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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
H-atom completeness 94%
Disorder in solvent or counterion
R factor = 0.038
wR factor = 0.098
Data-to-parameter ratio = 12.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Bis[triaqua(2,2'-diamino-4,4'-bi-1,3-thiazole)isonicotinatozinc(II)] bis(isonicotinate) diaqua(2,2'-diamino-4,4'-bi-1,3-thiazole)bis(isonicotinato)zinc(II) tetrahydrate**

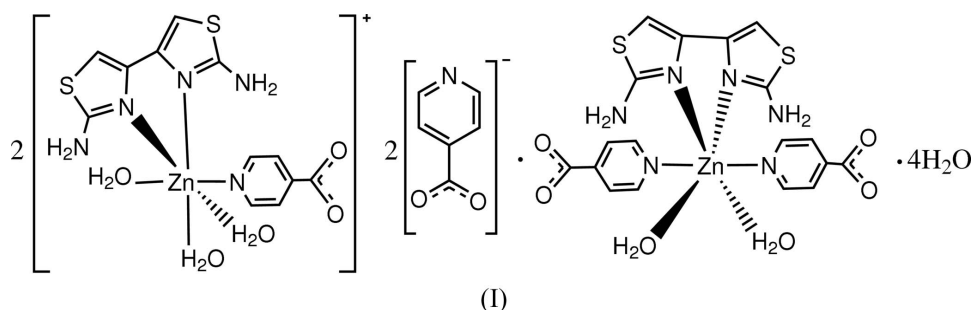
The crystal structure of the title compound, $[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_4\text{N}_4\text{S}_2)(\text{H}_2\text{O})_3]_2(\text{C}_6\text{H}_4\text{NO}_2)_2 \cdot [\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_6\text{H}_4\text{N}_4\text{S}_2)(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, consists of four discrete components. In the neutral complex the Zn ion is located on a crystallographic twofold axis. The two thiazole rings of the diaminobithiazole ligand are twisted with respect to each other [dihedral angle = $13.85(9)^\circ$] in the neutral complex but are coplanar [dihedral angle = $3.54(15)^\circ$] in the cationic complex. π - π stacking is observed between nearly parallel pyridine rings.

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Comment

Transition metal complexes of 2,2'-diamino-4,4'-bi-1,3-thiazole (DABT) have shown potential application in the field of soft magnetic materials (Sun *et al.*, 1997). As part of a series of structural investigations of metal complexes with DABT (Liu *et al.*, 2003), the title Zn^{II} complex has recently been prepared and its crystal structure is presented here.



The crystal structure of (I) consists of four discrete components: the Zn^{II} complex cation, isonicotinate anion, neutral Zn^{II} complex and uncoordinated water molecule (Fig. 1). Within the neutral complex, the Zn^{II} ion is located on a twofold axis and coordinated by one DABT ligand, two isonicotinate anions and two water molecules. The two thiazole rings of DABT are twisted with respect to each other, with a dihedral angle of $13.85(9)^\circ$, comparable to $14.7(3)^\circ$ found in a DABT complex of Cd^{II} (Zhang *et al.*, 2006) and $20.04(8)^\circ$ found in a DABT complex of Ni^{II} (Liu & Xu, 2005). Within the complex cation, the Zn^{II} ion is coordinated by one DABT ligand, one isonicotinate anion and three water molecules. The DABT ligand displays a planar configuration in the complex cation, the dihedral angle between the two thiazole rings being $3.54(15)^\circ$, comparable to $2.60(10)^\circ$ found in a DABT complex of Mn^{II} (Liu *et al.*, 2006). The isonicotinate anion coordinates to the Zn^{II} ion *via* the N atom. In both the neutral and the

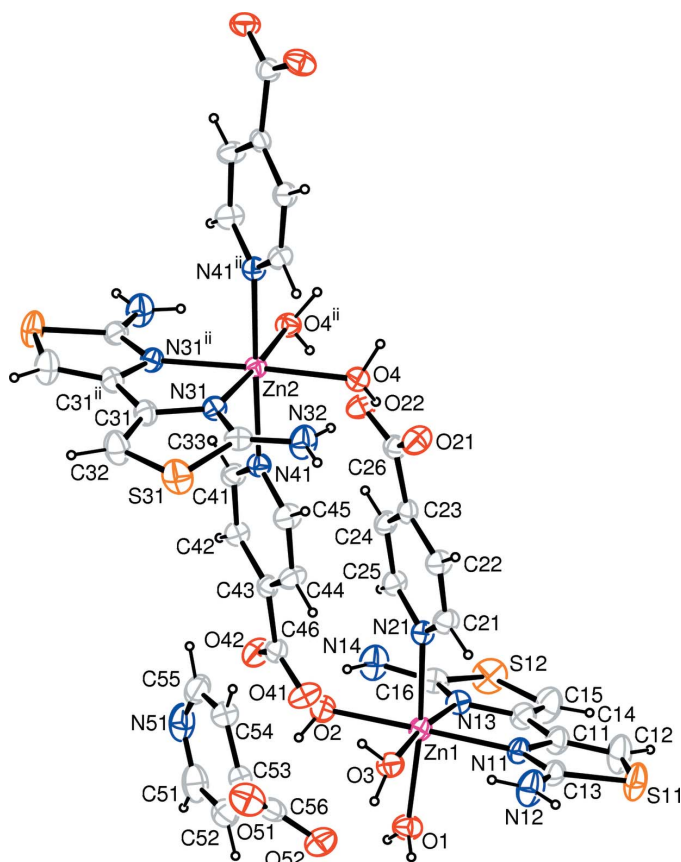


Figure 1
The structural components of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry codes: (ii) $1 - x, y, \frac{3}{2} - z$]. Solvent water molecules have been omitted for clarity.

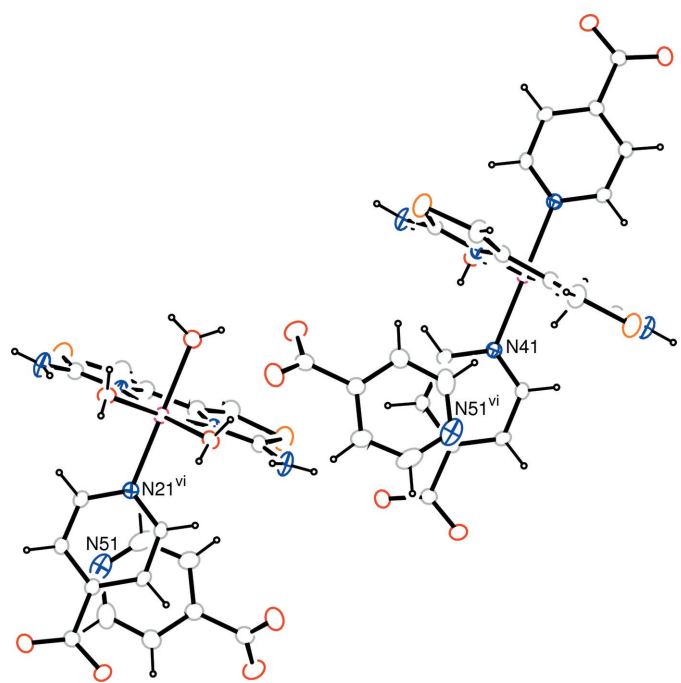


Figure 2
 π - π stacking between pyridine rings [symmetry code: (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$].

cationic complexes, the carboxylate groups of isonicotinate are coplanar with the pyridine rings. However, the carboxylate group of the free isonicotinate is twisted with respect to the pyridine plane, with a larger dihedral angle of $50.98(11)^\circ$, which is considered to be a result of $O-H \cdots O$ hydrogen bonding between the carboxylate group and coordinated water molecules of the adjacent cationic complex (Table 2).

A partially overlapped arrangement between pyridine rings is observed in the crystal structure (Fig. 2). The centroid-to-centroid separation of $3.7934(18) \text{ \AA}$ between nearly parallel N41-pyridine and N51^{vi}-pyridine rings [dihedral angle $3.13(2)^\circ$] and the centroid-to-centroid separation of $3.5634(17) \text{ \AA}$ between nearly parallel N51-pyridine and N21^{vi}-pyridine rings [dihedral angle $5.70(3)^\circ$] [symmetry code: (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$] indicate the existence of π - π stacking in the crystal structure of (I).

Experimental

An aqueous solution (20 ml) containing DABT (1 mmol) and $ZnCl_2$ (1 mmol) was mixed with an aqueous solution (10 ml) of isonicotinic acid (2 mmol) and NaOH (2 mmol). The mixture was refluxed for 5 h. The solution was filtered after cooling to room temperature. Yellow single crystals of (I) were obtained from the filtrate after one week.

Crystal data

$[Zn(C_6H_4NO_2)(C_6H_6N_4S_2) \cdot (H_2O)_3]_2(C_6H_4NO_2)_2 \cdot [Zn(C_6H_4NO_2)_2(C_6H_6N_4S_2) \cdot (H_2O)_2] \cdot 4H_2O$
 $M_r = 1739.72$
 Monoclinic, $C2/c$
 $a = 36.196(3) \text{ \AA}$
 $b = 10.1184(9) \text{ \AA}$
 $c = 20.4410(17) \text{ \AA}$
 $\beta = 108.967(12)^\circ$
 $V = 7079.9(11) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.632 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.27 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism, yellow
 $0.34 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.680, T_{max} = 0.780$
 17955 measured reflections
 6224 independent reflections
 5136 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.027$
 $\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.098$
 $S = 1.04$
 6224 reflections
 484 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 6.9519P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$
 $\Delta\rho_{max} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$

Table 1
Selected bond lengths (\AA).

Zn1—O1	2.2077 (19)	Zn1—N21	2.166 (2)
Zn1—O2	2.1218 (19)	Zn2—O4	2.1447 (18)
Zn1—O3	2.1178 (18)	Zn2—N31	2.146 (2)
Zn1—N11	2.102 (2)	Zn2—N41	2.161 (2)
Zn1—N13	2.140 (2)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1A···O52	0.81	2.08	2.856 (3)	161
O1—H1B···O51 ⁱ	0.85	2.02	2.859 (3)	172
O2—H2A···O51	0.85	1.85	2.702 (4)	179
O2—H2B···O42	0.84	1.84	2.660 (3)	166
O3—H3A···O52 ⁱ	0.82	1.89	2.686 (3)	165
O3—H3B···O41	0.84	1.79	2.634 (3)	177
O4—H4A···O22 ⁱⁱ	0.85	1.85	2.699 (3)	173
O4—H4B···O21	0.93	1.81	2.741 (3)	175
O1W—H1WA···O21	0.92	1.81	2.720 (4)	168
O1W—H1WB···O2WA	0.93	1.89	2.799 (14)	167
O1W—H1WB···O2WB	0.93	2.01	2.873 (19)	154
N12—H12A···O3	0.83	2.22	2.972 (4)	151
N12—H12B···O22 ⁱⁱⁱ	0.83	2.00	2.803 (3)	161
N14—H14A···O2	0.87	2.27	3.061 (4)	151
N14—H14B···O42 ^{iv}	0.82	2.12	2.929 (3)	171
N32—H32A···O4	0.84	2.35	3.117 (3)	153
N32—H32B···O41 ^v	0.83	2.19	2.980 (3)	159

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

One solvent water molecule is disordered over two sites; occupancies were refined and converged to 0.54 (3) and 0.46 (3). H atoms of the disordered water molecule were not located. H atoms of the amino groups and the ordered water molecules were located in a difference Fourier map and refined as riding in their as-found relative positions [O—H = 0.81–0.93 Å, N—H = 0.82–0.87 Å] with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{N})$. Other H atoms were placed in calculated positions with

C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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