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Bis(7-amino-1,3-benzothiazole-κN^3)-dichlorozinc(II)

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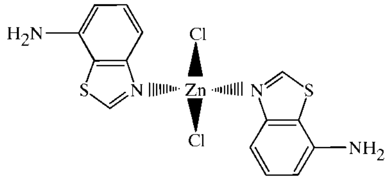
The title complex, $[ZnCl_2(C_7H_6N_2S)_2]$, contains a Zn centre with a distorted tetrahedral coordination sphere, involving two Cl^- ligands and two endocyclic N atoms from the thiazole moiety [Zn—Cl = 2.2284 (7) and 2.2236 (7) Å, and Zn—N = 2.081 (2) and 2.041 (2) Å]. The interplanar angle between the two ligands is 79.32 (6)°. The amino groups participate in intermolecular N—H···Cl hydrogen bonds, with N···Cl distances in the range 3.463 (2)–3.519 (2) Å.

Comment

As the activities of many enzymes depend upon the interaction of an imidazole or thiazole group with a metal ion (Kaim & Schwederski, 1996), the coordination behaviour of 1,3-benzothiazole (bta) and its derivatives towards Zn^{II} as a biogenic element is of particular interest. These ligands include both S and N heteroatoms, as well as π-donor aromatic systems. A search of the literature showed that the chemistry of the 7-amino-1,3-benzothiazole (7-NH_2-bta) ligand with Zn^{II} salts has apparently not been studied previously, in contrast with 2-amino-1,3-benzothiazole. As a general rule, 2-substituted derivatives of 1,3-benzothiazole (2-X-bta, where X is NH_2, CH_3, Cl or S) act as σ-monodentate ligands through either the ring N atom (Giusti & Peyronel, 1982) or the exocyclic S atom (X = S). In the case of 2-mercapto-1,3-benzothiazole derivatives, both *endo*-N and *exo*-S atoms can act as donor atoms, resulting in versatile coordination modes (McCleverty *et al.*, 1980; Raper, 1985, 1996, 1997; Baggio *et al.*, 1993; Castro *et al.*, 1993; Popović *et al.*, 2002).

A survey of the Cambridge Structural Database (Version 5.23 of April 2002; Allen, 2002) revealed the structure of neither the title ligand nor of any corresponding metal complex. There have been only a few structural reports of complexes of the form $[ZnX_2L_2]$ (where X is Cl, Br or I), with L = 2-NH_2-ta (ta is thiazole) or 2-NH_2-bta (Macíček & Davarski, 1993; Davarski *et al.*, 1996), namely $[ZnCl_2(2\text{-}NH_2\text{-}ta)_2]$, $[ZnBr_2(2\text{-}NH_2\text{-}ta)_2]$, $[ZnBr_2(2\text{-}NH_2\text{-}bta)_2]$ and $[ZnI_2(2\text{-}NH_2\text{-}ta)_2]$, all containing a distorted tetrahedral $[ZnN_2X_2]$ moiety. In this context, the title complex, (I), was prepared and its crystal structure is presented here.


(I)

In the structure of (I), the tetrahedral Zn coordination sphere is built up of two Cl^- ligands and the amino N atoms of two neutral monodentate 7-NH_2-bta ligands (Fig. 1). The $ZnCl_2$ moiety is preserved within the complex [Zn—Cl1 = 2.2285 (6) Å and Zn—Cl2 = 2.2235 (7) Å], accompanied by a Cl1—Zn—Cl2 angle of 116.81 (3)°. In $[ZnCl_2(2\text{-}NH_2\text{-}ta)_2]$ (Macíček & Davarski, 1993), the corresponding Zn—Cl bond distances are slightly longer [2.2548 (8) and 2.2386 (8) Å] and the Cl—Zn—Cl′ bond angle is smaller [113.47 (3)°]. The Zn—N bond lengths in (I) are 2.081 (2) and 2.041 (2) Å for Zn—N1 and Zn—N3, respectively, somewhat longer than in $[ZnCl_2(2\text{-}NH_2\text{-}ta)_2]$ [2.024 (2) and 2.011 (2) Å]. Such trends in Zn—Cl and Zn—N bond distances in $[ZnCl_2(2\text{-}NH_2\text{-}ta)_2]$ and (I) are influenced by the more pronounced delocalization in the benzothiazole fragment of (I) in comparison with the thiazole fragment of $[ZnCl_2(2\text{-}NH_2\text{-}ta)_2]$. The strength of the Zn—N bonds in (I) is consistent with valence-shell electron-pair repulsion considerations, reflected in the smallest bond angle in the Zn coordination sphere being 103.30 (7)° for N1—Zn—N3. A similar trend is found in the $[ZnBr_2(2\text{-}NH_2\text{-}ta)_2]$ and $[ZnI_2(2\text{-}NH_2\text{-}ta)_2]$ complexes [106.0 (2) and 104.6 (1)°, respectively], but not in the $[ZnBr_2(2\text{-}NH_2\text{-}bta)_2]$ complex, where the N—Zn—N angle is 116.1 (3)° (Davarski *et al.*, 1996). The reason for this exception is not clear.

The ligand geometry in (I) is normal (Allen *et al.*, 1987). The S1—C1 [1.709 (2) Å] and S2—C14 [1.707 (2) Å] bonds are slightly shorter than S1—C7 [1.736 (2) Å] and S2—C13 [1.734 (2) Å], due to the pronounced delocalization in the –S—C═N– fragment of the thiazole ring [N1—C1 = 1.303 (3) Å and N3—C14 = 1.297 (3) Å, *versus* N1—C2 =

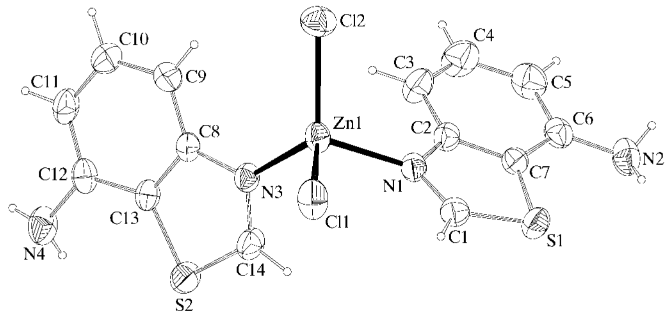


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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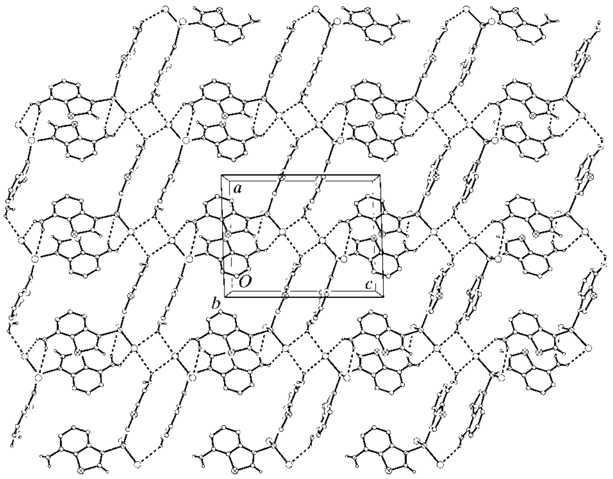

Figure 2
A packing diagram for (I). The view shows a layer parallel to the *ac* plane (see text); the view direction is parallel to the *b* axis. H atoms not involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

1.399 (3) and N3—C8 = 1.400 (2) Å]. The bond angles around the endocyclic S atoms are in agreement with the literature values (Allen *et al.*, 1987) for the geometry around an endocyclic S atom [C1—S1—C7 = 89.31 (10)° and C13—S2—C14 = 89.21 (10)°]. The ligands are planar, with the angles between the best planes calculated through the five- and six-membered rings of each ligand being 3.26 (10) and 1.14 (10)°. The ligands are mutually almost perpendicular, with an interplanar angle between the two ligands of 79.32 (6)°.

There are no intramolecular hydrogen bonds in the structure of (I). The NH_2 groups participate in hydrogen bonds with atoms Cl1 and Cl2, although the H···Cl distances are long. Atom H1N4 forms a three-centre hydrogen bond to two different Cl1 atoms, whereas the other three amine H atoms form normal two-centre hydrogen bonds. Four of these five interactions link the molecules into sheets parallel to the *ac* plane (Table 2 and Fig. 2). Atom Cl2 acts as a triple H-atom acceptor, forming one C—H···Cl and two N—H···Cl hydrogen bonds.

The solid-state IR spectrum of (I) in the region 4000–450 cm^{-1} is in agreement with the X-ray diffraction data with respect to the mode of coordination. Generally, the absorption bands in the spectrum of (I) were shifted towards lower wavenumbers upon coordination, *i.e.* by ~10–20 cm^{-1} with respect to the bands in the spectrum of the free ligand. The shift of ν(C—S) towards higher wavenumbers (from 627 to 653 cm^{-1}) implies an increased $d\pi$–$p\pi$ contribution between sulfur and the ring π system. The two shortest wavelength bands in the UV–vis spectrum of the free ligand, characterized by high molecular absorption coefficients, can be attributed to the π–π^* transition. The longest wavelength band, characterized by less strong absorption coefficients, is generally mixed in character and contains π–π^* and n–π^* transitions, due to the presence of the nitrogen lone pair of electrons.

Experimental

7-Amino-1,3-benzothiazole was prepared according to the procedure of Ward & Williams (1965). Spectroscopic analysis, IR (ν, cm^{-1}): 3389 (*s*), 3304 (*s*, *br*), 3200 (*s*–*vs*, *br*), 3073 (*s*), 1904 (*w*–*m*), 1640 (*s*), 1572 (*vs*), 1532 (*m*), 1480 (*s*–*vs*), 1462 (*vs*), 1407 (*s*–*vs*), 1336 (*s*), 1303 (*s*–*vs*), 1280 (*s*), 1232 (*m*), 1221 (*m*), 1137 (*m*), 1099 (*m*), 1045 (*s*), 1007 (*s*), 953 (*w*–*m*), 870 (*vs*), 854 (*vs*), 840 (*vs*), 781 (*vs*), 730 (*s*), 718 (*vs*), 671 (*s*), 627 (*s*), 537 (*m*), 484 (*m*); UV–vis [λ_{max} ($\varepsilon_{max} \times 10^{-3}$)]: 318 (2.7), 270 (3.8), 205 (234); ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 9.26 (*s*, 1H, H2), 7.34 (*d*, 1H, $J_{4,5}$ = 7.9 Hz, H4), 7.25 (*dd*, 1H, $J_{5,6}$ = 7.7 Hz, $J_{5,4}$ = 7.9 Hz, H5), 6.70 (*d*, 1H, $J_{6,5}$ = 7.7 Hz, H6), 5.68 (*s*, 2H, H–NH_2); ^{13}C NMR (DMSO-d_6, δ, p.p.m.): 154.4 (*s*), 154.4 (*d*), 143.4 (*s*), 127.0 (*d*), 119.0 (*s*), 110.9 (*d*), 108.6 (*d*). Zinc(II) chloride (0.15 g; 1 mmol) was dissolved in ethanol (30 ml). Into this solution, an ethanol solution of 7-amino-1,3-benzothiazole (0.33 g, 2.2 mmol in 20 ml) was added slowly. The reaction mixture was left to crystallize in a cool place. The crystals of (I) which formed were filtered off, washed with ethanol and dried [yield 67%; m.p. 547–549 K (decomposition)]. Analysis calculated for $C_{14}H_{12}Cl_2N_4S_2Zn$: C 38.51, H 2.77, N 12.83, S 14.68, Zn 14.97%; found: C 38.67, H 2.98, N 12.67, S 14.47, Zn 15.02%. Spectroscopic analysis, IR (ν, cm^{-1}): 3410 (*s*), 3390 (*s*), 3340 (*s*), 3323 (*s*), 3228 (*m*), 3066 (*m*–*s*), 3030 (*m*–*s*), 1900 (*vw*), 1631 (*s*), 1582 (*s*–*vs*), 1488 (*m*–*s*), 1458 (*vs*), 1407 (*m*–*s*), 1339 (*w*), 1317 (*m*), 1291 (*m*), 1251 (*m*), 1231 (*m*), 1139 (*m*), 1048 (*m*), 1013 (*m*), 955 (*w*–*m*), 886 (*s*), 868 (*m*), 785 (*s*), 775 (*s*), 723 (*m*), 712 (*s*), 653 (*m*, *br*). The melting point was determined on a Kofler block apparatus and is uncorrected. The IR spectra were recorded with a Nicolet Magna 760 IR spectrophotometer in KBr pellets. ^{1}H NMR and ^{13}C NMR data were determined with a Bruker Advance DPX 300 MHz NMR spectrometer with tetramethylsilane as the internal standard. The UV–vis spectra were recorded on a Perkin–Elmer UV–vis spectrometer Lambda 20 using 10^{-5} *M* methanol solutions at room temperature.

Crystal data

[$ZnCl_2(C_7H_6N_2S)_2$]
M_r = 436.67
Monoclinic, $P2_1/c$
a = 10.5620 (7) Å
b = 11.4321 (18) Å
c = 13.7109 (13) Å
β = 91.587 (9)°
V = 1654.9 (3) Å^3
Z = 4

D_x = 1.753 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 60 reflections
θ = 10–18°
μ = 2.06 mm^{-1}
T = 293 (2) K
Prism, green–grey
0.55 × 0.30 × 0.18 mm

Table 1
Selected geometric parameters (Å, °).

Zn1—N3	2.0405 (16)	S2—C13	1.734 (2)
Zn1—N1	2.0807 (17)	N1—C1	1.303 (3)
Zn1—Cl2	2.2235 (7)	N1—C2	1.399 (3)
Zn1—Cl1	2.2285 (6)	N2—C6	1.387 (3)
S1—C1	1.709 (2)	N3—C14	1.297 (3)
S1—C7	1.736 (2)	N3—C8	1.400 (2)
S2—C14	1.707 (2)	N4—C12	1.377 (3)
N3—Zn1—N1	103.30 (7)	C14—S2—C13	89.21 (10)
N3—Zn1—Cl2	115.92 (5)	C1—N1—C2	110.93 (18)
N1—Zn1—Cl2	107.79 (5)	C1—N1—Zn1	122.41 (15)
N3—Zn1—Cl1	108.67 (5)	C2—N1—Zn1	126.11 (14)
N1—Zn1—Cl1	102.60 (5)	C14—N3—C8	111.33 (17)
Cl2—Zn1—Cl1	116.81 (3)	C14—N3—Zn1	117.69 (14)
C1—S1—C7	89.31 (10)	C8—N3—Zn1	130.59 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N2···Cl2^{i}	0.82 (3)	2.73 (3)	3.463 (2)	148 (3)
N2—H2N2···Cl1^{i}	0.83 (3)	2.86 (3)	3.519 (2)	138 (3)
N4—H1N4···Cl1^{ii}	0.81 (4)	2.82 (4)	3.491 (2)	141 (4)
N4—H2N4···Cl2^{iii}	0.79 (3)	2.80 (3)	3.471 (2)	144 (3)
N4—H1N4···Cl1^{iv}	0.81 (4)	2.87 (4)	3.472 (2)	134 (4)
C1—H1···Cl2^{v}	0.93	2.78	3.619 (2)	150

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

Data collection

Philips PW1100 diffractometer (upgraded by Stoe)
$\theta/2\theta$ scans
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1995)
$T_{\min} = 0.486$, $T_{\max} = 0.690$
7185 measured reflections
4795 independent reflections
3220 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 30°$
$h = -14 \rightarrow 14$
$k = -5 \rightarrow 16$
$l = 0 \rightarrow 19$
5 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.075$
$S = 1.02$
4795 reflections
224 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.3308P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}

H atoms bonded to C atoms were introduced at calculated positions and refined using a riding model, with $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(C) and C—H distances of 0.93 Å. The H atoms of the NH_2 groups from both 7-aminobenzothiazole ligands were found in electron-density difference Fourier maps at the final stages of the refinement procedure and were refined freely.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1998) and *XP* (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1531). Services for accessing these data are described at the back of the journal.

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