

Bis(2-benzyl-1*H*-benzimidazole-*N*³)-dichlorozinc(II)

Fengli Bei,^a Fangfang Jian,^a Xujie Yang,^a Lude Lu,^a Xin Wang,^a Ibrahim Abdul Razak,^b S. Shanmuga Sundara Raj^b and Hoong-Kun Fun^{b*}

^aMaterials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

Received 25 August 2000

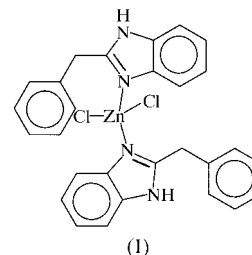
Accepted 23 October 2000

In the title compound, $[\text{ZnCl}_2(\text{C}_{14}\text{H}_{12}\text{N}_2)_2]$, the environment around the Zn atom is distorted tetrahedral formed by two Cl atoms and two tertiary N atoms of the 2-benzyl-1*H*-benzimidazole ligands. $\text{N}-\text{H}\cdots\text{Cl}$ intermolecular hydrogen bonds link the molecules into infinite chains in the $[101]$ direction.

Comment

Benzimidazole is an interesting heterocyclic ring because it is present in various naturally occurring drugs, such as omeprazole, astemizole and emedastine difumarate (Sakai *et al.*, 1989). The efficacy of substituted benzimidazoles in the treatment of parasitic infections is well known (Brown *et al.*, 1961; Preston, 1974; Sarkar *et al.*, 1984). Benzimidazole-substituted moieties are established pharmacophores in parasitic chemotherapy. Bis(2-benzimidazoles) and some substituted bis(benzimidazol-2-yl)alkanes have attracted much interest because of their wide-ranging antiviral activity (Tidwell *et al.*, 1993) and also because of the coordination chemistry of azoles acting as ligands in transition metal compounds. Such compounds are increasingly being studied in the context of modelling biological systems (Pujar *et al.*, 1988; Bouwman *et al.*, 1990). Zinc is a relatively abundant element in biological organisms and plays an essential role in a large number of enzymatic reactions (Liljas *et al.*, 1972). Zn^{II} , being a d^{10} ion, provides few spectroscopic signatures for the monitoring of structure. The structure of the zinc binding site can only be elucidated by X-ray crystallography.

In the title compound, (I), the molecule possesses near C_2 symmetry and the symmetry axis lies parallel to the b axis. The Zn atom is coordinated tetrahedrally by two Cl^- anions and two 2-benzyl-1*H*-benzimidazole ligands, *i.e.* ZnCl_2N_2 . The ZnCl_2N_2 tetrahedron is slightly distorted, with angles ranging from $103.32(7)$ to $116.67(7)^\circ$. The range of the tetrahedral angles is comparable with the corresponding values in the reported complex $\text{ZnCl}_2(5,7\text{-dimethyl-1,2,4-triazolo}[1,5-a]\text{-pyrimidine})_2$ [102.09 (9)–117.54 (4) $^\circ$; Salas *et al.*, 1994] but the coordination around the Zn atom in another complex, which also contains the ZnCl_2N_2 unit, namely $\text{ZnCl}_2(\text{purine})_2$ (Laity & Taylor, 1995), is severely distorted compared with the title complex, with angles ranging from $99.9(1)$ to $113.7(1)^\circ$.



(I)

The average Zn—Cl distance of $2.261(1)$ Å is longer than the average corresponding distances reported for related metal complexes with distorted ZnN_2Cl_2 tetrahedral environments, *cf.* $2.224(1)$ Å in $\text{ZnCl}_2(5,7\text{-dimethyl-1,2,4-triazolo}[1,5-a]\text{pyrimidine})_2$ (Salas *et al.*, 1994), $2.212(4)$ Å in $\text{ZnCl}_2(2,9\text{-dimethyl-1,10-phenanthroline})$ (Preston & Kennard, 1969), $2.226(2)$ Å in $\text{ZnCl}_2(\text{purine})_2$ (Laity & Taylor, 1995) and $2.209(3)$ Å in $\text{ZnCl}_2(4\text{-vinylpyridine})_2$ (Steffen & Palenik, 1977), but comparable to the value of $2.255(1)$ Å in $\text{ZnCl}_2[1-(5,6\text{-dimethylbenzimidazolyl})-3\text{-benzimidazolyl-2-thiapropane}]$ (Matthews *et al.*, 1998).

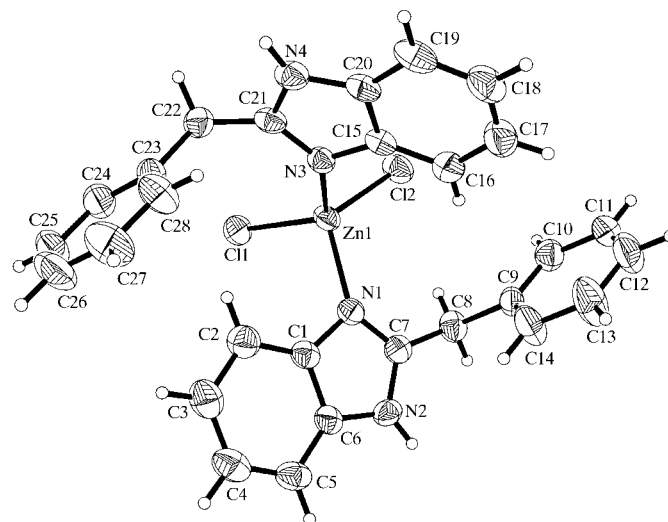


Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The average Zn—N bond distance of $2.042(3)$ Å is comparable to reported average values, *e.g.* $2.039(3)$ Å in $\text{ZnCl}_2(5,7\text{-dimethyl-1,2,4-triazolo}[1,5-a]\text{pyrimidine})_2$ (Salas *et al.*, 1994), $2.05(1)$ Å in $\text{ZnCl}_2(1\text{-methyltetrazole})_2$ (Baenziger & Schultz, 1971), $2.059(3)$ Å in $\text{ZnCl}_2(1\text{-methylcytosine})_2$ (Beauchamp, 1984) and $2.027(3)$ Å in $\text{ZnCl}_2[1-(5,6\text{-dimethylbenzimidazolyl})-3\text{-benzimidazolyl-2-thiapropane}]$ (Matthews *et al.*, 1998), but longer than the average value of $2.007(4)$ Å in $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{Cl}_2(1,2\text{-dimethylimidazole})_2$ (Bharadwaj *et al.*, 1991).

The dihedral angles between the benzimidazole moieties (involving N1/N2 and N3/N4) and the phenyl rings (C9–C14 and C23–C28) are 83.0 (2) and 79.4 (2)°, respectively. The mean planes of the two benzimidazole moieties form a dihedral angle of 69.7 (1)°, while the dihedral angle between the phenyl rings is 1.2 (2)°.

In the crystal, the N2 and N4 atoms of the benzimidazole moieties are involved in N—H...Cl intermolecular hydrogen bonds with the Cl atoms (Table 2). These intermolecular hydrogen bonds link the molecules into infinite one-dimensional chains in the [101] direction.

Experimental

Solid 2-benzyl-1H-benzimidazole was dissolved in EtOH/H₂O. Zinc dichloride was then added at 343–353 K with stirring and the resulting solution was refluxed for 4–5 h and then cooled. The red solution obtained was filtered and left to evaporate. After one day, red solids had separated out and were recrystallized from EtOH/H₂O. Single crystals suitable for X-ray analysis were obtained by slow evaporation from an EtOH solution at room temperature.

Crystal data

[ZnCl ₂ (C ₁₄ H ₁₂ N ₂) ₂]	$D_x = 1.438 \text{ Mg m}^{-3}$
$M_r = 552.78$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8192 reflections
$a = 11.8623 (2) \text{ \AA}$	$\theta = 1.92\text{--}28.32^\circ$
$b = 16.3674 (1) \text{ \AA}$	$\mu = 1.196 \text{ mm}^{-1}$
$c = 14.1767 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 111.943 (1)^\circ$	Slab, red
$V = 2553.08 (6) \text{ \AA}^3$	$0.28 \times 0.24 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	6226 independent reflections
ω scans	3898 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.073$
$T_{\text{min}} = 0.731$, $T_{\text{max}} = 0.796$	$\theta_{\text{max}} = 28.28^\circ$
17 665 measured reflections	$h = -7 \rightarrow 15$
	$k = -21 \rightarrow 21$
	$l = -18 \rightarrow 18$

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.039 (2)	Zn1—Cl1	2.2575 (8)
Zn1—N3	2.044 (2)	Zn1—Cl2	2.2626 (8)
N1—Zn1—N3	108.54 (9)	N1—Zn1—Cl2	115.44 (7)
N1—Zn1—Cl1	103.32 (7)	N3—Zn1—Cl2	104.47 (6)
N3—Zn1—Cl1	116.67 (7)	Cl1—Zn1—Cl2	108.84 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N2—H2A...Cl2 ⁱ	0.86	2.46	3.240 (3)	152
N4—H4A...Cl1 ⁱⁱ	0.86	2.55	3.314 (3)	148

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.133$
 $S = 0.93$
 6226 reflections
 316 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0592P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.51 \text{ e \AA}^{-3}$

After checking their presence in the difference map, the positions of all H atoms were calculated geometrically and allowed to ride on their attached atoms (N—H = 0.86 Å and C—H = 0.93–0.97 Å). The highest peak and deepest hole are located 0.91 and 0.82 Å, respectively, from the Zn atom. Examination of the structure with PLATON (Spek, 1990) showed that there were solvent-accessible voids of 34 Å³ in the crystal lattice, but there was no evidence of diffuse solvent in these holes.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R & D No. 305/PFIZIK/610942. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1109). Services for accessing these data are described at the back of the journal.

References

- Baenziger, N. C. & Schultz, R. J. (1971). *Inorg. Chem.* **10**, 661–667.
- Beauchamp, A. L. (1984). *Inorg. Chim. Acta*, **91**, 33–38.
- Bharadwaj, P. K., Schugar, H. J. & Potenza, J. A. (1991). *Acta Cryst.* **C47**, 754–757.
- Bouwman, E., Driessen, W. L. & Reedijk, J. (1990). *Coord. Chem. Rev.* **104**, 143–172.
- Brown, H. D., Matzuk, A. R., Ilves, I. R., Peterson, L. H., Harris, S. A., Sarett, L. H., Egerton, J. R., Yakstis, J. J., Campbell, W. C. & Cuckler, A. C. (1961). *J. Am. Chem. Soc.* **83**, 1764–1765.
- Laity, H. L. & Taylor, M. R. (1995). *Acta Cryst.* **C51**, 1791–1793.
- Liljas, A., Kannan, K. K., Bergsten, P. C., Waara, L., Fridborg, K., Strandberg, B., Caribom, V., Jarup, L., Lovgren, S. & Petef, M. (1972). *Nature New Biol.* **235**(57), 131–137.
- Matthews, C. J., Clegg, W., Heath, S. L., Martin, N. C., Hill, S. M. N. & Lockhart, J. C. (1998). *Inorg. Chem.* **37**, 199–207.
- Preston, H. S. & Kennard, C. H. L. (1969). *J. Chem. Soc. A*, pp. 1956–1961.
- Preston, P. N. (1974). *Chem. Rev.* **74**, 279–314.
- Pujar, M. A., Bharamgoudar, T. D. & Sathyanarayana, D. N. (1988). *Transition Met. Chem.* **13**, 423–425.
- Sakai, T., Hamada, T., Awata, N. & Watanabe, J. (1989). *J. Pharmacobiodyn.* **12**, 530–536.
- Salas, J. M., Romero, M. A. & Rahmani, A. (1994). *Acta Cryst.* **C50**, 510–512.
- Sarkar, B. R., Pathak, B., Dutta, S. & Lahiri, S. C. (1984). *J. Indian Chem. Soc.* **61**, 151–153.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Steffen, W. L. & Palenik, G. J. (1977). *Inorg. Chem.* **16**, 1119–1127.
- Tidwell, R. R., Jones, S. K., Naiman, N. A., Berger, L. C., Brake, W. B., Dykstra, C. C. & Hall, J. E. (1993). *Antimicrob. Agents Chemother.* **37**, 1713–1716.