Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(μ-pyridazine-3,6-carboxylato-$\kappa^4N,O:N',O'$)-bis[diaquazinc(II)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.101
Data-to-parameter ratio = 15.8

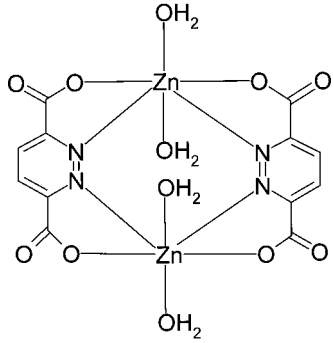
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 9 November 2006
Accepted 16 November 2006

The title crystal structure, $[Zn_2(C_6H_2N_2O_4)_2(H_2O)_4]$, is composed of discrete centrosymmetric molecular dimers in which two Zn^{II} atoms are coordinated by two fully deprotonated pyridazine-3,6-dicarboxylate ligands *via* *N*,*O*-bonding and two water O atoms in axial positions forming slightly distorted octahedral environments. In the crystal structure, a three-dimensional network is formed *via* intermolecular O—H···O hydrogen bonds [H···O = 2.04 (4)–2.10 (5) Å]

Comment

The structure of the title compound, (I), is composed of discrete centrosymmetric dinuclear units consisting of two Zn^{II} atoms bridged by two fully deprotonated pyridazine-3,4-dicarboxylate ligands. Each Zn^{II} atom is chelated by two *N*,*O*-bonding groups, each donated by a different ligand molecule, and two water O atoms in axial positions, forming a slightly distorted octahedral environment. The relevant bond distances and angles are listed in Table 1. They are close to those commonly observed in Zn^{II} complexes with *N*-heterocyclic carboxylate ligands (see for example Gryz *et al.*, 2004*a*, 2005). Also bond distances and angles within the anionic ligand molecule agree well with those reported for both modifications of the parent acid (Sueur *et al.*, 1987; Starosta & Leciejewicz, 2004).



(I)

Fig. 1 shows the molecular structure of the title dimer with the atom-labelling scheme. The dimer molecules lie on crystallographic inversion centres. The Zn^{II} atoms and the pyridazine rings are coplanar, with an r.m.s. deviation of 0.0408 (10) Å. The carboxylate groups deviate from the mean ring plane by 5.4 (5) (C7/O1/O2) and 5.0 (5)° (C8/O3/O4). There are hydrogen bonds between coordinated water molecules, and carboxylate group O atoms belonging to adjacent dimers. In the crystal structure, a three-dimensional network is

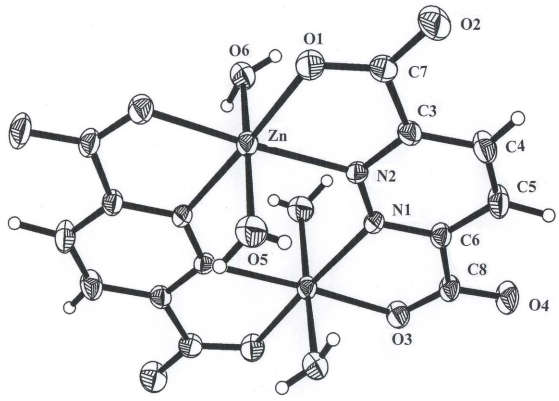


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y + 2, -z + 1)$.

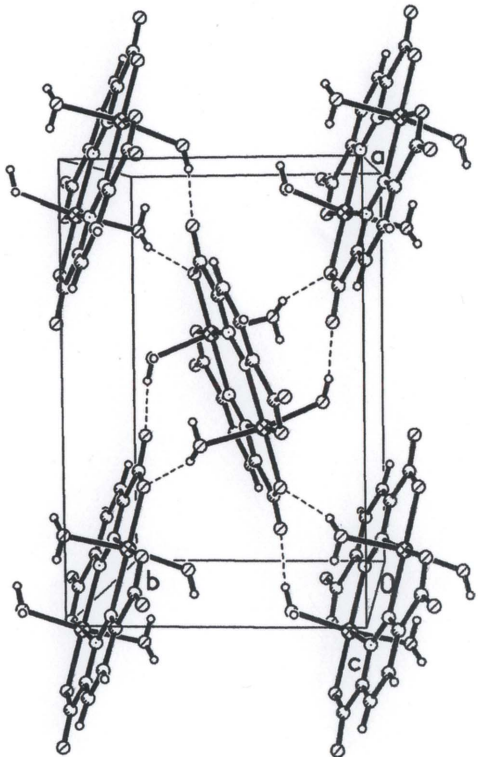


Figure 2
Part of the crystal structure of (I), with hydrogen bonds shown as dashed lines.

formed *via* these intermolecular O—H···O hydrogen bonds (Table 2 and Fig. 2). The Ni^{II} analogue is isostructural with the title compound (Escuer *et al.*, 1997). On the other hand, the structure of the Mn^{II} complex $Mn(HC_6H_2N_2O_4)_2(H_2O)_2$ contains monomeric molecular units with singly deprotonated ligand molecules and Mn^{II} atoms having an octahedral coordination environment (El Gueddi *et al.*, 1996), while the structure of the Mg^{II} complex is composed of monomeric anions $[Mg(C_6H_2N_2O_4)_2]^{2-}$ with fully deprotonated ligand molecules and protonated hydrazine cations $(H_2N—NH_3)^+$ (Gryz *et al.*, 2004*b*).

Experimental

A hot aqueous solution (100 ml) of pyridazine-3,6-dicarboxylic acid dihydrate (1 mmol) was mixed with a hot solution (50 ml) of zinc acetate dihydrate (1 mmol). The mixture was boiled with stirring for 1 h. After cooling to room temperature, hydrazine (3 ml) was added to maintain the pH at about 5. After standing for *ca* two weeks, colourless single crystals in the form of prismatic blocks deposited in the mother liquid. They were washed with cold water and dried in air.

Crystal data

$[Zn_2(C_6H_2N_2O_4)_2(H_2O)_4]$
M_r = 535.0
Orthorhombic, *Pbca*
a = 13.393 (3) Å
b = 8.8039 (18) Å
c = 14.622 (3) Å
V = 1724.2 (6) Å^3
Z = 4
D_x = 2.061 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.86 mm^{-1}
T = 293 (2) K
Prismatic blocks, colourless
0.13 × 0.11 × 0.06 mm

Data collection

Kuma KM-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2000)
T_{min} = 0.687, T_{max} = 0.836
3043 measured reflections
2535 independent reflections
1684 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 30.1°
3 standard reflections
every 200 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.101
S = 1.03
2535 reflections
160 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.0332 (18)	Zn1—O5	2.145 (2)
Zn1—O3^{i}	2.0445 (18)	Zn1—N1^{i}	2.1600 (18)
Zn1—O6	2.121 (2)	Zn1—N2	2.1720 (19)
O1—Zn1—O3^{i}	99.39 (7)	O1—Zn1—N2	78.04 (7)
O6—Zn1—O5	172.68 (9)	N1^{i}—Zn1—N2	104.54 (7)
O3^{i}—Zn1—N1^{i}	77.99 (7)		

Symmetry code: (i) $-x, -y + 2, -z + 1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O2^{ii}	0.74 (5)	2.06 (5)	2.773 (3)	162 (5)
O5—H52···O3^{iii}	0.77 (4)	2.04 (4)	2.745 (3)	153 (4)
O6—H61···O4^{iv}	0.71 (4)	2.04 (4)	2.743 (3)	170 (4)
O6—H62···O2^{v}	0.74 (5)	2.10 (5)	2.816 (3)	163 (6)

Symmetry codes: (ii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{5}{2}, -z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

H atoms were refined independently with isotropic displacement parameters [C—H = 0.89 (3) and 1.01 (3) Å; O—H distances as in Table 2].

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1992); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Ministry of Scientifc Research and Information Technology (grant No. 3 T0907828).

References

El Gueddi, A., Guesmi, S., Mernari, B., Stoeckli-Evans, H., Ribas, J., Vicente, R. & Laggrenee, M. (1996). *Polyhedron*, **15**, 4283–4288.

Escuer, A., Vicente, R., Mernari, B., El Gueddi, A. & Pierrot, M. (1997). *Inorg. Chem.* **36**, 2511–2516.

Gryz, M., Starosta, W. & Leciejewicz, J. (2004*a*). *Acta Cryst.* E**60**, m1481–m1483.

Gryz, M., Starosta, W. & Leciejewicz, J. (2004*b*). *J. Coord. Chem.* **57**, 917–922.

Gryz, M., Starosta, W. & Leciejewicz, J. (2005). *J. Coord. Chem.* **58**, 931–935.

Kuma (1996). *KM-4 Software*. Kuma Diffraction, Wroclaw, Poland.

Kuma (2001). *DATAPROC*. Version 10.0.7. Kuma Diffraction, Wroclaw, Poland.

Oxford Diffraction (2000). *CrysAlis RED*. Version 1.69. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1992). *XP*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.

Starosta, W. & Leciejewicz, J. (2004). *Acta Cryst.* E**60**, o2219–o2220.

Sueur, S., Lagrenee, M., Abraham, F. & Bremard, C. (1987). *J. Heterocycl. Chem.* **24**, 1285–1289.