0017 (12)	−0.0052 (13)	0.0017 (13)
C14	0.0296 (16)	0.0491 (16)	0.053 (2)	−0.0052 (12)	−0.0021 (17)	−0.0081 (19)
C15	0.0341 (16)	0.0471 (18)	0.047 (2)	−0.0004 (13)	−0.0007 (15)	−0.0036 (15)
C16	0.0327 (14)	0.0492 (17)	0.0467 (19)	0.0021 (12)	−0.0048 (15)	−0.0069 (17)
N12	0.0349 (14)	0.0582 (18)	0.053 (2)	0.0051 (13)	−0.0076 (13)	−0.0151 (15)
O11	0.0322 (12)	0.0719 (17)	0.0728 (19)	0.0104 (11)	−0.0097 (14)	−0.0258 (18)

Geometric parameters (Å, °)

Zn1—N1 ⁱ	1.921 (3)	C12—H12	0.9500
Zn1—N1	1.921 (3)	C13—C14	1.385 (4)
Zn1—N11	2.033 (3)	C13—C16	1.495 (5)
Zn1—N11 ⁱ	2.033 (3)	C14—C15	1.378 (5)
N1—C1	1.165 (5)	C14—H14	0.9500
C1—S1	1.605 (4)	C15—H15	0.9500
N11—C15	1.336 (4)	C16—O11	1.233 (4)
N11—C11	1.344 (4)	C16—N12	1.326 (5)
C11—C12	1.376 (5)	N12—H12A	0.8800
C11—H11	0.9500	N12—H12B	0.8800
C12—C13	1.387 (5)		
N1 ⁱ —Zn1—N1	123.6 (2)	C13—C12—H12	120.2
N1 ⁱ —Zn1—N11	109.39 (13)	C14—C13—C12	117.8 (3)
N1—Zn1—N11	104.32 (13)	C14—C13—C16	122.9 (3)
N1 ⁱ —Zn1—N11 ⁱ	104.32 (13)	C12—C13—C16	119.3 (3)
N1—Zn1—N11 ⁱ	109.40 (13)	C15—C14—C13	119.5 (3)
N11—Zn1—N11 ⁱ	104.42 (17)	C15—C14—H14	120.2
C1—N1—Zn1	177.2 (4)	C13—C14—H14	120.2
N1—C1—S1	178.8 (5)	N11—C15—C14	122.6 (3)
C15—N11—C11	118.2 (3)	N11—C15—H15	118.7
C15—N11—Zn1	118.4 (2)	C14—C15—H15	118.7
C11—N11—Zn1	123.3 (2)	O11—C16—N12	122.1 (4)
N11—C11—C12	122.3 (3)	O11—C16—C13	120.1 (3)
N11—C11—H11	118.9	N12—C16—C13	117.8 (3)
C12—C11—H11	118.9	C16—N12—H12A	120.0
C11—C12—C13	119.7 (3)	C16—N12—H12B	120.0
C11—C12—H12	120.2	H12A—N12—H12B	120.0

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

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>
C14—H14 \cdots O11 ⁱⁱ	0.95	2.54	3.365 (6)	145
N12—H12A \cdots S1 ⁱⁱⁱ	0.88	2.62	3.407 (3)	150
N12—H12B \cdots O11 ⁱⁱ	0.88	1.97	2.821 (4)	162

Symmetry codes: (ii) $x+1/4, -y+5/4, z+1/4$; (iii) $-x+3/4, y+1/4, z+7/4$.