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Bis(1*H*-benzotriazole-κN^3)bis(isothiocyanato-κN)-zinc(II) 1*H*-benzotriazole hemisolvate

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Key indicators

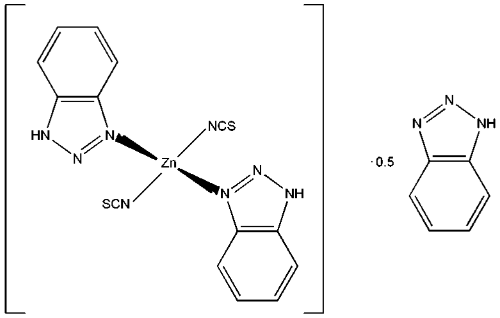
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.049
wR factor = 0.103
Data-to-parameter ratio = 17.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the asymmetric unit of the title complex, $[Zn(NCS)_2(C_6H_5N_3)_2]\cdot 0.5C_6H_5N_3$, there are two independent Zn^{II} atoms, which are four-coordinated in a distorted tetrahedral coordination environment defined by four N atoms from two monodentate 1*H*-benzotriazole ligands and two terminal isothiocyanate ligands.

Comment

The coordination chemistry of benzotriazoles (Hbta) has been explored in recent years (Himes *et al.*, 1981; Handley *et al.*, 1993; Hursthouse *et al.*, 1986). One reason for this is the anticorrosion action of benzotriazoles towards certain metals, particularly copper, zinc and their alloys (Sockalingum *et al.*, 1991). To understand the complex surface chemistry that leads to corrosion inhibition and to create new inhibitors more efficient than Hbta, chemical, physical and structural studies on realistic model complexes are required. Despite the extensive use of Hbta and its derivatives as corrosion inhibitors for zinc and its alloys, only a few zinc compounds have been structurally characterized by X-ray diffraction (Inger & Kurt, 1981; Li *et al.*, 2002). We report here the preparation and crystal structure of a new Zn^{II} complex incorporating the Hbta ligand, *viz*. $[Zn(NCS)_2(Hbta)_2]\cdot 0.5Hbta$, (I).



(I)

As shown in Fig. 1, the asymmetric unit of compound (I) contains two independent coordinated Zn^{II} atoms and one Hbta solvent molecule. Atoms Zn1 and Zn2 are similarly four-coordinated by two N atoms from two Hbta ligands and by two N atoms from two terminal isothiocyanate ions, giving distorted tetrahedral geometries. This coordination environment is similar to that found in $[Zn(NCS)_2(4\text{-dmap})_2]$ [4-dmap = 4-(*N*,*N*-dimethylamino)pyridine; Secondo *et al.*, 2000] and $[Zn(NCS)_2(PPz)_2]_n$ (PPz = piperazine; Suen *et al.*, 2002). The Hbta ligand coordinates one Zn^{II} atom in a monodentate mode, similar to that in compounds $[ZnCl_2(Hbta)_2]$ (Inger & Kurt, 1981) and $[Zn(Hbta)_4(H_2O)_2](ClO_4)_2$ (Li *et al.*, 2002). The Zn—N(Hbta) bond lengths are 2.016 (2) and 2.018 (2) Å

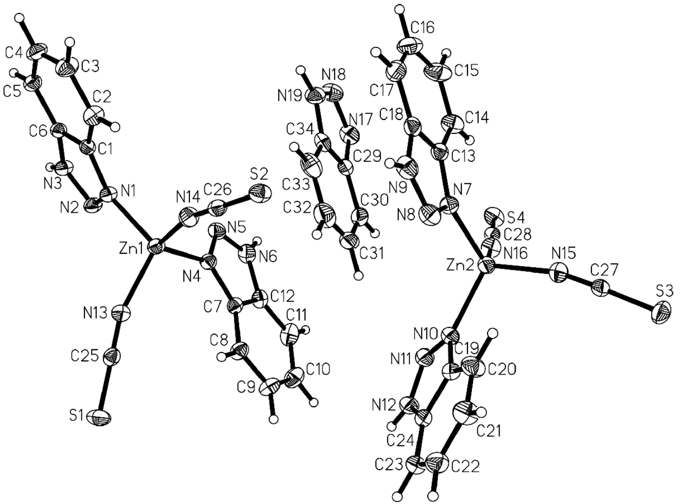


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.

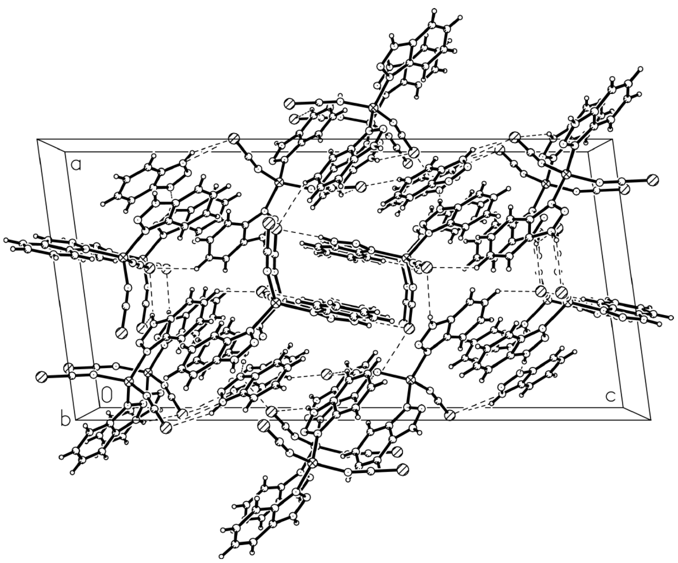


Figure 2
Unit-cell packing diagram for (I). Dashed lines indicate hydrogen bonds.

for Zn1, and 2.000 (2) and 2.017 (2) Å for Zn2, close to the corresponding value of 2.024 (10) Å (mean) in the distorted tetrahedral compound [$ZnCl_2(Hbta)_2$] (Inger & Kurt, 1981) and shorter than the corresponding value of 2.171 (3) Å (mean) in the distorted octahedral compound [$Zn(Hbta)_4(H_2O)_2$](ClO_4)$_2$ (Li *et al.*, 2002). The Zn—N(NCS) bond lengths (Table 1) can be compared with the values found in [$Zn(NCS)_2(4\text{-dmap})_2$] [1.936 (6) and 1.941 (5) Å; Secondo *et al.*, 2000] and [$Zn(NCS)_2(PPz)_2$]$_n$ [1.940 (3) and 1.953 (3) Å; Suen *et al.*, 2002]. The N—Zn—N bond angles of the distorted tetrahedral Zn1 atom are in the range 104.43 (11)–112.40 (11)°, close to the corresponding values of the Zn2 atom, which are in the range 105.21 (10)–112.91 (12)°. The isothiocyanate anions are almost linear (Table 1), in good agreement with the results usually obtained for terminal N-bonded isothiocyanate anions. The bond angles involving isothiocyanate for Zn1 (C25—N13—Zn1 and C26—N14—Zn1) are 156.7 (2) and 165.4 (2)°, respectively, slightly smaller than the corresponding values for Zn2 [C27—N15—Zn2 = 166.5 (2)° and C28—N16—Zn2 = 174.9 (3)°], and similar to the values observed in [$Zn(NCS)_2(4\text{-dmap})_2$] [164.2((5) and 166.1 (5)°; Secondo *et al.*, 2000] and [$Zn(NCS)_2(PPz)_2$]$_n$ [161.4 (3) and 162.1 (3)°; Suen *et al.*, 2002].

The four coordinated benzotriazole rings, *viz*. C1–C6/N1–N3, C7–12/N4–N6, C13–C18/N7–N9 and C19–C24/N10–N12, are planar, with r.m.s. deviations of 0.009 (2), 0.006 (3), 0.009 (2) and 0.013 (3) Å, respectively. The benzotriazole solvent molecule is also planar, with an r.m.s. deviation of 0.008 (3) Å. There are weak S···H—N and N···H—N hydrogen-bonding interactions between S atoms of coordinated isothiocyanate anions or an N atom of an Hbta molecule and H atoms from N atoms of adjacent Hbta molecules (Table 2). There are also weak S···H—C interactions between S atoms of coordinated isothiocyanate anions and H atoms from benzene-ring C atoms of adjacent Hbta molecules [S1···H11*A*($2 - x$, $1 - y$, $-z$) = 2.903 Å, S1···H32*A*($2 - x$, $2 - y$, $-z$) = 2.823 Å, S3···H9*A*($1 - x$, $2 - y$, $-z$) = 2.949 Å, S4···H4 ($2 - x$, $1 - y$, $\frac{1}{2} - z$) = 2.871 Å, S4···H20*A*(x, $y - 1$, z) = 2.668 Å] (Fig. 2).

There are π–π stacking interactions between Hbta molecules in the crystal. The dihedral angle between the C1–C6/N1–N3 Hbta plane and the adjacent C13–C18/N7–N9($2 - x$, $y - \frac{1}{2}$, $-\frac{1}{2} - z$) Hbta plane is 8.2 (7)° and the centre-to-centre distance between the two benzene rings is 3.849 (4) Å (the two triazole rings are offset). The C7–C12/N4–N6 Hbta molecule and the symmetry-related C7–C12/N4–N6($2 - x$, $1 - y$, $-z$) Hbta plane are parallel stacked (the benzene ring stacks above the triazole ring); the centre-to-centre distance between the benzene ring of one Hbta and one triazole ring of the other Hbta is 3.706 (4) Å. The dihedral angle between the C7–C12/N4–N6 Hbta molecular plane and the adjacent C29–C34/N17–N19 Hbta solvent molecule is 10.0 (1)°; the centre-to-centre distance between the C7/C12/N4–N6 triazole ring and the C29–C34 benzene ring is 3.656 (6) Å (the C7–C12 benzene ring and the C29/C34/N17–N19 triazole ring are offset). The C19–24/N10–N12 Hbta molecule and the symmetry-related C19–C24/N10–N12($1 - x$, $2 - y$, $-z$) Hbta molecule are parallel stacked (the two benzene rings are offset); the centre-to-centre distance between the triazole rings is 3.705 (5) Å. All the above dihedral angles and distances show obvious π–π stacking interactions between Hbta molecules (Tong *et al.*, 1999; Li *et al.*, 2001) in the crystal structure. The centre-to-centre distances between two benzene rings and triazole rings from the coordinated C13–C18/N7–N9 Hbta molecule and the neighbouring C29–C34/N17–N19 Hbta solvent molecule are 4.002 (6) and 5.007 (6) Å, showing no π–π interactions. These weak interactions sustain the stability of (I) in the solid state.

Experimental

An ethanol solution (10 ml) of benzotriazole (0.060 g, 0.5 mmol) was added to an aqueous solution (10 ml) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.149 g, 0.5 mmol) and KSCN (0.107 g, 1.1 mmol) with stirring. The mixture was stirred at room temperature for 30 min and the resultant solution was filtered. After allowing the filtrate to stand in air at room temperature for one week, well shaped colourless single crystals of (I) were obtained. Analysis found: C 42.52, H 2.54, N 27.63; calculated for $C_{34}H_{25}N_{19}S_4Zn_2$: C 42.59, H 2.63, N 27.76%.

Crystal data

$[Zn(NCS)_2(C_6H_5N_3)_2]\cdot0.5C_6H_5N_3$
$M_r = 479.35$
Monoclinic, $P2_1/c$
$a = 14.9344$ (12) Å
$b = 9.2160$ (6) Å
$c = 30.256$ (3) Å
$\beta = 97.811$ (2)°
$V = 4125.7$ (6) Å^3
$Z = 8$

$D_x = 1.543$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 892 reflections
$\theta = 3.0$–27.5°
$\mu = 1.42$ mm^{-1}
$T = 193.2$ K
Block, colourless
0.32 × 0.29 × 0.15 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.650$, $T_{max} = 0.811$
43 832 measured reflections

9425 independent reflections
7842 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 19$
$k = -11 \rightarrow 10$
$l = -39 \rightarrow 39$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.103$
$S = 1.09$
9425 reflections
533 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 3.6940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N13	1.938 (2)	Zn2—N16	1.917 (3)
Zn1—N14	1.943 (3)	Zn2—N15	1.963 (3)
Zn1—N1	2.016 (2)	Zn2—N7	2.000 (2)
Zn1—N4	2.018 (2)	Zn2—N10	2.017 (2)
N13—Zn1—N14	112.40 (11)	N15—Zn2—N10	105.21 (10)
N13—Zn1—N1	111.95 (10)	N7—Zn2—N10	112.15 (10)
N14—Zn1—N1	110.77 (10)	C25—N13—Zn1	156.7 (2)
N13—Zn1—N4	104.43 (10)	C26—N14—Zn1	165.4 (2)
N14—Zn1—N4	112.04 (10)	C27—N15—Zn2	166.5 (2)
N1—Zn1—N4	104.86 (9)	C28—N16—Zn2	174.9 (3)
N16—Zn2—N15	112.91 (12)	N13—C25—S1	179.4 (3)
N16—Zn2—N7	109.56 (10)	N14—C26—S2	179.1 (3)
N15—Zn2—N7	105.28 (11)	N15—C27—S3	177.9 (3)
N16—Zn2—N10	111.55 (11)	N16—C28—S4	179.6 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···S4^{i}	0.88	2.67	3.330 (2)	132
N3—H3B···S3^{ii}	0.88	2.82	3.482 (3)	133
N6—H6A···S2^{iii}	0.88	2.62	3.377 (3)	145
N9—H9B···N17^{iv}	0.88	1.90	2.768 (4)	169
N12—H12A···S3^{v}	0.88	2.58	3.446 (3)	168
N19—H19A···S2^{vi}	0.88	2.49	3.288 (3)	151

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

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and with N—H distances of 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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