

# Crystal structures of tetrakis(pyridine-4-thioamide- $\kappa N$ )bis(thiocyanato- $\kappa N$ )cobalt(II) monohydrate and bis(pyridine-4-thioamide- $\kappa N$ )bis(thiocyanato- $\kappa N$ )-zinc(II)

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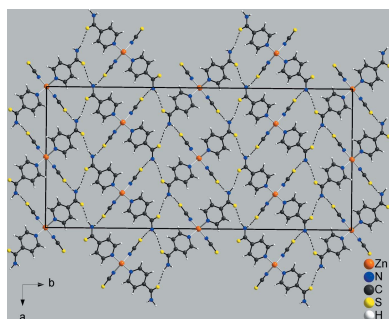
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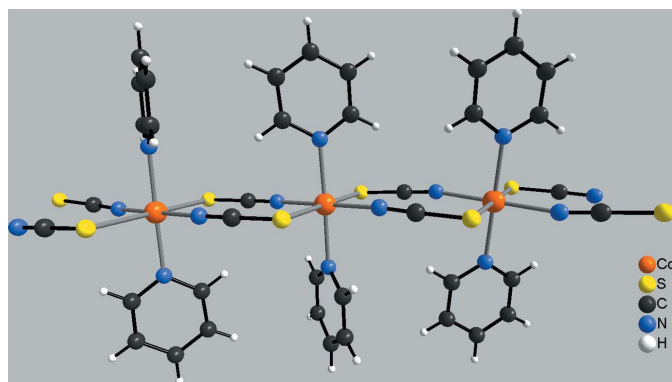
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Reaction of  $\text{Co}(\text{NCS})_2$  and  $\text{Zn}(\text{NCS})_2$  with 4-pyridinethioamide led to the formation of compounds with composition  $[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{S})_4]\cdot\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{S})_2]$  (**2**), respectively. The asymmetric unit of compound **1**, consists of one cobalt(II) cation, two thiocyanate anions, four 4-pyridinethioamide ligands and one water molecule whereas that of compound **2** comprises one zinc(II) cation that is located on a twofold rotation axis as well as one thiocyanate anion and one 4-pyridinethioamide ligand in general positions. In the structure of compound **1**, the cobalt(II) cations are octahedrally coordinated by two terminal N-bonding thiocyanate anions and by the N atoms of four 4-pyridinethioamide ligands, resulting in discrete and slightly distorted octahedral complexes. These complexes are linked into a three-dimensional network *via* intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonding between the amino H atoms and the thiocyanate S atoms. From this arrangement, channels are formed in which the water molecules are embedded and linked to the host structure by intermolecular  $\text{O}-\text{H}\cdots\text{S}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding. In the structure of compound **2**, the zinc(II) cations are tetrahedrally coordinated by two N-bonding thiocyanate anions and the N atoms of two 4-pyridinethioamide ligands into discrete complexes. These complexes are likewise connected into a three-dimensional network by intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonding between the amino H atoms and the thioamide S atoms.

## 1. Chemical context

Thio- and selenocyanate anions are useful ligands for the synthesis of new coordination compounds and polymers, because of their versatile coordination behaviour (Massoud *et al.*, 2013; Mousavi *et al.*, 2012; Prananto *et al.*, 2017; Kabešová *et al.*, 1995). In this regard, compounds with general composition  $[\text{M}(\text{NCS})_2(\text{L})_2]_n$  ( $\text{M} = \text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$ ;  $\text{L} =$  neutral N-donor co-ligand) in which the metal cations are linked by these anionic ligands are of special interest, because magnetic exchange can be mediated (Palion-Gazda *et al.*, 2015; Wöhlert *et al.*, 2013a). In this context, we are especially interested in cobalt(II) compounds in which the metal cations are octahedrally coordinated by two neutral co-ligands and four anionic ligands, which link the central metal cations into chains by pairs of anionic ligands, as symbolized in Fig. 1. Some of these compounds show a slow relaxation of the magnetization, which in most cases can be traced back to single-chain magnetism (Rams *et al.*, 2017a,b; Wöhlert *et al.*, 2012, 2013b). To study the influence of the neutral co-ligand on the magnetic properties, different pyridine derivatives




**Figure 1**

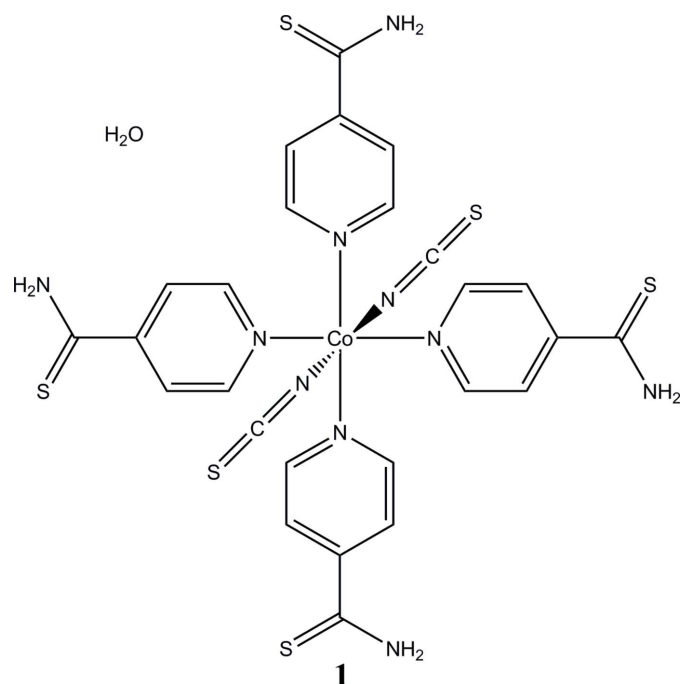
View of a part of a chain in  $[\text{Co}(\text{NCS})_2(\text{pyridine})_2]_n$ , as a representative of compounds with the general composition  $[\text{M}(\text{NCS})_2(\text{L})_2]_n$  ( $\text{M} = \text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$  and  $\text{L} =$  neutral N-donor co-ligand).

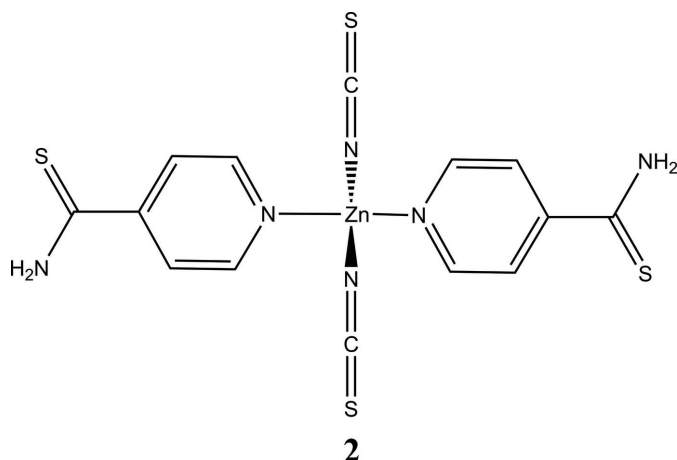
substituted in the 4-position such as 4-benzoylpyridine, 4-vinylpyridine, 4-acetylpyridine, 4-ethylpyridine were investigated (Rams *et al.*, 2017b; Werner *et al.*, 2015; Wöhlert *et al.*, 2014). It was found that all these compounds can be divided magnetically into two groups, even if the same  $\text{Co}(\text{NCS})_2$  chains are observed. In one group, the compounds exhibit an antiferromagnetic ground state and the relaxations observed in the magnetic measurements can be attributed to those of single chains. In the second group, the compounds show a ferromagnetic ground state and the relaxations observed at zero field do not correspond to single-chain relaxations. To gain a better insight into this behaviour, additional examinations of such chain compounds are required, which is of extraordinary importance for our project.

Therefore we became interested in the monodentate ligand 4-pyridinethioamide. In contrast to all ligands used previously, this ligand might be able to link the  $\text{Co}(\text{NCS})_2$  chains into layers by pairs of intermolecular hydrogen bonds between the amino H atoms and the thioamide S atom, which is observed, for example, in the crystal structure of the pure ligand (Coller & Gadret, 1967; Eccles *et al.*, 2014). It should be noted that only one such coordination polymer, namely with 4-pyridinethioamide and Cd, is reported in the literature (Neumann *et al.*, 2016). Here the  $\text{Cd}^{\text{II}}$  cations are linked by pairs of anionic ligands into a linear chain, which corresponds exactly to the structure we are interested in. However, irrespective of the ratio between  $\text{Co}(\text{NCS})_2$  and the co-ligand, a compound with composition  $\text{Co}(\text{NCS})_2(4\text{-pyridinethioamide})_2$  could not be obtained from solution. IR spectroscopic studies of all products showed bands for the CN stretching vibrations at about  $2060\text{ cm}^{-1}$ , thus indicating only terminal N-coordinating anionic ligands. Therefore the formation of compounds with bridging anionic ligands can be excluded (Bailey *et al.*, 1971), presumably because cobalt shows no high affinity to bond with sulfur atoms. Hence the formation of discrete complexes with only terminal N-bonding thiocyanate anions is preferred. The situation is reversed for cadmium, which shows a high affinity to sulfur, and this is obviously the reason why a cadmium compound with a chain structure can easily be obtained from solution. In an alternative approach

we tried to synthesize discrete complexes with terminal N-bonding thiocyanate anions and with additional N-donor co-ligand in the coordination sphere, or mixed ligand complexes with 4-pyridinethioamide and other volatile ligands *e.g.* water. Such compounds can easily be transformed into compounds with anion bridges by thermal annealing, as shown previously (Suckert *et al.*, 2017). In most of these cases, half of the N-bonding co-ligands are replaced by the sulfur atom of the (then bridging) thiocyanate anion, thus enabling the coordination number of 6 to be maintained. In the course of these investigations, crystals of  $[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{S})_4] \cdot \text{H}_2\text{O}$  (**1**) were obtained from aqueous solution and characterized by single crystal X-ray diffraction, which revealed the formation of a discrete complex. Unfortunately, the powder pattern of all batches revealed multi-phase formation, and in several cases large amounts of the 4-pyridinethioamide ligand were present in the products (see Fig. S1 in the supporting information).

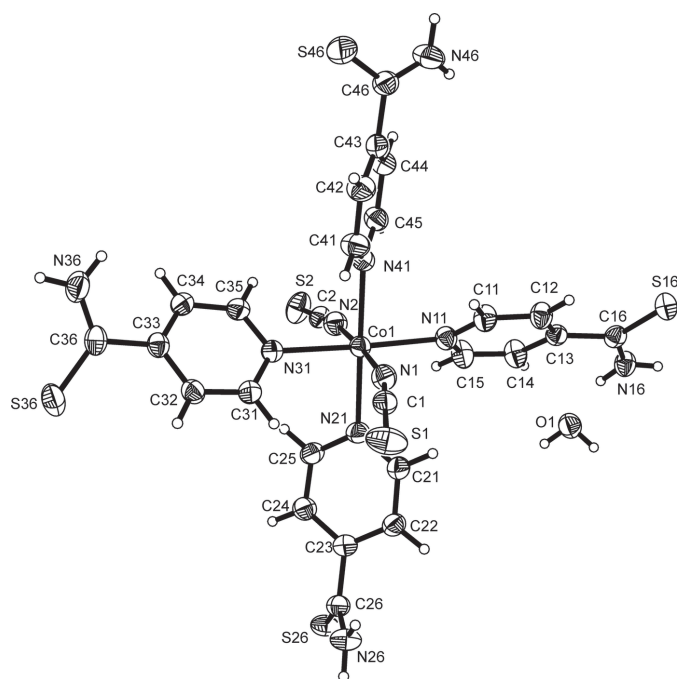
$\text{Co}^{\text{II}}$  sometimes forms discrete complexes with composition  $\text{Co}(\text{NCS})_2(\text{L})_2$  in which the cations are tetrahedrally coordinated by two terminal N-bonding thiocyanate anions and the N atoms of two neutral co-ligands. In several cases these complexes are isotopic with the corresponding zinc analogues, which enables a simple method for checking whether a tetrahedral Co complex might be present in the mixture. Hence we synthesized a compound with composition  $[\text{Zn}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{S})_4]$  (**1**) that shows the expected tetrahedral coordination of zinc(II). However, the calculated X-ray powder diffraction pattern of **2** does not match with the additional reflections observed in some of the X-ray powder diffraction pattern of products obtained during synthesis of **1**. Because of the unknown phase(s), no further investigations were performed.





## 2. Structural commentary

The asymmetric unit of compound **1** consists of one  $\text{Co}^{\text{II}}$  cation, two thiocyanate anions, one water molecule and four 4-pyridinethioamide co-ligands. The  $\text{Co}^{\text{II}}$  cations are sixfold coordinated by two terminal N-bonding thiocyanate anions and the N atoms of four 4-pyridinethioamide ligands, forming discrete octahedral complexes, in which all coordinating atoms are in *trans*-positions (Fig. 2). This corresponds to the most common arrangement for structures of compounds with general composition  $M(\text{NCS})_2(L)_4$ , where  $M$  is a divalent 3d metal cation and  $L$  a monodentate N-donor co-ligand (Małeck, *et al.*, 2011). In this context, it is noted that for bridging N-donor co-ligands, like pyrazine or 4,4'-bipyridine, two-dimensional networks are obtained, in which the anionic ligands are still terminal coordinating (Real *et al.*, 1991; Lu *et*



**Figure 2**

View of the asymmetric unit of compound **1** with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for **1**.

Co1—N1	2.0944 (18)	Co1—N41	2.1723 (16)
Co1—N2	2.0956 (19)	Co1—N21	2.1730 (16)
Co1—N11	2.1640 (16)	Co1—N31	2.1761 (16)
N1—Co1—N2	175.82 (7)	N11—Co1—N21	92.44 (6)
N1—Co1—N11	90.78 (7)	N41—Co1—N21	176.64 (7)
N2—Co1—N11	91.08 (7)	N1—Co1—N31	88.11 (7)
N1—Co1—N41	90.49 (7)	N2—Co1—N31	90.22 (7)
N2—Co1—N41	93.31 (7)	N11—Co1—N31	176.76 (6)
N11—Co1—N41	88.03 (6)	N41—Co1—N31	88.93 (6)
N1—Co1—N21	86.18 (7)	N21—Co1—N31	90.53 (6)
N2—Co1—N21	90.00 (7)		

**Table 2**

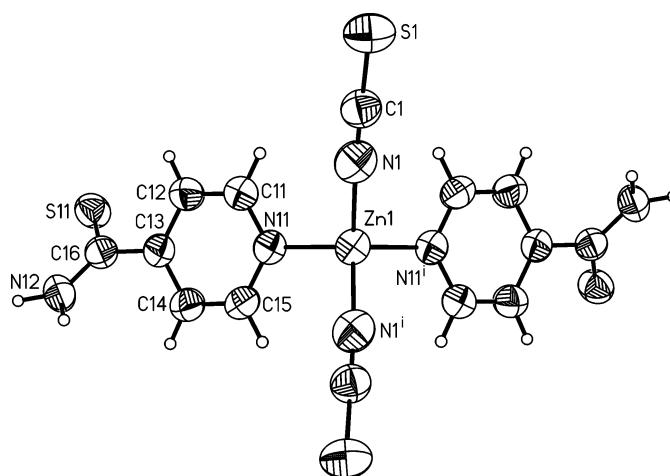
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for **2**.

Zn1—N1 <sup>i</sup>	1.935 (6)	Zn1—N11 <sup>i</sup>	2.022 (5)
Zn1—N1	1.935 (6)	Zn1—N11	2.023 (5)
N1 <sup>i</sup> —Zn1—N1	118.4 (4)	N1 <sup>i</sup> —Zn1—N11	105.9 (2)
N1 <sup>i</sup> —Zn1—N11 <sup>i</sup>	106.8 (2)	N1—Zn1—N11	106.8 (2)
N1—Zn1—N11 <sup>i</sup>	105.9 (2)	N11 <sup>i</sup> —Zn1—N11	113.3 (3)

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

*al.*, 1997). The Co—N bond lengths to the thiocyanate anions of 2.0944 (18) and 2.0956 (19)  $\text{\AA}$  are significantly shorter than those to the pyridine N atoms of the 4-pyridinethioamide ligand [2.1640 (16) – 2.1761 (16)  $\text{\AA}$ ], which is in agreement with related coordination modes reported in the literature (Table 1; Goodgame *et al.*, 2003; Prananto *et al.*, 2017). The bond angles around the central metal cation deviate from the ideal values, indicating a slight distortion (Table 1). For each co-ligand, the thioamide group is rotated differently out of the pyridine ring plane, with dihedral angles of 11.8 (2), 55.5 (1), 40.1 (2) and 38.3 (1) $^\circ$ .

In the structure of compound **2**, the asymmetric unit consists of a  $\text{Zn}^{\text{II}}$  cation that is located on a twofold rotation axis, and one thiocyanate anion as well as one 4-pyridinethioamide ligand in general positions. The  $\text{Zn}^{\text{II}}$  cation is coordinated by the N atoms of two anionic and two neutral co-



**Figure 3**

View of the asymmetric unit of compound **2** with the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ .]

**Table 3**  
Hydrogen-bond geometry (Å, °) for **1**.

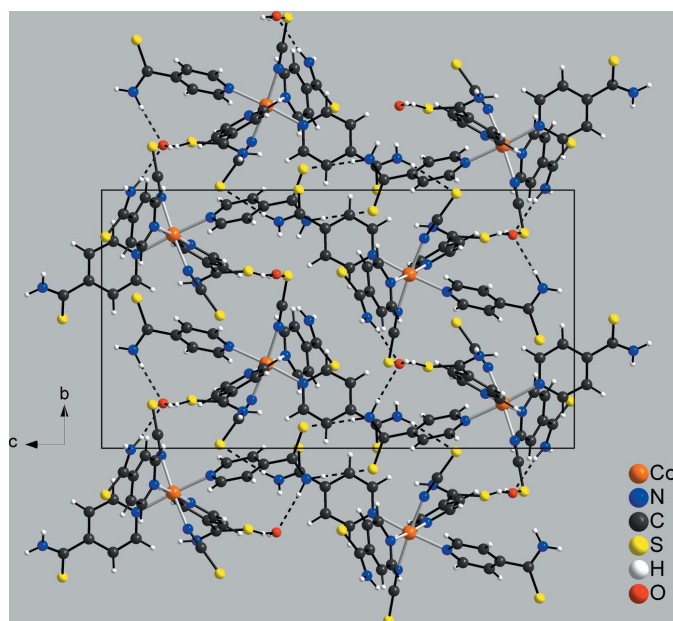
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C11—H11···S46 <sup>i</sup>	0.95	2.85	3.674 (2)	145
C12—H12···S26 <sup>ii</sup>	0.95	2.94	3.695 (2)	137
C14—H14···O1	0.95	2.65	3.531 (3)	154
C15—H15···S36 <sup>iii</sup>	0.95	2.91	3.581 (2)	129
N16—H2N···O1	0.88	2.06	2.893 (2)	159
C22—H22···S36 <sup>iv</sup>	0.95	2.96	3.668 (2)	133
N26—H3N···S26 <sup>v</sup>	0.88	2.64	3.5155 (18)	179
N26—H4N···O1 <sup>ii</sup>	0.88	2.21	3.078 (2)	170
N36—H5N···S26 <sup>vi</sup>	0.88	2.78	3.618 (2)	159
N36—H6N···S1 <sup>vii</sup>	0.88	2.96	3.812 (2)	165
C41—H41···N1	0.95	2.58	3.104 (3)	115
N46—H7N···S2 <sup>viii</sup>	0.88	2.91	3.782 (2)	174
N46—H8N···S1 <sup>i</sup>	0.88	2.60	3.466 (2)	170
O1—H2O1···S36 <sup>iii</sup>	0.84	2.53	3.2356 (16)	142
O1—H1O1···S2 <sup>iv</sup>	0.84	2.59	3.2394 (16)	135

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $x - 1, y, z$ ; (v)  $-x + 1, -y + 1, -z + 2$ ; (vi)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $x + 1, y, z$ ; (viii)  $-x + 1, -y + 1, -z + 1$ .

ligands within a slightly distorted tetrahedron (Fig. 3). Bond lengths and angles (Table 2) are in agreement with values retrieved from the literature. The dihedral angle between the thioamide group and the pyridine ring is 43.8 (4)°.

### 3. Supramolecular features

In the crystal of compound **1**, the discrete complexes are linked by centrosymmetric pairs of intermolecular N—H···S hydrogen bonds between the amino H atoms and the thiocyanate S atoms into chains extending parallel to [100], which are further connected by additional N—H···S hydrogen bonds into a three-dimensional network (Fig. 4 and Table 3). By this arrangement, channels along the *a* axis are formed in



**Figure 4**  
Crystal structure of compound **1** viewed along the *a* axis with intermolecular hydrogen bonds shown as dashed lines.

**Table 4**  
Hydrogen-bond geometry (Å, °) for **2**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C15—H15···S1 <sup>ii</sup>	0.95	2.96	3.690 (6)	135
N12—H1N···S11 <sup>iii</sup>	1.01	2.41	3.358 (5)	156
N12—H2N···S1 <sup>iv</sup>	1.03	2.41	3.424 (6)	166

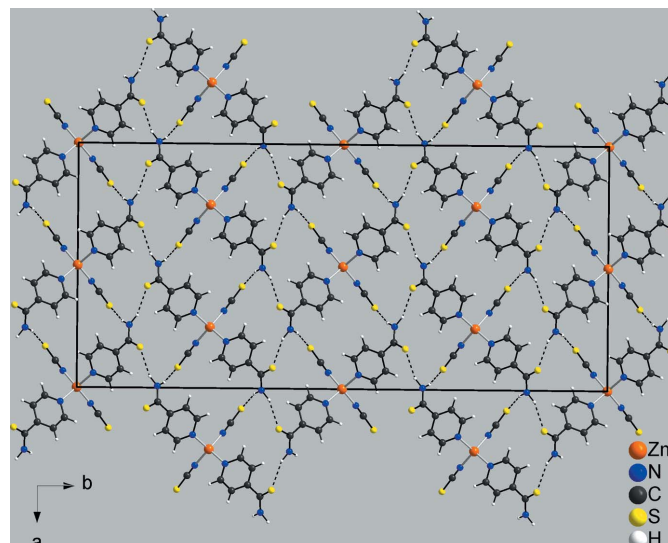
Symmetry codes: (ii)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z + 1$ ; (iii)  $x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{4}$ ; (iv)  $x - \frac{1}{2}, y, z + \frac{1}{2}$ .

which the water molecules are located (Fig. 4). These solvent molecules are linked to the network *via* intermolecular O—H···S hydrogen bonding between the water H atoms and the thiocyanate S atoms (Table 3). The water molecules additionally act as acceptors for N—H···O hydrogen bonding to the amino H atoms. There are additional short contacts between some of the aromatic hydrogen atoms and the thiocyanate S atoms (Table 3).

In the crystal of compound **2**, the discrete complexes are linked by intermolecular N—H···S hydrogen-bonding interactions between the H atoms of the amino group and thioamide (S1) and thiocyanate (S11) S atoms, so forming a three-dimensional hydrogen-bonded framework (Fig. 5 and Table 4). There is also a weak C15—H15···S1<sup>ii</sup> interaction present within the framework (Table 4).

### 4. Database survey

There is only one cobalt thiocyanate compound with 4-pyridinethioamide reported in the Cambridge Structure Database (Version 5.39; Groom *et al.*, 2016). In tetrakis(pyridine-4-carbothioamide- $\kappa N^1$ )bis-(thiocyanato- $\kappa N$ )cobalt(II) methanol monosolvate, the Co<sup>II</sup> cations are octahedrally coordinated by four pyridine-4-carbothioamide ligands and two thiocyanate anions, and the solvent molecules are located in the cavities of the structure (Neumann *et al.*, 2017). More-



**Figure 5**  
Crystal structure of compound **2** viewed along the *c* axis with intermolecular hydrogen bonds shown as dashed lines.

**Table 5**  
Experimental details.

	<b>1</b>	<b>2</b>
<b>Crystal data</b>		
Chemical formula	[Co(NCS) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> S) <sub>4</sub> ·H <sub>2</sub> O	[Zn(NCS) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> S) <sub>2</sub> ]
<i>M<sub>r</sub></i>	745.89	457.91
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/n</i>	Orthorhombic, <i>Fdd2</i>
Temperature (K)	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.9256 (2), 12.9595 (6), 24.1116 (6)	18.965 (3), 41.216 (7), 5.1117 (7)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 100.763 (2), 90	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	3353.91 (19)	3995.6 (11)
<i>Z</i>	4	8
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.92	1.66
Crystal size (mm)	0.18 × 0.14 × 0.11	0.11 × 0.08 × 0.06
<b>Data collection</b>		
Diffractometer	Stoe IPDS2	Stoe IPDS2
Absorption correction	Numerical ( <i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe, 2008)	Numerical ( <i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe, 2008)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.787, 0.886	0.789, 0.894
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	35796, 7301, 6291	6296, 1919, 1711
<i>R<sub>int</sub></i>	0.031	0.087
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.639	0.617
<b>Refinement</b>		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.078, 1.07	0.040, 0.109, 1.07
No. of reflections	7301	1919
No. of parameters	397	114
No. of restraints	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.37, -0.38	0.41, -0.36
Absolute structure	–	Flack <i>x</i> determined using 638 quotients [( <i>I</i> <sup>+</sup> ) – ( <i>I</i> <sup>–</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>–</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	–	0.014 (18)

Computer programs: *X-AREA* (Stoe, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1990) and *pubCIF* (Westrip, 2010).

over, there is one compound with cadmium, in which the Cd<sup>II</sup> cations are octahedrally coordinated by two terminal N-bonding pyridinethioamide ligands and four thiocyanate anions and linked by pairs of anionic ligands into linear chains (Neumann *et al.*, 2016). Other coordination compounds with this ligand are unknown. Therefore, the title compound is the third structurally characterized coordination compound with 4-pyridinethioamide as a ligand. However, the pure 4-pyridinethioamide ligand is also known and in its structure the molecules are linked by pairs of hydrogen bonds between the amino H atoms and the thioamide S atom (Colleter & Gadret, 1967; Eccles *et al.*, 2014). Finally, the protonated form with iodine as counter-anion was reported by Shotonwa & Boeré (2014).

## 5. Synthesis and crystallization

Co(NCS)<sub>2</sub> and 4-pyridinethioamide were purchased from Alfa Aesar. Zn(NCS)<sub>2</sub> was prepared by the reaction of equimolar amounts of Ba(SCN)<sub>2</sub>·3H<sub>2</sub>O with ZnSO<sub>4</sub>·H<sub>2</sub>O in water. The white precipitate of BaSO<sub>4</sub> was filtered off, and the resulting clear solution was evaporated until complete dryness. The purity of the obtained Zn(NCS)<sub>2</sub> was checked by X-ray powder diffraction (XRPD) measurements.

Crystals of compound **1** were obtained by the reaction of 8.8 mg of Co(NCS)<sub>2</sub> (0.05 mmol) with 6.9 mg of 4-pyridinethioamide (0.05 mmol) in a mixture of 1 ml of methanol and 1 ml of water. The reaction mixture was heated to boiling and then slowly cooled to ambient temperature, leading to crystals of the title compound suitable for single crystal X-ray diffraction. XRPD revealed impurities by crystals of the employed 4-pyridinethioamide ligand as the major phase (see Fig. S1 in the supporting information). Some crystals were selected by hand to measure an infrared spectrum (see Fig. S2 in the supporting information). We also tried to obtain pure samples by using different amounts of Co(NCS)<sub>2</sub> and 4-pyridinethioamide, however without any success.

For the synthesis of compound **2**, 18.2 mg Zn(NCS)<sub>2</sub> (0.1 mmol) were reacted with 6.9 mg of 4-pyridinethioamide (0.05 mmol) in 1.0 ml of water which was then overlaid with 1.0 ml of chloroform. After a few days, crystals suitable for single crystal X-ray diffraction formed at the interface of the solvents.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. For both compounds, the aromatic hydrogen atoms were positioned with idealized geometry and

were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  using a riding model. The N–H and O–H hydrogen atoms were located in difference-Fourier maps. For compound **1**, their bond lengths were set to ideal values (N–H = 0.88 Å, O–H = 0.84 Å), and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N,O})$  using a riding model. For compound **2**, the N–H atoms were initially refined and then held fixed (N–H = 1.01 and 1.03 Å) and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N,O})$  using a riding model. The absolute structure of compound **2** was determined by resonant scattering [Fleck parameter = 0.014 (18); Table 5].

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## supporting information

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## Crystal structures of tetrakis(pyridine-4-thioamide- $\kappa N$ )bis(thiocyanato- $\kappa N$ )cobalt(II) monohydrate and bis(pyridine-4-thioamide- $\kappa N$ )bis(thiocyanato- $\kappa N$ )zinc(II)

Tristan Neumann, Inke Jess and Christian Näther

### Computing details

For both structures, 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: *DIAMOND* (Brandenburg, 1990); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tetrakis(pyridine-4-thioamide- $\kappa N$ )bis(thiocyanato- $\kappa N$ )cobalt(II) monohydrate (1)

#### Crystal data

$[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{S})_4] \cdot \text{H}_2\text{O}$

$M_r = 745.89$

Monoclinic,  $P2_1/n$

$a = 10.9256(2) \text{ \AA}$

$b = 12.9595(6) \text{ \AA}$

$c = 24.1116(6) \text{ \AA}$

$\beta = 100.763(2)^\circ$

$V = 3353.91(19) \text{ \AA}^3$

$Z = 4$

$F(000) = 1532$

$D_x = 1.477 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7301 reflections

$\theta = 3.1\text{--}54.0^\circ$

$\mu = 0.92 \text{ mm}^{-1}$

$T = 200 \text{ K}$

Block, light red

$0.18 \times 0.14 \times 0.11 \text{ mm}$

#### Data collection

Stoe IPDS-2  
diffractometer

$\omega$  scans

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

$T_{\min} = 0.787$ ,  $T_{\max} = 0.886$

35796 measured reflections

7301 independent reflections

6291 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 1.7^\circ$

$h = -13 \rightarrow 13$

$k = -16 \rightarrow 16$

$l = -30 \rightarrow 30$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.078$

$S = 1.07$

7301 reflections

397 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 1.8302P]$

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

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

$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.56386 (2)	0.32716 (2)	0.65116 (2)	0.02828 (7)
N1	0.50992 (16)	0.18701 (14)	0.68256 (8)	0.0350 (4)
C1	0.50476 (18)	0.11498 (17)	0.71023 (9)	0.0334 (4)
S1	0.49655 (7)	0.01363 (5)	0.74981 (3)	0.05452 (17)
N2	0.62178 (16)	0.47098 (14)	0.62584 (8)	0.0362 (4)
C2	0.65867 (18)	0.55240 (17)	0.61831 (9)	0.0340 (4)
S2	0.71112 (5)	0.66765 (5)	0.60707 (3)	0.05095 (16)
N11	0.37335 (14)	0.35882 (13)	0.61109 (7)	0.0310 (3)
C11	0.30074 (18)	0.28333 (16)	0.58515 (9)	0.0353 (4)
H11	0.3365	0.2171	0.5823	0.042*
C12	0.17590 (18)	0.29742 (16)	0.56226 (9)	0.0356 (4)
H12	0.1281	0.2420	0.5436	0.043*
C13	0.12101 (17)	0.39272 (15)	0.56661 (8)	0.0284 (4)
C14	0.19731 (19)	0.47126 (16)	0.59235 (10)	0.0383 (5)
H14	0.1644	0.5384	0.5955	0.046*
C15	0.32153 (19)	0.45127 (17)	0.61330 (10)	0.0388 (5)
H15	0.3726	0.5064	0.6302	0.047*
C16	-0.01659 (17)	0.40709 (15)	0.54605 (8)	0.0309 (4)
S16	-0.10407 (5)	0.31858 (4)	0.50805 (2)	0.03728 (12)
N16	-0.06492 (15)	0.49408 (14)	0.56133 (8)	0.0361 (4)
H1N	-0.1449	0.5073	0.5508	0.054*
H2N	-0.0220	0.5408	0.5833	0.054*
N21	0.53727 (15)	0.39399 (13)	0.73071 (7)	0.0318 (3)
C21	0.43666 (18)	0.37052 (17)	0.75246 (9)	0.0348 (4)
H21	0.3684	0.3381	0.7286	0.042*
C22	0.42671 (19)	0.39088 (17)	0.80772 (9)	0.0344 (4)
H22	0.3534	0.3730	0.8214	0.041*
C23	0.52596 (18)	0.43786 (15)	0.84273 (8)	0.0305 (4)
C24	0.62852 (19)	0.46660 (17)	0.82001 (9)	0.0354 (4)
H24	0.6963	0.5020	0.8425	0.042*
C25	0.63077 (19)	0.44304 (16)	0.76421 (9)	0.0337 (4)
H25	0.7017	0.4625	0.7491	0.040*
C26	0.51995 (18)	0.45985 (16)	0.90307 (8)	0.0322 (4)
S26	0.53825 (5)	0.58106 (4)	0.92626 (2)	0.03722 (12)
N26	0.49702 (18)	0.38057 (14)	0.93325 (8)	0.0396 (4)
H3N	0.4892	0.3904	0.9685	0.059*
H4N	0.4850	0.3200	0.9167	0.059*
N31	0.75564 (14)	0.28842 (13)	0.68796 (7)	0.0302 (3)
C31	0.78932 (18)	0.23749 (16)	0.73696 (8)	0.0333 (4)



H31	0.7276	0.2243	0.7591	0.040*
C32	0.90894 (18)	0.20355 (16)	0.75667 (9)	0.0328 (4)
H32	0.9293	0.1692	0.7920	0.039*
C33	0.99949 (17)	0.22025 (15)	0.72412 (8)	0.0298 (4)
C34	0.96583 (18)	0.27467 (16)	0.67424 (8)	0.0322 (4)
H34	1.0257	0.2890	0.6513	0.039*
C35	0.84442 (18)	0.30784 (16)	0.65808 (8)	0.0323 (4)
H35	0.8229	0.3463	0.6241	0.039*
C36	1.12841 (18)	0.17958 (16)	0.74238 (9)	0.0344 (4)
S36	1.19683 (5)	0.18531 (5)	0.80975 (3)	0.04698 (14)
N36	1.18076 (17)	0.14209 (16)	0.70151 (9)	0.0458 (5)
H5N	1.1414	0.1379	0.6662	0.069*
H6N	1.2580	0.1195	0.7067	0.069*
N41	0.58869 (15)	0.25150 (13)	0.57362 (7)	0.0324 (4)
C41	0.6140 (2)	0.15032 (17)	0.57289 (9)	0.0396 (5)
H41	0.6274	0.1137	0.6076	0.048*
C42	0.6215 (2)	0.09683 (18)	0.52419 (9)	0.0403 (5)
H42	0.6413	0.0254	0.5257	0.048*
C43	0.59981 (17)	0.14867 (17)	0.47296 (9)	0.0337 (4)
C44	0.57594 (19)	0.25345 (17)	0.47372 (9)	0.0364 (4)
H44	0.5627	0.2920	0.4396	0.044*
C45	0.57158 (19)	0.30155 (16)	0.52443 (9)	0.0345 (4)
H45	0.5556	0.3736	0.5243	0.041*
C46	0.60338 (19)	0.09230 (17)	0.41907 (9)	0.0374 (5)
S46	0.70646 (6)	0.00009 (5)	0.41673 (3)	0.05019 (15)
N46	0.51894 (19)	0.12246 (17)	0.37506 (8)	0.0481 (5)
H7N	0.4664	0.1733	0.3767	0.072*
H8N	0.5204	0.0945	0.3419	0.072*
O1	0.01279 (14)	0.67371 (12)	0.63019 (7)	0.0425 (4)
H2O1	0.0695	0.6686	0.6588	0.064*
H1O1	-0.0504	0.6648	0.6448	0.064*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.02703 (12)	0.03082 (14)	0.02647 (13)	0.00297 (10)	0.00368 (9)	-0.00167 (10)
N1	0.0347 (8)	0.0343 (9)	0.0356 (9)	-0.0011 (7)	0.0053 (7)	-0.0004 (7)
C1	0.0310 (9)	0.0368 (11)	0.0320 (10)	0.0019 (8)	0.0050 (8)	-0.0077 (9)
S1	0.0897 (5)	0.0383 (3)	0.0367 (3)	-0.0010 (3)	0.0148 (3)	0.0037 (2)
N2	0.0357 (9)	0.0364 (10)	0.0364 (9)	0.0014 (7)	0.0068 (7)	0.0007 (7)
C2	0.0276 (9)	0.0423 (12)	0.0330 (10)	0.0064 (8)	0.0076 (8)	0.0012 (9)
S2	0.0403 (3)	0.0413 (3)	0.0735 (4)	0.0019 (2)	0.0164 (3)	0.0135 (3)
N11	0.0283 (8)	0.0305 (8)	0.0332 (9)	0.0038 (6)	0.0033 (6)	-0.0007 (7)
C11	0.0310 (10)	0.0292 (10)	0.0449 (12)	0.0031 (8)	0.0050 (8)	-0.0045 (9)
C12	0.0305 (9)	0.0309 (11)	0.0448 (12)	-0.0018 (8)	0.0056 (8)	-0.0040 (9)
C13	0.0289 (9)	0.0295 (10)	0.0271 (9)	0.0004 (7)	0.0060 (7)	0.0030 (7)
C14	0.0341 (10)	0.0283 (10)	0.0496 (13)	0.0050 (8)	0.0002 (9)	-0.0029 (9)
C15	0.0327 (10)	0.0311 (11)	0.0492 (13)	0.0029 (8)	-0.0010 (9)	-0.0074 (9)

C16	0.0309 (9)	0.0316 (10)	0.0311 (10)	-0.0001 (8)	0.0079 (8)	0.0065 (8)
S16	0.0319 (2)	0.0361 (3)	0.0416 (3)	-0.0025 (2)	0.0012 (2)	-0.0011 (2)
N16	0.0287 (8)	0.0348 (9)	0.0441 (10)	0.0032 (7)	0.0056 (7)	-0.0021 (8)
N21	0.0340 (8)	0.0332 (9)	0.0291 (8)	0.0002 (7)	0.0083 (7)	-0.0033 (7)
C21	0.0311 (9)	0.0407 (11)	0.0331 (10)	-0.0035 (8)	0.0073 (8)	-0.0054 (9)
C22	0.0330 (9)	0.0380 (11)	0.0337 (10)	-0.0050 (8)	0.0104 (8)	-0.0022 (8)
C23	0.0365 (10)	0.0264 (9)	0.0297 (10)	0.0024 (8)	0.0089 (8)	0.0009 (7)
C24	0.0363 (10)	0.0363 (11)	0.0337 (10)	-0.0074 (8)	0.0069 (8)	-0.0058 (8)
C25	0.0352 (10)	0.0350 (11)	0.0333 (10)	-0.0051 (8)	0.0121 (8)	-0.0050 (8)
C26	0.0344 (10)	0.0342 (11)	0.0284 (10)	0.0009 (8)	0.0070 (8)	0.0004 (8)
S26	0.0519 (3)	0.0308 (3)	0.0302 (2)	-0.0042 (2)	0.0112 (2)	-0.0028 (2)
N26	0.0589 (11)	0.0319 (9)	0.0301 (9)	-0.0003 (8)	0.0136 (8)	0.0011 (7)
N31	0.0277 (7)	0.0349 (9)	0.0278 (8)	0.0033 (7)	0.0047 (6)	0.0004 (7)
C31	0.0301 (9)	0.0403 (11)	0.0297 (10)	-0.0003 (8)	0.0060 (7)	0.0031 (8)
C32	0.0316 (9)	0.0362 (11)	0.0292 (10)	0.0002 (8)	0.0022 (8)	0.0037 (8)
C33	0.0277 (9)	0.0268 (9)	0.0338 (10)	-0.0011 (7)	0.0028 (7)	-0.0025 (8)
C34	0.0307 (9)	0.0355 (11)	0.0316 (10)	0.0008 (8)	0.0084 (8)	0.0008 (8)
C35	0.0329 (9)	0.0369 (11)	0.0274 (9)	0.0022 (8)	0.0062 (7)	0.0021 (8)
C36	0.0276 (9)	0.0282 (10)	0.0461 (12)	-0.0017 (8)	0.0032 (8)	0.0020 (9)
S36	0.0340 (3)	0.0548 (4)	0.0469 (3)	0.0003 (2)	-0.0058 (2)	0.0079 (3)
N36	0.0307 (9)	0.0502 (12)	0.0555 (12)	0.0077 (8)	0.0058 (8)	-0.0066 (9)
N41	0.0303 (8)	0.0368 (9)	0.0290 (8)	0.0061 (7)	0.0031 (6)	-0.0039 (7)
C41	0.0467 (12)	0.0394 (12)	0.0323 (11)	0.0134 (9)	0.0062 (9)	0.0002 (9)
C42	0.0440 (11)	0.0372 (12)	0.0398 (12)	0.0080 (9)	0.0079 (9)	-0.0042 (9)
C43	0.0269 (9)	0.0396 (11)	0.0341 (10)	-0.0016 (8)	0.0048 (8)	-0.0067 (8)
C44	0.0373 (10)	0.0389 (11)	0.0325 (10)	-0.0009 (9)	0.0050 (8)	-0.0018 (9)
C45	0.0354 (10)	0.0342 (11)	0.0327 (10)	0.0012 (8)	0.0034 (8)	-0.0025 (8)
C46	0.0373 (10)	0.0399 (12)	0.0367 (11)	-0.0070 (9)	0.0111 (9)	-0.0066 (9)
S46	0.0470 (3)	0.0524 (4)	0.0524 (4)	0.0055 (3)	0.0126 (3)	-0.0179 (3)
N46	0.0593 (12)	0.0506 (12)	0.0334 (10)	0.0037 (10)	0.0060 (9)	-0.0092 (9)
O1	0.0393 (8)	0.0445 (9)	0.0423 (9)	-0.0037 (7)	0.0037 (7)	-0.0009 (7)

*Geometric parameters (Å, °)*

Co1—N1	2.0944 (18)	C26—N26	1.310 (3)
Co1—N2	2.0956 (19)	C26—S26	1.667 (2)
Co1—N11	2.1640 (16)	N26—H3N	0.8801
Co1—N41	2.1723 (16)	N26—H4N	0.8800
Co1—N21	2.1730 (16)	N31—C35	1.336 (2)
Co1—N31	2.1761 (16)	N31—C31	1.343 (3)
N1—C1	1.155 (3)	C31—C32	1.377 (3)
C1—S1	1.636 (2)	C31—H31	0.9500
N2—C2	1.156 (3)	C32—C33	1.390 (3)
C2—S2	1.640 (2)	C32—H32	0.9500
N11—C15	1.331 (3)	C33—C34	1.384 (3)
N11—C11	1.339 (3)	C33—C36	1.491 (3)
C11—C12	1.385 (3)	C34—C35	1.380 (3)
C11—H11	0.9500	C34—H34	0.9500

C12—C13	1.385 (3)	C35—H35	0.9500
C12—H12	0.9500	C36—N36	1.321 (3)
C13—C14	1.387 (3)	C36—S36	1.658 (2)
C13—C16	1.504 (3)	N36—H5N	0.8803
C14—C15	1.381 (3)	N36—H6N	0.8800
C14—H14	0.9500	N41—C45	1.334 (3)
C15—H15	0.9500	N41—C41	1.341 (3)
C16—N16	1.326 (3)	C41—C42	1.379 (3)
C16—S16	1.656 (2)	C41—H41	0.9500
N16—H1N	0.8799	C42—C43	1.387 (3)
N16—H2N	0.8800	C42—H42	0.9500
N21—C21	1.338 (3)	C43—C44	1.384 (3)
N21—C25	1.339 (3)	C43—C46	1.497 (3)
C21—C22	1.382 (3)	C44—C45	1.381 (3)
C21—H21	0.9500	C44—H44	0.9500
C22—C23	1.385 (3)	C45—H45	0.9500
C22—H22	0.9500	C46—N46	1.328 (3)
C23—C24	1.387 (3)	C46—S46	1.650 (2)
C23—C26	1.496 (3)	N46—H7N	0.8800
C24—C25	1.384 (3)	N46—H8N	0.8802
C24—H24	0.9500	O1—H2O1	0.8400
C25—H25	0.9500	O1—H1O1	0.8400
N1—Co1—N2	175.82 (7)	N21—C25—C24	122.76 (18)
N1—Co1—N11	90.78 (7)	N21—C25—H25	118.6
N2—Co1—N11	91.08 (7)	C24—C25—H25	118.6
N1—Co1—N41	90.49 (7)	N26—C26—C23	116.01 (18)
N2—Co1—N41	93.31 (7)	N26—C26—S26	125.19 (16)
N11—Co1—N41	88.03 (6)	C23—C26—S26	118.78 (15)
N1—Co1—N21	86.18 (7)	C26—N26—H3N	119.2
N2—Co1—N21	90.00 (7)	C26—N26—H4N	118.4
N11—Co1—N21	92.44 (6)	H3N—N26—H4N	122.3
N41—Co1—N21	176.64 (7)	C35—N31—C31	117.37 (17)
N1—Co1—N31	88.11 (7)	C35—N31—Co1	118.52 (13)
N2—Co1—N31	90.22 (7)	C31—N31—Co1	123.83 (13)
N11—Co1—N31	176.76 (6)	N31—C31—C32	123.17 (18)
N41—Co1—N31	88.93 (6)	N31—C31—H31	118.4
N21—Co1—N31	90.53 (6)	C32—C31—H31	118.4
C1—N1—Co1	163.19 (17)	C31—C32—C33	119.03 (18)
N1—C1—S1	179.4 (2)	C31—C32—H32	120.5
C2—N2—Co1	172.22 (18)	C33—C32—H32	120.5
N2—C2—S2	179.5 (2)	C34—C33—C32	117.95 (17)
C15—N11—C11	117.21 (17)	C34—C33—C36	121.32 (18)
C15—N11—Co1	122.27 (14)	C32—C33—C36	120.73 (18)
C11—N11—Co1	120.44 (13)	C35—C34—C33	119.33 (18)
N11—C11—C12	122.93 (19)	C35—C34—H34	120.3
N11—C11—H11	118.5	C33—C34—H34	120.3
C12—C11—H11	118.5	N31—C35—C34	123.07 (18)

C11—C12—C13	119.70 (19)	N31—C35—H35	118.5
C11—C12—H12	120.1	C34—C35—H35	118.5
C13—C12—H12	120.1	N36—C36—C33	115.24 (19)
C12—C13—C14	117.11 (18)	N36—C36—S36	124.65 (16)
C12—C13—C16	120.37 (18)	C33—C36—S36	120.10 (16)
C14—C13—C16	122.48 (18)	C36—N36—H5N	122.8
C15—C14—C13	119.58 (19)	C36—N36—H6N	123.6
C15—C14—H14	120.2	H5N—N36—H6N	113.6
C13—C14—H14	120.2	C45—N41—C41	117.31 (18)
N11—C15—C14	123.4 (2)	C45—N41—Co1	121.76 (14)
N11—C15—H15	118.3	C41—N41—Co1	120.79 (14)
C14—C15—H15	118.3	N41—C41—C42	123.2 (2)
N16—C16—C13	116.05 (18)	N41—C41—H41	118.4
N16—C16—S16	121.60 (15)	C42—C41—H41	118.4
C13—C16—S16	122.33 (15)	C41—C42—C43	119.2 (2)
C16—N16—H1N	120.7	C41—C42—H42	120.4
C16—N16—H2N	123.8	C43—C42—H42	120.4
H1N—N16—H2N	115.4	C44—C43—C42	117.70 (19)
C21—N21—C25	117.49 (17)	C44—C43—C46	121.7 (2)
C21—N21—Co1	120.68 (14)	C42—C43—C46	120.6 (2)
C25—N21—Co1	120.61 (13)	C45—C44—C43	119.5 (2)
N21—C21—C22	123.54 (19)	C45—C44—H44	120.2
N21—C21—H21	118.2	C43—C44—H44	120.2
C22—C21—H21	118.2	N41—C45—C44	123.1 (2)
C21—C22—C23	118.55 (18)	N41—C45—H45	118.5
C21—C22—H22	120.7	C44—C45—H45	118.5
C23—C22—H22	120.7	N46—C46—C43	115.02 (19)
C22—C23—C24	118.41 (18)	N46—C46—S46	124.22 (17)
C22—C23—C26	120.34 (17)	C43—C46—S46	120.76 (17)
C24—C23—C26	121.22 (18)	C46—N46—H7N	123.1
C25—C24—C23	119.14 (19)	C46—N46—H8N	118.4
C25—C24—H24	120.4	H7N—N46—H8N	118.1
C23—C24—H24	120.4	H2O1—O1—H1O1	100.5

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11—H11 $\cdots$ S46 <sup>i</sup>	0.95	2.85	3.674 (2)	145
C12—H12 $\cdots$ S26 <sup>ii</sup>	0.95	2.94	3.695 (2)	137
C14—H14 $\cdots$ O1	0.95	2.65	3.531 (3)	154
C15—H15 $\cdots$ S36 <sup>iii</sup>	0.95	2.91	3.581 (2)	129
N16—H2N $\cdots$ O1	0.88	2.06	2.893 (2)	159
C22—H22 $\cdots$ S36 <sup>iv</sup>	0.95	2.96	3.668 (2)	133
N26—H3N $\cdots$ S26 <sup>v</sup>	0.88	2.64	3.5155 (18)	179
N26—H4N $\cdots$ O1 <sup>ii</sup>	0.88	2.21	3.078 (2)	170
N36—H5N $\cdots$ S26 <sup>vi</sup>	0.88	2.78	3.618 (2)	159
N36—H6N $\cdots$ S1 <sup>vii</sup>	0.88	2.96	3.812 (2)	165
C41—H41 $\cdots$ N1	0.95	2.58	3.104 (3)	115

N46—H7N...S2 <sup>viii</sup>	0.88	2.91	3.782 (2)	174
N46—H8N...S1 <sup>i</sup>	0.88	2.60	3.466 (2)	170
O1—H2O1...S36 <sup>iii</sup>	0.84	2.53	3.2356 (16)	142
O1—H1O1...S2 <sup>iv</sup>	0.84	2.59	3.2394 (16)	135

Symmetry codes: (i)  $-x+1, -y, -z+1$ ; (ii)  $-x+1/2, y-1/2, -z+3/2$ ; (iii)  $-x+3/2, y+1/2, -z+3/2$ ; (iv)  $x-1, y, z$ ; (v)  $-x+1, -y+1, -z+2$ ; (vi)  $-x+3/2, y-1/2, -z+3/2$ ; (vii)  $x+1, y, z$ ; (viii)  $-x+1, -y+1, -z+1$ .

### Bis(pyridine-4-thioamide- $\kappa$ N)bis(thiocyanato- $\kappa$ N)zinc(II) (2)

#### Crystal data

[Zn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>S)<sub>2</sub>]

$M_r = 457.91$

Orthorhombic, *Fdd2*

$a = 18.965$  (3) Å

$b = 41.216$  (7) Å

$c = 5.1117$  (7) Å

$V = 3995.6$  (11) Å<sup>3</sup>

$Z = 8$

$F(000) = 1856$

$D_x = 1.522$  Mg m<sup>-3</sup>

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

Cell parameters from 6296 reflections

$\theta = 2.0$ – $26.0^\circ$

$\mu = 1.66$  mm<sup>-1</sup>

$T = 200$  K

Block, colorless

$0.11 \times 0.08 \times 0.06$  mm

#### Data collection

Stoe IPDS-2

diffractometer

$\omega$  scans

Absorption correction: numerical

(*X-RED32* and *X-SHAPE*; Stoe, 2008)

$T_{\min} = 0.789$ ,  $T_{\max} = 0.894$

6296 measured reflections

1919 independent reflections

1711 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.087$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -23 \rightarrow 23$

$k = -50 \rightarrow 50$

$l = -5 \rightarrow 6$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.109$

$S = 1.07$

1919 reflections

114 parameters

1 restraint

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 3.6629P]$

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

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

$\Delta\rho_{\max} = 0.41$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

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

Absolute structure parameter: 0.014 (18)

#### 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<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.7500	0.2500	0.4335 (2)	0.0566 (3)
N1	0.8164 (3)	0.22371 (14)	0.2398 (12)	0.0719 (17)
C1	0.8585 (3)	0.20935 (15)	0.1215 (13)	0.0598 (15)

S1	0.91578 (10)	0.18998 (5)	-0.0532 (5)	0.0774 (5)
N11	0.6912 (2)	0.21920 (10)	0.6510 (12)	0.0554 (12)
C11	0.7150 (3)	0.18989 (13)	0.7237 (13)	0.0572 (14)
H11	0.7618	0.1839	0.6781	0.069*
C12	0.6743 (3)	0.16827 (14)	0.8614 (13)	0.0601 (15)
H12	0.6932	0.1479	0.9129	0.072*
C13	0.6053 (3)	0.17635 (12)	0.9247 (14)	0.0550 (12)
C14	0.5813 (3)	0.20657 (14)	0.8525 (14)	0.0616 (16)
H14	0.5348	0.2131	0.8962	0.074*
C15	0.6250 (3)	0.22727 (13)	0.7169 (15)	0.0645 (16)
H15	0.6076	0.2480	0.6681	0.077*
C16	0.5580 (3)	0.15290 (13)	1.0657 (13)	0.0563 (14)
N12	0.4930 (3)	0.15183 (13)	0.9681 (12)	0.0618 (13)
H1N	0.4537	0.1374	1.0313	0.093*
H2N	0.4786	0.1644	0.8012	0.093*
S11	0.58394 (9)	0.13158 (4)	1.3212 (4)	0.0673 (5)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0576 (5)	0.0490 (4)	0.0632 (5)	-0.0008 (4)	0.000	0.000
N1	0.080 (4)	0.066 (3)	0.070 (4)	0.001 (3)	-0.001 (3)	-0.003 (3)
C1	0.063 (4)	0.060 (3)	0.057 (4)	0.003 (3)	-0.001 (3)	-0.003 (3)
S1	0.0802 (11)	0.0795 (10)	0.0724 (11)	0.0212 (9)	0.0063 (11)	-0.0055 (10)
N11	0.053 (3)	0.048 (2)	0.064 (3)	-0.0019 (19)	0.000 (3)	-0.006 (2)
C11	0.052 (3)	0.055 (3)	0.065 (4)	0.001 (2)	0.000 (3)	0.002 (3)
C12	0.053 (3)	0.056 (3)	0.071 (4)	0.003 (3)	0.000 (3)	0.007 (3)
C13	0.052 (3)	0.049 (2)	0.064 (3)	-0.002 (2)	0.001 (3)	-0.007 (3)
C14	0.058 (3)	0.052 (3)	0.075 (4)	0.003 (2)	0.010 (3)	0.000 (3)
C15	0.060 (3)	0.045 (2)	0.088 (5)	0.004 (2)	0.009 (4)	0.002 (3)
C16	0.054 (3)	0.054 (3)	0.061 (3)	0.001 (2)	0.004 (3)	-0.009 (3)
N12	0.052 (3)	0.066 (3)	0.067 (3)	-0.009 (2)	-0.001 (2)	-0.003 (3)
S11	0.0588 (9)	0.0727 (9)	0.0705 (10)	0.0005 (8)	0.0039 (8)	0.0091 (9)

*Geometric parameters (Å, °)*

Zn1—N1 <sup>i</sup>	1.935 (6)	C12—H12	0.9500
Zn1—N1	1.935 (6)	C13—C14	1.376 (8)
Zn1—N11 <sup>i</sup>	2.022 (5)	C13—C16	1.502 (8)
Zn1—N11	2.023 (5)	C14—C15	1.376 (9)
N1—C1	1.163 (8)	C14—H14	0.9500
C1—S1	1.617 (7)	C15—H15	0.9500
N11—C15	1.342 (8)	C16—N12	1.331 (8)
N11—C11	1.342 (7)	C16—S11	1.649 (7)
C11—C12	1.373 (8)	N12—H1N	1.0078
C11—H11	0.9500	N12—H2N	1.0347
C12—C13	1.389 (8)		

N1 <sup>i</sup> —Zn1—N1	118.4 (4)	C13—C12—H12	120.2
N1 <sup>i</sup> —Zn1—N11 <sup>i</sup>	106.8 (2)	C14—C13—C12	117.8 (5)
N1—Zn1—N11 <sup>i</sup>	105.9 (2)	C14—C13—C16	120.9 (5)
N1 <sup>i</sup> —Zn1—N11	105.9 (2)	C12—C13—C16	121.3 (5)
N1—Zn1—N11	106.8 (2)	C13—C14—C15	119.8 (6)
N11 <sup>i</sup> —Zn1—N11	113.3 (3)	C13—C14—H14	120.1
C1—N1—Zn1	176.5 (6)	C15—C14—H14	120.1
N1—C1—S1	177.8 (7)	N11—C15—C14	122.4 (6)
C15—N11—C11	117.9 (5)	N11—C15—H15	118.8
C15—N11—Zn1	119.9 (4)	C14—C15—H15	118.8
C11—N11—Zn1	122.1 (4)	N12—C16—C13	113.2 (6)
N11—C11—C12	122.5 (5)	N12—C16—S11	123.7 (5)
N11—C11—H11	118.8	C13—C16—S11	123.0 (5)
C12—C11—H11	118.8	C16—N12—H1N	125.8
C11—C12—C13	119.6 (5)	C16—N12—H2N	122.6
C11—C12—H12	120.2	H1N—N12—H2N	111.3

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

*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>
C15—H15 $\cdots$ S1 <sup>ii</sup>	0.95	2.96	3.690 (6)	135
N12—H1N $\cdots$ S11 <sup>iii</sup>	1.01	2.41	3.358 (5)	156
N12—H2N $\cdots$ S1 <sup>iv</sup>	1.03	2.41	3.424 (6)	166

Symmetry codes: (ii)  $-x+3/2, -y+1/2, z+1$ ; (iii)  $x-1/4, -y+1/4, z-1/4$ ; (iv)  $x-1/2, y, z+1/2$ .