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Aqua(2,2′-diamino-4,4′-bi-1,3-thiazole-κ^2N,N')(oxydiacetato-κ^3O,O',O'')zinc(II) dihydrate

Hong Li,[a] Yue Luo,[a] Duan-Jun Xu,[a]* Jing-Yun Wu[b] and Michael Y. Chiang[b]

[a]Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, People's Republic of China, and [b]Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan

Correspondence e-mail: xudj@mail.hz.zj.cn

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Key indicators

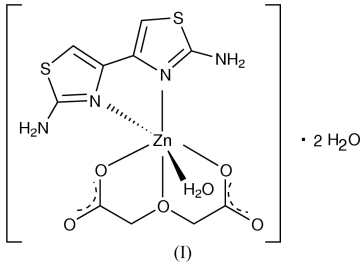
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.012 Å
H-atom completeness 88%
Disorder in solvent or counterion
R factor = 0.054
wR factor = 0.189
Data-to-parameter ratio = 15.5

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

The title Zn^{II} complex, $[Zn(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot 2H_2O$, with ligands consisting of an oxydiacetate dianion (ODA), a diaminobithiazole (DABT) molecule and a water molecule, displays a distorted octahedral coordination geometry. The tridentate ODA chelates to the Zn^{II} in a meridional configuration, with the Zn—O(ether) distance of 2.216 (5) Å, much longer than the Zn—O(carboxyl) distances of 2.051 (5) and 2.071 (5) Å. The overlapped arrangement of parallel DABT ligands, with a separation of 3.509 (9) Å between neighboring DABT rings, suggests π–π stacking between neighboring molecules.

Comment

Transition metal complexes with 2,2′-diamino-4,4′-bithiazole (DABT) have shown interesting properties and potential applications in many fields. For example, a Co^{II} complex and a Ni^{II} complex with DABT have been found to be effective inhibitors of the DNA synthesis of tumor cells (Waring, 1981; Fisher *et al.*, 1985). The X-ray structure of the title Zn^{II} complex, (I), is presented here.



(I)

The molecular structure of (I) is shown in Fig. 1. The complex molecule, with ligands consisting of an oxydiacetate dianion (ODA), a diaminobithiazole (DABT) molecule and a water molecule, has a distorted octahedral coordination geometry. The two thiazole rings of DABT are almost coplanar, with a small dihedral angle of 2.0 (5)°; this differs from the twisted structure of the bithiazole ligand found in a DABT complex of Cd^{II} (Liu *et al.*, 2003).

The tridentate ODA ligand chelates the Zn^{II} in a meridional configuration, as found in most metal complexes involving the ODA ligand (Cambridge Structural Database; Allen, 2002). The Zn—O3 bond distance of 2.216 (5) Å is essentially identical to the Zn—O6 distance of 2.219 (4) Å, but significantly longer than Zn—O1 [2.051 (5) Å] and Zn—O4 [2.071 (5) Å].

An overlapped arrangement of neighboring DABT ligands is observed, as shown in Fig. 2. The separation of 3.509 (9) Å

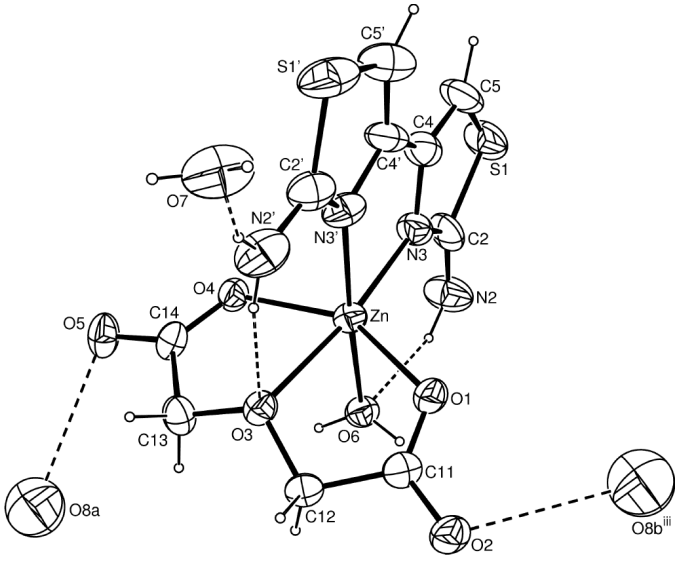


Figure 1
The structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding. [Symmetry code: (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.]

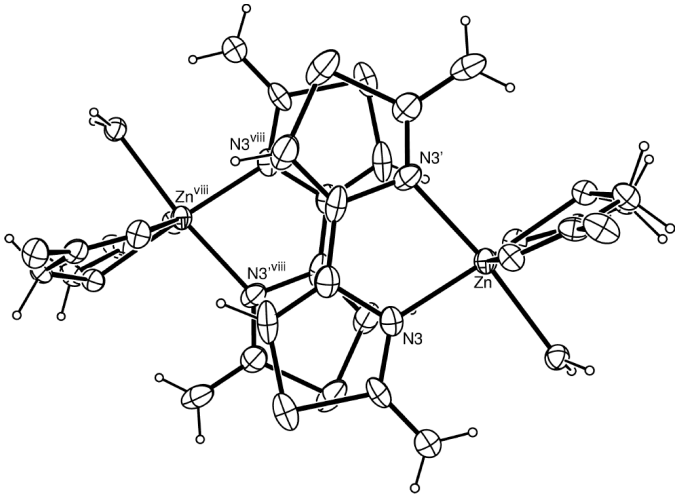


Figure 2
The overlapped arrangement of neighboring DABT ligands, showing the π–π stacking. [Symmetry code: (viii) $-x, 1-y, 1-z$.]

between the parallel N3-DABT and N3^{viii}-DABT ligands [symmetry code: (viii) $-x, 1-y, 1-z$] suggests the existence of π–π stacking between neighboring DABT ligands.

The O atoms of the uncoordinated water molecules, O7 and O8, hydrogen bond to the complex molecule, as shown in Fig. 1. Atom O8 is disordered over two sites, O8*a* and O8*b*, separated by 1.25 (3) Å; one site is close to carboxyl atom O5 while the other is close to carboxyl atom O2 of an adjacent complex molecule. The O···O distances of 2.98 (2) and 3.06 (2) Å suggest hydrogen bonding between atoms O8*a* and O5, and between atoms O8*b*($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$) and O2 (see Fig. 1). A packing diagram (Fig. 3) reveals the considerable space around the disordered water molecule; this might be considered as a factor contributing to the disorder in the structure.

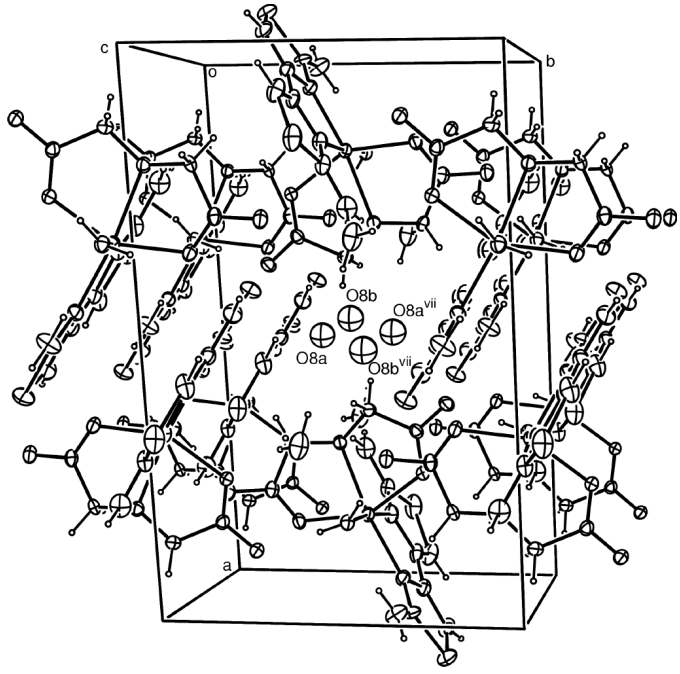


Figure 3
A packing diagram, showing the considerable space around the disordered water molecule. [Symmetry code: (vii) $1-x, 1-y, 1-z$.]

Experimental

The title complex was prepared by refluxing a mixture of DABT (0.10 g, 0.5 mmol), $H_2ODA{\cdot}H_2O$ (0.075 g, 0.5 mmol) and $ZnCl_2$ (0.070 g, 0.5 mmol) in an aqueous solution (10 ml) containing NaOH (0.40 g 1 mmol) for 3 h. The pale-yellow solution was then cooled to room temperature and filtered. Colorless single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[Zn(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]{\cdot}2H_2O$
$M_r = 449.76$
Monoclinic, $P2_1/n$
$a = 16.682$ (4) Å
$b = 10.083$ (3) Å
$c = 11.1718$ (17) Å
$\beta = 108.907$ (2)°
$V = 1777.8$ (7) Å^3
$Z = 4$
$D_x = 1.680$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 4.8$–$10.2°$
$\mu = 1.66$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.30 × 0.25 × 0.14 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.602$, $T_{max} = 0.790$
3688 measured reflections
3496 independent reflections
1589 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0°$
$h = -20 \rightarrow 19$
$k = -12 \rightarrow 0$
$l = 0 \rightarrow 13$
3 standard reflections
every 150 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.189$
$S = 1.01$
3496 reflections
225 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—O1	2.051 (5)	Zn—N3′	2.124 (6)
Zn—N3	2.066 (6)	Zn—O3	2.216 (5)
Zn—O4	2.069 (4)	Zn—O6	2.219 (4)
O1—Zn—N3	112.6 (2)	O4—Zn—N3′	94.1 (2)
N3—Zn—O4	97.8 (2)	N3—Zn—O3	172.3 (2)
O1—Zn—N3′	96.5 (2)	N3′—Zn—O3	97.9 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O6	0.86	2.09	2.878 (10)	152
N2—H22···O5^{i}	0.86	1.95	2.799 (10)	168
N2′—H23···O3	0.86	2.39	3.169 (8)	151
N2′—H24···O7	0.86	2.06	2.897 (9)	163
O6—H61···O2^{ii}	0.92	1.78	2.696 (7)	173
O6—H62···O5^{iii}	0.87	1.81	2.674 (7)	174
O7—H71···O8*b*^{iv}	0.99	2.47	3.43 (2)	163
O7—H72···O2^{v}	0.98	2.31	2.792 (9)	110
C5′—H5′···O8*a*^{vi}	0.93	2.43	3.14 (2)	133
C13—H13A···O8*a*^{vii}	0.97	2.46	3.24 (2)	138

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

One water molecule (O8) was found to be disordered over two sites (O8*a* and O8*b*), each with a site-occupancy factor of 0.5. Atoms O8*a* and O8*b* were refined isotropically and their attached H atoms were not located. The H atoms of the other uncoordinated water molecule and the coordinated water molecule were positioned theoretically (Nardelli, 1999) and included in the structure-factor calculations with fixed positional parameters and an isotropic displacement parameter of 0.1 Å^2. The H atoms attached to carbon were placed in calculated positions, with C—H = 0.93 Å (DABT), 0.97 Å (ODA) and N—H = 0.86 Å, and included in the final cycles of refinement as riding atoms, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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