Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Triaqua(4-hydroxypyridine-2,6-dicarboxylato-κ^3*N*,*O*,*O*′)zinc(II)–acetonitrile–water(1/0.25/1)

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Received 15 August 2003
Accepted 8 September 2003
Online 18 September 2003

Key indicators

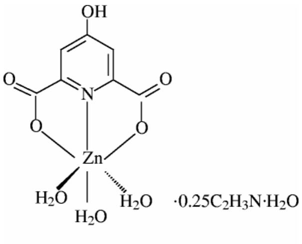
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
H-atom completeness 38%
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.154
Data-to-parameter ratio = 11.1

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

The title compound, $[Zn(C_7H_2NO_5)(H_2O)_3]\cdot 0.25CH_3CN\cdot H_2O$, was synthesized by the reaction of $Zn(CH_3COO)_2\cdot 2H_2O$ and chelidamic acid. The coordination geometry of the Zn atom is a distorted octahedron, with one N and two O atoms from the chelidamate ligand and three water O atoms. A three-dimensional network is formed by the O—H···O hydrogen bonds between the O atoms of the chelidamate ligand and the aqua ligands and water molecule of crystallization.

Comment

Research on the behavior of metal chelation, which has been one of the most active areas in the fields of chemistry and material sciences, shows promising prospects in applications (Schnebeck *et al.*, 1999; Abrahams *et al.*, 1998; Goodgame *et al.*, 1999; Albrecht, 1985). Chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid), an polydentate ligand, is of considerable interest in coordination chemistry. It is also important in biochemistry, organic chemistry, and medical chemistry, even in HIV investigations (Berl *et al.*, 2001; Ng, 1999; Nakatsuji *et al.*, 1985; Boger *et al.*, 1999; Fessmann & Kilburn, 1999; Bridger *et al.*, 1999; Searcey *et al.*, 1998). Metal complexes containing the chelidamate ligand have been reported for Fe^{III}, Cr^{III}, Sn^{IV}, Gd^{III} and V^{V} (Ng, 1998, 1999; Riegel, 1926; Hall *et al.*, 2000; Cline *et al.*, 1979; Yang *et al.*, 2002; Thich *et al.*, 1976). Here we report the synthesis and crystal structure of a new Zn^{II} compound, (I), with a chelidamate ligand.



(I)

As shown in Fig. 1, the Zn^{II} atom is chelated by two O atoms [average Zn—O 2.216 (2) Å] and one N atom from the chelidamate ligand, and coordinated by three water molecules [mean Zn—O = 2.101 (2) Å]. The Zn—N distance of 2.0232 (13) Å in (I) is slightly shorter than that of 2.089 (3) Å in a related compound, tetraaqua(uracil-6-carboxylato)zinc(II) monohydrate (Karipides & Thomas, 1986). The coordination geometry of the Zn atom can be described as a distorted octahedron (Table 1). The largest distortion from

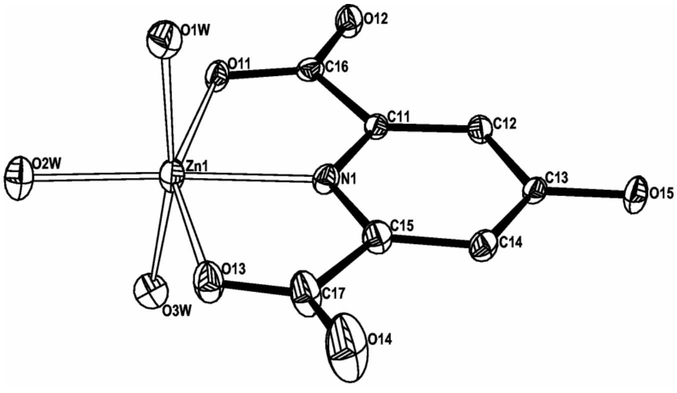


Figure 1
A view of the complex molecule in (I), showing 30% displacement ellipsoids for non-H atoms. H atoms are omitted.

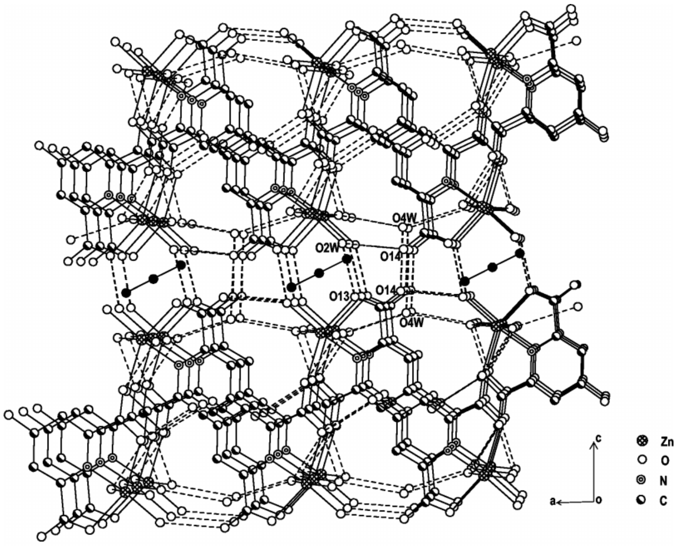


Figure 2
Packing diagram of (I). Dashed lines represent the hydrogen bonds. Thick dashed lines indicate the interlayer hydrogen bonds.

octahedral symmetry is seen in the O13—Zn1—O11 bond angle of 151.80 (4)°; this is due to the tridentate chelation. Atom Zn1 and the chelidamate ligand are coplanar, with a mean deviation of 0.021 Å. The C13—O15 bond distance of 1.3428 (19) Å, which is close to 1.36 Å characteristic of C—O bonds in aromatic alcohols (Sutton, 1965; Penfold, 1953), indicates that the pyridine ring exhibits the enolic form upon coordination (Gaspar *et al.*, 2001).

Atoms O14 and O11 act as hydrogen-bond acceptors, forming intermolecular hydrogen bonds with atoms O2*W* and O15 [O2*W*···O14 2.833 (2), O15···O11 2.6427 (16) Å]. These hydrogen bonds link the zinc complex, forming an infinite chain in the [110] direction. Neighboring chains are connected into an infinite layer in the [010] direction through the hydrogen bonds between O1*W*, O3*W*, O4*W* and O12 [O1*W*···O4*W* = 2.814 (2), O1*W*···O12 = 2.719 (2), O3*W*···O4*W* = 2.862 (2), O3*W*···O12 = 2.818 (2) Å]. The layers are inter-linked through the O4*W*···O14 and O2*W*···O13 hydrogen bonds [O14···O4*W* = 2.747 (2), O2*W*···O13 = 2.662 (2) Å], forming a three-dimensional framework along the [001] direction, as shown in Fig. 2. Positionally disordered acetonitrile molecules are located between the layers.

Experimental

A mixture of $Zn(CH_3COO)_2·2H_2O$ (64 mg, 0.29 mmol) and chelidamic acid (50 mg, 0.25 mmol) was dissolved in a 1:1 mixture of water and acetonitrile (20 ml). After adding 1–2 drops of KOH (0.1 mmol, 1 mol/l) to the solution and stirring for about 4 h, the mixed solution was filtered. The filtrate was allowed to stand at room temperature. Yellow crystals of (I) were formed over a period of 4–5 d, in a yield of 63%.

Crystal data

$[Zn(C_7H_2NO_5)(H_2O)_3]·0.25C_2H_3N·H_2O$
M_r = 327.79
Monoclinic, $C2/c$
a = 14.6504 (3) Å
b = 7.0380 (2) Å
c = 22.6423 (5) Å
β = 91.866 (1)°
V = 2333.4 (1) Å^3
Z = 8
D_x = 1.866 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2863 reflections
θ = 2.8–25.0°
μ = 2.15 mm^{-1}
T = 293 (2) K
Prism, pale yellow
0.64 × 0.40 × 0.38 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.296, T_{max} = 0.442
3823 measured reflections
2059 independent reflections
1759 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.0°
$h = -13 \rightarrow 17$
$k = -5 \rightarrow 8$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.154
S = 1.00
2059 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2 + 10.2923P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −1.05 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O2*W*	2.0081 (12)	Zn1—O13	2.1854 (13)
Zn1—N1	2.0232 (13)	Zn1—O11	2.2473 (12)
Zn1—O3*W*	2.1409 (13)	O15—C13	1.3428 (19)
Zn1—O1*W*	2.1541 (14)		
O2*W*—Zn1—N1	172.22 (5)	O3*W*—Zn1—O13	94.75 (5)
O2*W*—Zn1—O3*W*	86.46 (5)	O1*W*—Zn1—O13	93.95 (5)
N1—Zn1—O3*W*	96.78 (5)	O2*W*—Zn1—O11	111.92 (5)
O2*W*—Zn1—O1*W*	84.25 (5)	N1—Zn1—O11	75.35 (5)
N1—Zn1—O1*W*	93.41 (5)	O3*W*—Zn1—O11	87.92 (5)
O3*W*—Zn1—O1*W*	167.90 (5)	O1*W*—Zn1—O11	88.38 (5)
O2*W*—Zn1—O13	96.27 (5)	O13—Zn1—O11	151.80 (4)
N1—Zn1—O13	76.46 (5)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O15—H15$\cdots$O11^{i}	0.83 (3)	1.82 (3)	2.6427 (16)	175 (3)
O4W—H4$W\cdots$O14^{ii}	0.95 (2)	1.91 (2)	2.747 (2)	145.9 (19)

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

C-bound H atoms, except for those of the acetonitrile molecule, were placed at calculated positions, riding on their parent atoms. One of the H atoms of O4*W* and the H atom bonded to O15 were located in difference Fourier maps and refined isotropically. The other H atoms of the water molecules were not included in the calculation. The acetonitrile molecule lies on a site of symmetry 2, and its occupancy was refined to *ca* 0.25 and finally set to 0.25. The minimum peak in final difference map is -1.05 Å^{-3} from the Zn1 atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 20001007, 20131020), the Natural Sciences Foundation of the Chinese Academy of Sciences (KJCX2-H3) and Fujian Province (2000F006).

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