research communications

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

Tristan Neumann,* Inke Jess and Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth Strasse 2, D-24118 Kiel, Germany. *Correspondence e-mail: t.neumann@ac.uni-kiel.de

The asymmetric unit of the title complex, $[Zn(SCN)_2(C_6H_6N_2O)_2]$, 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⋯O and N—H⋯O, and weak intermolecular N—H⋯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 isotypic 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 $Zn(SCN)_2$. The synthesis and crystal structure of the resulting compound, $[Zn(NCS)_2(C_6H_6N_2O)_2]$, are reported here.
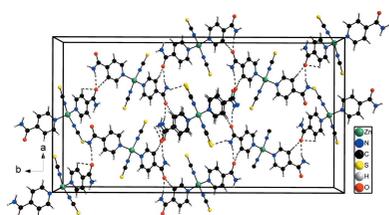
OPEN ACCESS

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 Zn—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 N—Zn—N angles ranging from 104.32 (13) to 123.6 (2)°.

Table 1
Selected bond lengths (Å).

Zn1—N1	1.921 (3)	Zn1—N11	2.033 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C14—H14$\cdots$O11^i	0.95	2.54	3.365 (6)	145
N12—H12$A\cdots$S1^{ii}	0.88	2.62	3.407 (3)	150
N12—H12$B\cdots$O11^i	0.88	1.97	2.821 (4)	162

Symmetry codes: (i) $x+\frac{1}{4}, -y+\frac{5}{4}, z+\frac{1}{4}$; (ii) $-x+\frac{3}{4}, y+\frac{1}{4}, z+\frac{7}{4}$.
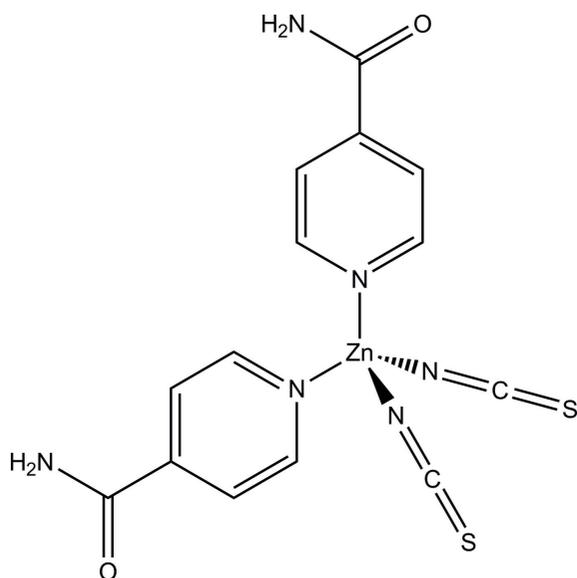
3. Supramolecular features

In the crystal structure, the discrete complexes are stacked along the c axis and are linked by intermolecular N—H$\cdots$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 NH₂ group is involved in intermolecular N—H$\cdots$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-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

Ba(NCS)₂·3H₂O, ZnSO₄·H₂O and isonicotinamide were purchased from Alfa Aesar. Zn(NCS)₂ was synthesized by stirring 3.076 g Ba(NCS)₂·3H₂O (10 mmol) with 1.795 g
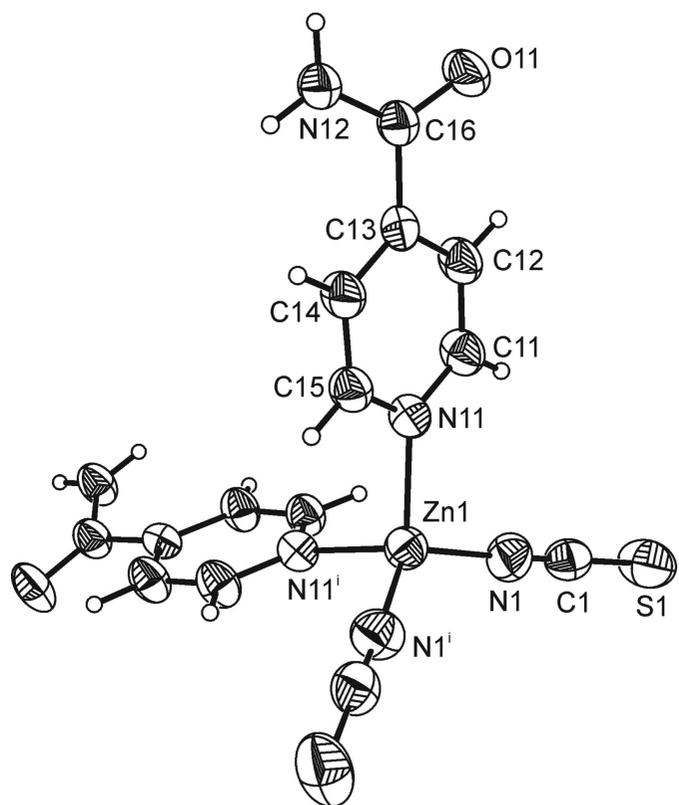

Figure 1
View of the discrete complex with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, z$.]

Table 3
Experimental details.

Crystal data

Chemical formula	[Zn(NCS)$_2$(C$_6$H$_6$N$_2$O)$_2$]
M_r	425.79
Crystal system, space group	Orthorhombic, $Fdd2$
Temperature (K)	200
a, b, c (Å)	19.1926 (9), 36.3044 (12), 5.2930 (2)
V (Å^3)	3688.0 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.58
Crystal size (mm)	$0.20 \times 0.16 \times 0.11$

Data collection

Diffractometer	Stoe IPDS2
Absorption correction	Numerical (X-$SHAPE$ and X-$RED32$; Stoe, 2008)
T_{min}, T_{max}	0.595, 0.742
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15338, 2132, 2012
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.662

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.27
Absolute structure	Flack x determined using 819 quotients [$(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons $et~al.$, 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).

ZnSO$_4$·H$_2$O (10 mmol) in 350 ml water. The white residue was filtered off and the filtrate was dried using a rotary evaporator. The homogenity 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 methylcyanide (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) = 1.2U_{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)].
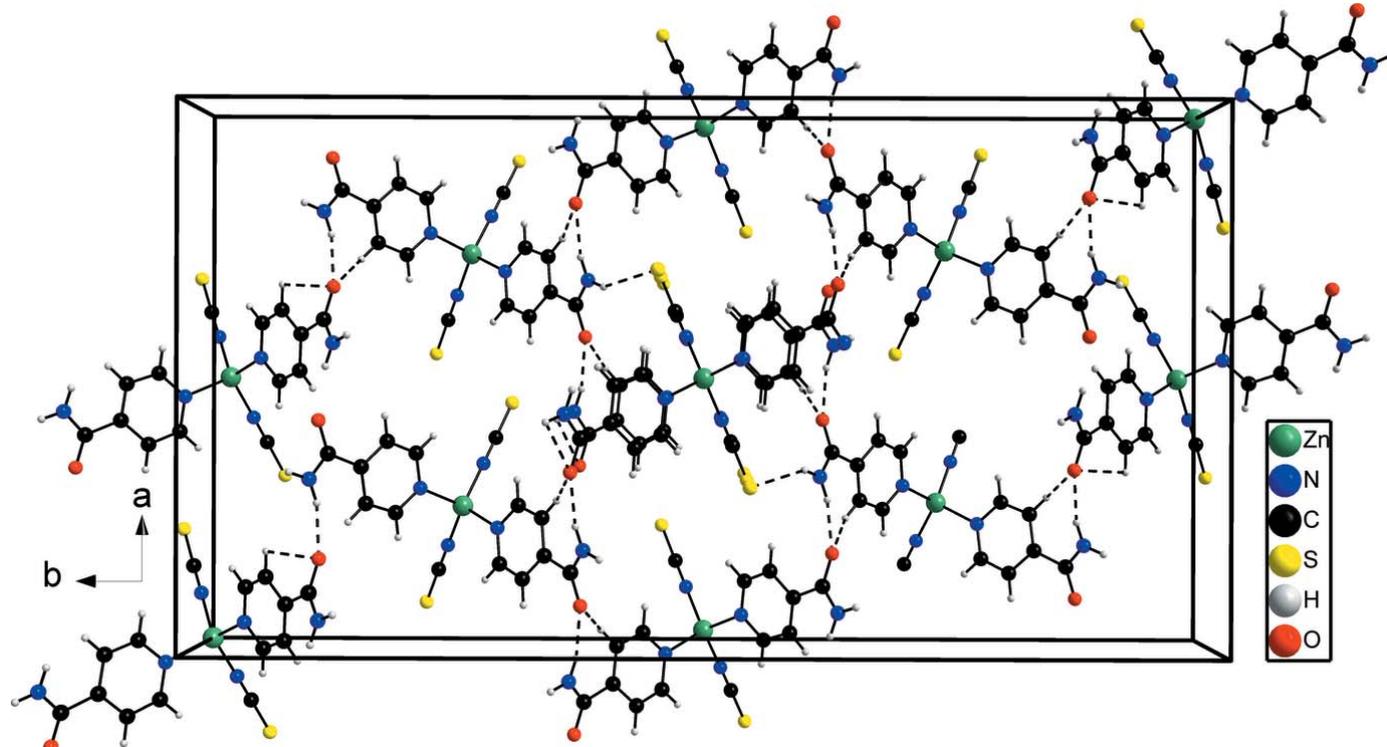
Figure 2
The packing of the complexes in the title compound, in a view along the c axis. Intermolecular hydrogen bonding is shown as dashed lines.

References

Banerjee, S., Drew, M. G. B., Lu, C.-Z., Tercero, J., Diaz, C. & Ghosh, A. (2005). *Eur. J. Inorg. Chem.* pp. 2376–2383.

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Đaković, M., Jagličić, Z., Kozlevčar, B. & Popović, Z. (2010). *Polyhedron*, **29**, 1910–1917.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Liu, X.-T., Wang, W.-Z., Zhang, W.-X., Cui, P. & Gao, S. (2006). *Adv. Mater.* **18**, 2852–2856.

Näther, C., Wöhlert, S., Boeckmann, J., Wriedt, M. & Jess, I. (2013). *Z. Anorg. Allg. Chem.* **639**, 2696–2714.

Palion-Gazda, J., Machura, B., Lloret, F. & Julve, M. (2015). *Cryst. Growth Des.* **15**, 2380–2388.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Sekiya, R. & Nishikiori, S. (2005). *Chem. Lett.* **34**, 1076–1077.

Sekiya, R., Nishikiori, S. & Kuroda, R. (2009). *CrystEngComm*, **11**, 2251–2253.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Stoe (2008). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.

Werner, J., Rams, M., Tomkowicz, Z. & Näther, C. (2014). *Dalton Trans.* **43**, 17333–17342.

Werner, J., Rams, M., Tomkowicz, Z., Runčevski, T., Dinnebier, R. E., Suckert, S. & Näther, C. (2015a). *Inorg. Chem.* **54**, 2893–2901.

Werner, J., Runčevski, T., Dinnebier, R. E., Ebbinghaus, S. G., Suckert, S. & Näther, C. (2015b). *Eur. J. Inorg. Chem.* **2015**, 3236–3245.

Werner, J., Tomkowicz, Z., Rams, M., Ebbinghaus, S. G., Neumann, T. & Näther, C. (2015c). *Dalton Trans.* **44**, 14149–14158.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Wöhlert, S., Peters, L. & Näther, C. (2013). *Dalton Trans.* **42**, 10746–10758.

Yang, G., Zhu, H.-G., Liang, B.-H. & Chen, X.-M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 580–585.

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

Tristan Neumann, Inke Jess and Christian Näther

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

$[Zn(NCS)_2(C_6H_6N_2O)_2]$	$D_x = 1.534$ Mg m^{-3}
$M_r = 425.79$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Fdd2$	Cell parameters from 15683 reflections
$a = 19.1926$ (9) Å	$\theta = 4.2–56.2°$
$b = 36.3044$ (12) Å	$\mu = 1.58$ mm^{-1}
$c = 5.2930$ (2) Å	$T = 200$ K
$V = 3688.0$ (3) Å^3	Block, colorless
$Z = 8$	$0.20 \times 0.16 \times 0.11$ mm
$F(000) = 1728$	

Data collection

Stoe IPDS-2 diffractometer	2132 independent reflections
ω scans	2012 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe, 2008)	$R_{int} = 0.035$
	$\theta_{max} = 28.1°$, $\theta_{min} = 2.2°$
$T_{min} = 0.595$, $T_{max} = 0.742$	$h = -25 \rightarrow 25$
15338 measured reflections	$k = -47 \rightarrow 47$
	$l = -6 \rightarrow 6$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 4.6943P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.031$	
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.13$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
2132 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}
114 parameters	Absolute structure: Flack x determined using 819 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
1 restraint	
Hydrogen site location: inferred from neighbouring sites	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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O11^{ii}	0.95	2.54	3.365 (6)	145
N12—H12*A*···S1^{iii}	0.88	2.62	3.407 (3)	150
N12—H12*B*···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.