

## Bis[*N*-aminocarbonyl-*N'*-(3-pyridylmethylene)hydrazine]diaquabis-(thiocyanato- $\kappa$ *N*)zinc(II)

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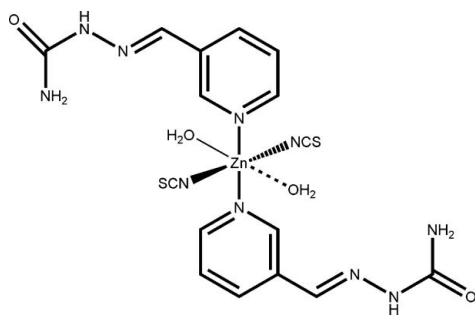
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.032;  $wR$  factor = 0.107; data-to-parameter ratio = 13.6.

The Zn atom of the title complex,  $[\text{Zn}(\text{NCS})_2(\text{C}_7\text{H}_8\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$  or  $[\text{Zn}(\text{SCN})_2(\text{H-Pysc})_2(\text{H}_2\text{O})_2]$  [ $\text{H-Pysc} = N$ -aminocarbonyl-*N'*-(3-pyridylmethylene)hydrazine], derived from the condensation of pyridine-3-carbaldehyde and semicarbazone, is located at a crystallographic centre of inversion and is octahedrally coordinated by two thiocyanate anions, two aqua molecules and two molecules of the neutral Schiff base ligand H-Pysc. The Schiff base molecules act as monodentate ligands coordinating the metal through the pyridyl N atom, whereas the amide O and imine N atoms remain uncoordinated. The crystal packing is stabilized by intermolecular hydrogen bonds involving H-Pysc ligands, thiocyanate anions and water molecules.

### Related literature

For related literature, see: Beraldo *et al.* (2001); Chen, Zhou, Liang *et al.* (2004); Chen, Zhou, Li *et al.* (2004); Li *et al.* (2006); Mendes *et al.* (2001); Zhong *et al.* (2007).



### Experimental

#### Crystal data

$[\text{Zn}(\text{NCS})_2(\text{C}_7\text{H}_8\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$   
 $M_r = 545.91$   
 Triclinic,  $P\bar{1}$   
 $a = 6.661$  (1) Å  
 $b = 9.251$  (2) Å  
 $c = 10.328$  (2) Å  
 $\alpha = 65.765$  (2)°  
 $\beta = 82.438$  (2)°  
 $\gamma = 74.637$  (2)°  
 $V = 559.4$  (2) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.33$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.36 \times 0.30 \times 0.22$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.626$ ,  $T_{\max} = 0.742$   
 4371 measured reflections  
 2169 independent reflections  
 2028 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.107$   
 $S = 1.01$   
 2169 reflections  
 159 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.74$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.58$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{O1}^{\text{i}}$	0.79 (3)	1.99 (3)	2.723 (3)	155 (3)
$\text{O2}-\text{H2B}\cdots\text{S1}^{\text{ii}}$	0.87 (3)	2.49 (3)	3.355 (2)	170 (3)
$\text{N3}-\text{H3A}\cdots\text{O1}^{\text{iii}}$	0.88	1.98	2.862 (3)	174

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2038).

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**supplementary materials**

*Acta Cryst.* (2007). E63, m2696-m2697 [ doi:10.1107/S1600536807048908 ]

**Bis[*N*-aminocarbonyl-*N'*-(3-pyridylmethylene- $\kappa$ N)hydrazine]diaquabis(thiocyanato- $\kappa$ N)zinc(II)**

**J.-H. Deng, G.-Q. Guo and D.-C. Zhong**

**Comment**

Metal complexes based on Schiff base ligands being synthesized by condensation of pyridine-3-carbaldehyde and thiosemicarbazone, semicarbazone and other amines (Mendes *et al.*, 2001; Li *et al.*, 2006) have attracted numerous chemists and biologists due to their antimicrobial, cytotoxic and antioxidant activities. Structurally characterized metal-organic complexes of Schiff bases derived from the condensation of pyridine-3-carbaldehyde and semicarbazone have been reported during the last several years. (Chen, Zhou, Liang *et al.*, 2004; Chen, Zhou, Li *et al.*, 2004; Beraldo *et al.* 2001). As a consecutive work of our studies, we report herein the synthesis and crystal structure of the title compound, (I).

The title compound, (I) (Fig. 1), is isostructural with the manganese derivative of the same ligand (Zhong *et al.*, 2007). The central Zn atom is situated at an crystallographic center of inversion and is hexa-coordinated by two O atoms of water molecules and four N atoms, two of which come from two thiocyanate anions and the others from H-Pysc ligands (Fig. 1), forming a slightly distorted octahedral geometry. The molecules are held together by intermolecular hydrogen bonding interactions forming a three-dimensional supramolecular network. The coordinated water molecules (O2) donate H atoms to the terminal O1 atom and thiocyanate S atoms to form O—H $\cdots$ O<sup>ii</sup> and O—H $\cdots$ S<sup>iii</sup> hydrogen bonds, respectively [symmetry codes ii = -1 + x, y, -1 + z; iii = 1 + x, y, z]. The O1 atoms also accept H atom from N to form N—H $\cdots$ O<sup>iv</sup> hydrogen bonds [symmetry codes iv = 3 - x, 1 - y, 2 - z] (Table 1, Fig. 2).

**Experimental**

1.0 mmol H-Pysc and 0.5 mmol Zn(Ac)<sub>2</sub> × 4H<sub>2</sub>O were dissolved in a water-methanol mixture (1:1 v/v; 10 ml) at room temperature. After stirring for *ca* 1 h, 10 ml of the same mixture solvent containing 1.0 mmol of (NH<sub>4</sub>)SCN was added, then the mixture was further stirred for another 1 h. The resulting filtrate was left to stand for slow evaporation at room temperature. Colorless single crystals of (I) suitable for X-ray structure analysis were obtained after two weeks (yield 85%).

**Refinement**

Hydrogen atoms attached to carbon atoms and nitrogen atoms were positioned geometrically refined using a riding model, with C—H = 0.95 Å, N—H = 0.88 Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$ . Water Hydrogen atoms were located in difference maps and constrained to ride at the as-found O—H distances (0.85 Å), with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

**Figures**

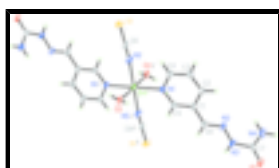


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-labeling scheme. [symmetry code: (i) 1 - x, 1 - y, 1 - z.]

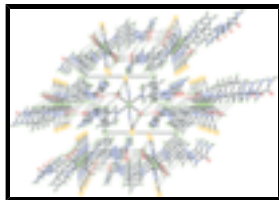


Fig. 2. Three-dimensional supramolecular network constructed by hydrogen bonding interactions (dashed lines).

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### Crystal data

$[\text{Zn}(\text{NCS})_2(\text{C}_7\text{H}_8\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$	$V = 559.4 (2) \text{ \AA}^3$
$M_r = 545.91$	$Z = 1$
Triclinic, $P\bar{1}$	$F_{000} = 280$
Hall symbol: $-P\ 1$	$D_x = 1.621 \text{ Mg m}^{-3}$
$a = 6.661 (1) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.251 (2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 10.328 (2) \text{ \AA}$	$\theta = 2.2\text{--}26.0^\circ$
$\alpha = 65.765 (2)^\circ$	$\mu = 1.33 \text{ mm}^{-1}$
$\beta = 82.438 (2)^\circ$	$T = 173 (2) \text{ K}$
$\gamma = 74.637 (2)^\circ$	Block, white
	$0.36 \times 0.30 \times 0.22 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	2169 independent reflections
Radiation source: fine-focus sealed tube	2028 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.073$
$T = 173(2) \text{ K}$	$\theta_{\text{max}} = 26.0^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.626$ , $T_{\text{max}} = 0.742$	$k = -11 \rightarrow 11$
4371 measured reflections	$l = -10 \rightarrow 12$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.0984P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
2169 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$

159 parameters

$$\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.5000	0.5000	0.01975 (16)
C1	0.9145 (3)	0.3158 (3)	0.8704 (2)	0.0194 (4)
C2	0.8475 (3)	0.1800 (3)	0.9697 (2)	0.0230 (5)
H2	0.9054	0.1234	1.0614	0.028*
C3	0.6960 (4)	0.1300 (3)	0.9317 (2)	0.0280 (5)
H3	0.6530	0.0346	0.9956	0.034*
C4	0.6054 (4)	0.2192 (3)	0.7997 (2)	0.0248 (5)
H4	0.4991	0.1837	0.7761	0.030*
C5	0.8161 (3)	0.3982 (3)	0.7395 (2)	0.0215 (4)
H5	0.8609	0.4910	0.6719	0.026*
C6	1.0788 (4)	0.3762 (3)	0.8988 (2)	0.0232 (5)
H6	1.1187	0.4698	0.8285	0.028*
C7	1.4282 (4)	0.2913 (3)	1.1602 (2)	0.0231 (5)
N1	0.6620 (3)	0.3537 (2)	0.70405 (18)	0.0191 (4)
N2	1.1687 (3)	0.3027 (2)	1.01843 (19)	0.0222 (4)
N3	1.3182 (3)	0.3681 (2)	1.03825 (19)	0.0245 (4)
H3A	1.3433	0.4593	0.9726	0.029*
N4	1.3754 (4)	0.1569 (3)	1.2579 (2)	0.0365 (5)
H4A	1.4414	0.1037	1.3386	0.044*
H4B	1.2748	0.1218	1.2414	0.044*
O1	1.5688 (3)	0.3483 (2)	1.17600 (17)	0.0269 (4)
O2	0.7266 (3)	0.3584 (2)	0.40154 (18)	0.0262 (4)
H2A	0.672 (5)	0.331 (4)	0.355 (3)	0.038 (8)*
H2B	0.819 (5)	0.276 (4)	0.455 (3)	0.034 (8)*
N5	0.3130 (3)	0.3310 (3)	0.5528 (2)	0.0286 (4)
C8	0.2314 (3)	0.2262 (3)	0.5733 (2)	0.0217 (5)
S1	0.11985 (9)	0.07746 (7)	0.60024 (7)	0.02934 (19)

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0215 (2)	0.0237 (2)	0.0187 (2)	-0.00941 (15)	-0.00541 (14)	-0.00894 (17)
C1	0.0178 (10)	0.0241 (11)	0.0205 (10)	-0.0042 (8)	-0.0029 (8)	-0.0126 (9)
C2	0.0232 (11)	0.0272 (11)	0.0198 (10)	-0.0048 (9)	-0.0049 (8)	-0.0098 (9)
C3	0.0296 (12)	0.0293 (12)	0.0245 (11)	-0.0137 (9)	-0.0049 (9)	-0.0046 (9)
C4	0.0254 (11)	0.0275 (12)	0.0258 (11)	-0.0105 (9)	-0.0050 (9)	-0.0108 (10)
C5	0.0238 (11)	0.0234 (11)	0.0200 (10)	-0.0076 (8)	-0.0038 (8)	-0.0090 (9)
C6	0.0255 (11)	0.0254 (11)	0.0217 (10)	-0.0084 (9)	-0.0061 (9)	-0.0090 (9)
C7	0.0261 (11)	0.0275 (11)	0.0195 (10)	-0.0021 (9)	-0.0064 (9)	-0.0137 (9)
N1	0.0178 (8)	0.0243 (9)	0.0194 (8)	-0.0053 (7)	-0.0031 (7)	-0.0117 (7)
N2	0.0219 (9)	0.0266 (9)	0.0237 (9)	-0.0060 (7)	-0.0063 (7)	-0.0136 (8)
N3	0.0262 (10)	0.0268 (10)	0.0243 (9)	-0.0087 (8)	-0.0106 (8)	-0.0095 (8)
N4	0.0436 (13)	0.0440 (13)	0.0234 (10)	-0.0202 (10)	-0.0125 (9)	-0.0051 (9)
O1	0.0285 (9)	0.0323 (9)	0.0265 (8)	-0.0067 (7)	-0.0114 (7)	-0.0152 (7)
O2	0.0291 (9)	0.0309 (9)	0.0235 (8)	-0.0049 (7)	-0.0093 (7)	-0.0144 (7)
N5	0.0314 (11)	0.0318 (10)	0.0262 (10)	-0.0125 (8)	-0.0105 (8)	-0.0087 (8)
C8	0.0229 (11)	0.0254 (11)	0.0179 (10)	-0.0060 (9)	-0.0079 (8)	-0.0073 (8)
S1	0.0290 (3)	0.0257 (3)	0.0373 (4)	-0.0123 (3)	-0.0048 (3)	-0.0115 (3)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Zn1—N5	2.109 (2)	C5—N1	1.343 (3)
Zn1—N5 <sup>i</sup>	2.109 (2)	C5—H5	0.9500
Zn1—O2 <sup>i</sup>	2.1611 (16)	C6—N2	1.280 (3)
Zn1—O2	2.1611 (16)	C6—H6	0.9500
Zn1—N1	2.2182 (18)	C7—O1	1.247 (3)
Zn1—N1 <sup>i</sup>	2.2182 (18)	C7—N4	1.340 (3)
C1—C2	1.396 (3)	C7—N3	1.364 (3)
C1—C5	1.400 (3)	N2—N3	1.369 (3)
C1—C6	1.463 (3)	N3—H3A	0.8800
C2—C3	1.373 (3)	N4—H4A	0.8800
C2—H2	0.9500	N4—H4B	0.8800
C3—C4	1.391 (3)	O2—H2A	0.79 (4)
C3—H3	0.9500	O2—H2B	0.87 (3)
C4—N1	1.344 (3)	N5—C8	1.167 (3)
C4—H4	0.9500	C8—S1	1.641 (2)
N5—Zn1—N5 <sup>i</sup>	180.0	C3—C4—H4	118.7
N5—Zn1—O2 <sup>i</sup>	90.68 (8)	N1—C5—C1	123.8 (2)
N5 <sup>i</sup> —Zn1—O2 <sup>i</sup>	89.32 (8)	N1—C5—H5	118.1
N5—Zn1—O2	89.32 (8)	C1—C5—H5	118.1
N5 <sup>i</sup> —Zn1—O2	90.68 (8)	N2—C6—C1	119.9 (2)
O2 <sup>i</sup> —Zn1—O2	180.000 (1)	N2—C6—H6	120.1
N5—Zn1—N1	90.02 (7)	C1—C6—H6	120.1
N5 <sup>i</sup> —Zn1—N1	89.98 (7)	O1—C7—N4	123.7 (2)

O2 <sup>i</sup> —Zn1—N1	90.58 (6)	O1—C7—N3	119.6 (2)
O2—Zn1—N1	89.42 (6)	N4—C7—N3	116.8 (2)
N5—Zn1—N1 <sup>i</sup>	89.98 (7)	C5—N1—C4	117.08 (18)
N5 <sup>i</sup> —Zn1—N1 <sup>i</sup>	90.02 (7)	C5—N1—Zn1	121.60 (14)
O2 <sup>i</sup> —Zn1—N1 <sup>i</sup>	89.42 (6)	C4—N1—Zn1	121.28 (15)
O2—Zn1—N1 <sup>i</sup>	90.58 (6)	C6—N2—N3	116.5 (2)
N1—Zn1—N1 <sup>i</sup>	180.0	C7—N3—N2	119.70 (19)
C2—C1—C5	117.9 (2)	C7—N3—H3A	120.1
C2—C1—C6	122.8 (2)	N2—N3—H3A	120.1
C5—C1—C6	119.3 (2)	C7—N4—H4A	120.0
C3—C2—C1	118.5 (2)	C7—N4—H4B	120.0
C3—C2—H2	120.8	H4A—N4—H4B	120.0
C1—C2—H2	120.8	Zn1—O2—H2A	111 (2)
C2—C3—C4	120.0 (2)	Zn1—O2—H2B	118.7 (19)
C2—C3—H3	120.0	H2A—O2—H2B	110 (3)
C4—C3—H3	120.0	C8—N5—Zn1	170.6 (2)
N1—C4—C3	122.7 (2)	N5—C8—S1	178.9 (2)
N1—C4—H4	118.7		

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

*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>
O2—H2A $\cdots$ O1 <sup>ii</sup>	0.79 (3)	1.99 (3)	2.723 (3)	155 (3)
O2—H2B $\cdots$ S1 <sup>iii</sup>	0.87 (3)	2.49 (3)	3.355 (2)	170 (3)
N3—H3A $\cdots$ O1 <sup>iv</sup>	0.88	1.98	2.862 (3)	174

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



Fig. 1

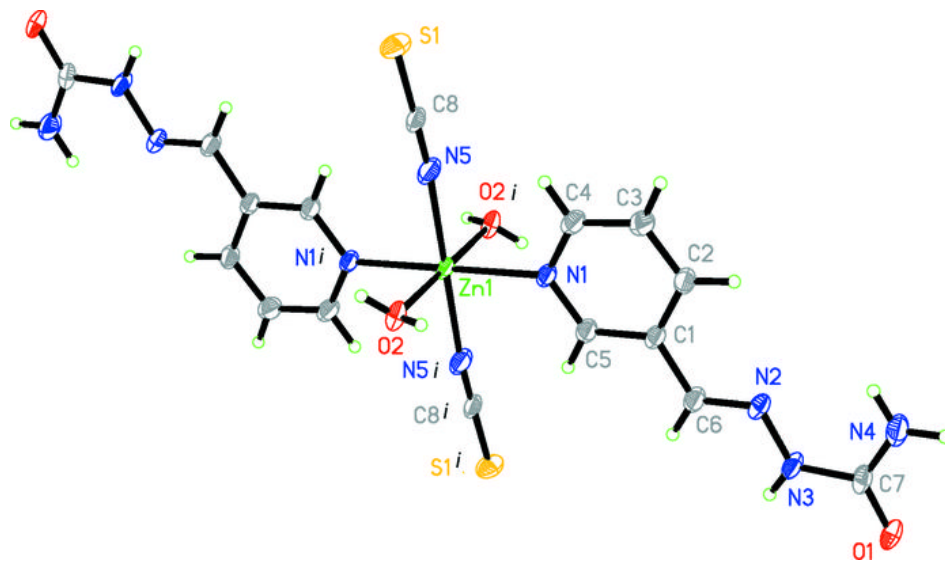


Fig. 2

