

## A new polymeric phase of zinc(II) oxydiacetate

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Received 31 October 2002

Accepted 25 November 2002

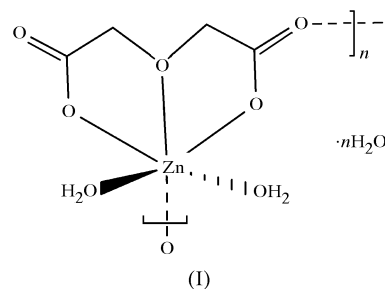
Online 24 December 2002

A new polymeric phase of zinc(II) oxydiacetate, *catenapoly*[[[diaquazinc(II)]- $\mu$ -oxydiacetato] hydrate],  $\{[\text{Zn}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$ , isomorphous with the Co homologue [Hatfield, Helms, Rohrs, Singh, Wasson & Weller (1987). *Proc. Indian Acad. Sci. Chem. Sci.* **98**, 23–31], is reported. It presents a chain-like structure, generated by  $\text{ZnO}_6$  cores which are bridged by carboxylate groups in an *anti-anti* conformation along the unique crystallographic *b* axis. The chains are held together through hydrogen-bonding interactions with the three water molecules.

### Comment

The interactions of the  $\text{Zn}^{\text{II}}$  ion with carboxylic acids are the subject of extensive research, due to the role of Zn–carboxylate bonds in the active sites of a variety of metallo-enzymes and in precursor systems for Zn-containing ceramic materials. Because of the lack of ligand field stabilization energy, the  $\text{Zn}^{\text{II}}$  cation exhibits no preferential coordination numbers and the actual coordination polyhedra are mainly determined by electrostatic forces and the steric effects of the ligands (Prince, 1987). Oxydiacetate (oda,  $^-\text{OOC}-\text{CH}_2-\text{O}-\text{CH}_2-\text{COO}^-$ ) is a versatile complexing agent, having five potential O-donor atoms in different orientations, thus allowing the construction of networks of different dimensionalities. A thorough review of related structures has been reported in a recent study, in which the density functional theory (DFT) method was applied to investigate the flexibility of this ligand (Grirrane *et al.*, 2002). The only binary zinc oxydiacetate complex known to date is the two-dimensional compound  $\{[\text{Zn}(\text{oda})\cdot 0.3\text{H}_2\text{O}]\}_n$ , hereinafter (II), which consists of sheets perpendicular to the *z* axis, composed of  $\text{ZnO}_5$  units bridged by carboxylate groups in an *anti-syn* conformation (Baggio *et al.*, 1996). For the related  $\text{Cd}^{\text{II}}$  compounds, however, three different phases of binary cadmium oxydiacetates have been identified (Boman, 1974,

1977*a,b,c*), with discrete units, chains and layers containing  $\text{CdO}_7$  cores. We report here another polymeric phase of  $\text{Zn}^{\text{II}}$  oxydiacetate, formulated as  $\{[\text{Zn}(\text{oda})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$ , (I), and compare it with (II).



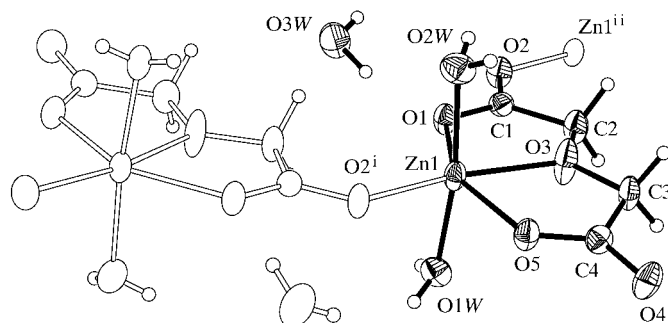
The structure of (I) is isomorphous with the homologous cobalt compound,  $\{[\text{Co}(\text{oda})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$  [Hatfield *et al.*, 1987; Cambridge Structural Database (Allen, 2002) refcode FICSUF]. Comparison of the two structures shows them to be almost identical. A least-squares fit of both coordination polyhedra (*XP* in *SHELXTL-NT*; Bruker, 2000) showed them to fit into one another, with deviations ranging from a minimum of 0.007 Å (for atom O1W) to a maximum of 0.027 Å (for atom O5), and with an overall mean of 0.017 Å.

The environment of the Zn atom in (I) consists of a distorted octahedron, with the basal plane defined by atoms O1, O3 and O5 of the tridentate oda ligand, and atom O2 from an outer carboxylate group of a neighbouring oda ligand. The latter serves as the link in the resulting one-dimensional polymer formed along the unique crystallographic *b* axis (Fig. 1). The apical sites are occupied by two water molecules, and an additional hydrate water molecule completes the unit-cell contents. The resulting polyhedron shows basal angles of  $\sim 74$  and  $166^\circ$ , instead of the regular values of  $90$  and  $180^\circ$ , respectively, and the apical Zn–O semi-axes subtend angles of  $\sim 5^\circ$  to the vertical. This is a likely result of the hydrogen-bonding interactions linking atom O1W to atoms O4 and O5, and atom O2W to atoms O4 and O3W (Table 2 and Fig. 2).

We note that the large Zn– $\text{O}_{\text{ether}}$  bonds in structures (I) and (II) are identical, at 2.114 (1) and 2.115 (1) Å, respectively. However, the mean length of the Zn– $\text{O}_{\text{carboxy}}$  bond is slightly larger in (I), at 2.095 (1) Å, versus 2.057 (1) Å in (II), due to the higher coordination number in the former. This corresponds to a smaller out-of-plane deformation of the ligand, the dihedral angle formed by the lateral planar wings (Zn–O3–C2–C1–O1 and Zn–O3–C3–C4–O5) around the Zn–O3 bond being  $6.5(1)^\circ$  in (I) and  $10.1(1)^\circ$  in (II).

The major difference between the two polymeric forms of zinc oxydiacetate is in their crystal packing. In form (I), adjacent  $\text{ZnO}_6$  coordination polyhedra bridged by carboxylate groups in an *anti-anti* conformation define linear arrays along **b**, with  $\text{Zn}\cdots\text{Zn}$  nearest-neighbour distances of 5.009 (1) Å within the chains [5.041 (1) Å in the homologous Co compound]. In compound (II), the adjacent  $\text{ZnO}_5$  polyhedra are bridged by the carboxylate groups in an *anti-syn* conformation along two mutually orthogonal directions, leading to a two-dimensional structure with closer  $\text{Zn}\cdots\text{Zn}$  contacts within the planes [4.867 (1) Å].

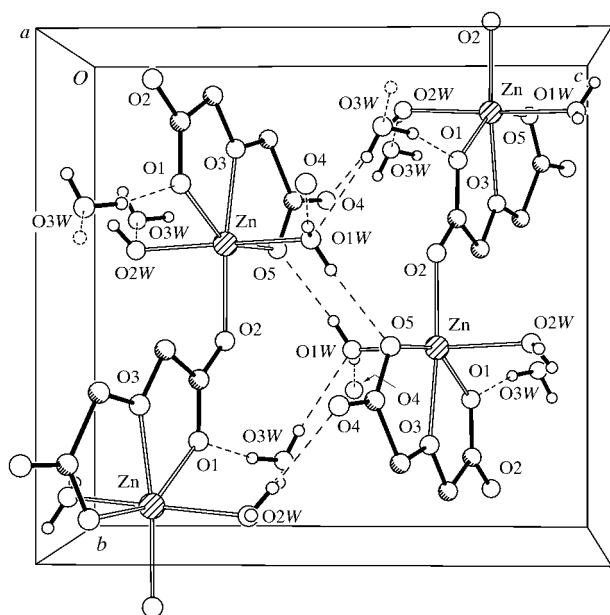
In spite of the differences in the Zn···Zn nearest-neighbour distances in the polymeric arrays, the overall densities in both structures are almost identical [2.034 (1) and 2.032 (1) Mg m<sup>-3</sup> for (I) and (II), respectively], suggesting that the 'less dense'



**Figure 1**

A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as small spheres of arbitrary radii and chain formation is indicated [symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ].

chains in (I) pack more closely than the 'more condensed' planes in (II). The reason for this is to be found in the marked differences of the hydrogen-bonding interactions. In structure (II), hydrogen-bond contacts are few and weak; one of them mediated by a disordered hydrate water molecule and another is of the C—H···O type. In form (I), by contrast, the hydrogen-bond contacts involve all six water H atoms, and the contacts tightly connect the chains to each other.



**Figure 2**

A schematic packing view of (I) along **a**, showing the way in which the chains (running along **b**) interact to form a three-dimensional network. Hydrogen bonds are shown as broken lines. H atoms attached to C atoms have been omitted for clarity.

## Experimental

Analytical grade zinc acetate dihydrate (Fluka) and oxydiacetic acid (Fluka) were used without further purification. Zinc acetate dihydrate (0.20 g, 1 mmol) was dissolved in an aqueous solution (25 ml) of oxydiacetic acid (0.20 g, 1.5 mmol) and stirred at room temperature for 4 h. After four weeks, colourless crystals of (I) suitable for X-ray diffraction were filtered and dried in air. Recrystallization was from water–ethanol (1:1). Analysis calculated for C<sub>4</sub>H<sub>10</sub>O<sub>8</sub>Zn: C 19.10, H 4.00, Zn 26%; found: C 19.00, H 4.05, Zn 25.5%.

### Crystal data

[Zn(C<sub>4</sub>H<sub>4</sub>O<sub>5</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O  
*M<sub>r</sub>* = 251.49  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 7.132 (1) Å  
*b* = 10.375 (1) Å  
*c* = 11.100 (1) Å  
 $\beta$  = 91.35 (1)°  
*V* = 821.1 (1) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.034 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 97 reflections  
 $\theta$  = 7.2–19.3°  
 $\mu$  = 3.01 mm<sup>-1</sup>  
*T* = 296 (2) K  
 Needle, colourless  
 0.32 × 0.14 × 0.10 mm

### Data collection

Bruker SMART APEX CCD  
 area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: refined  
 on  $\Delta F$  (SADABS in  
 SAINT-NT; Bruker, 2000)  
*T<sub>min</sub>* = 0.53, *T<sub>max</sub>* = 0.74  
 6664 measured reflections

1826 independent reflections  
 1654 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.020  
 $\theta_{\max}$  = 27.5°  
*h* = -9 → 8  
*k* = -13 → 13  
*l* = -14 → 14

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.025  
*wR* (*F*<sup>2</sup>) = 0.064  
*S* = 1.09  
 1826 reflections  
 142 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.1545P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.48 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

**Table 1**

Selected interatomic distances (Å).

Zn1—O2 <sup>i</sup>	2.0143 (14)	O1—C1	1.258 (2)
Zn1—O2W	2.0775 (18)	O2—C1	1.254 (2)
Zn1—O5	2.0848 (14)	O3—C2	1.396 (2)
Zn1—O1	2.1058 (13)	O3—C3	1.412 (2)
Zn1—O3	2.1143 (15)	O4—C4	1.238 (2)
Zn1—O1W	2.1272 (17)	O5—C4	1.270 (2)

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

**Table 2**

Hydrogen-bonding 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>
O3W—H3WB···O1W <sup>i</sup>	0.71 (3)	2.20 (3)	2.877 (3)	162 (3)
O3W—H3WA···O1	0.92 (5)	1.91 (5)	2.817 (2)	167 (4)
O2W—H2WB···O4 <sup>i</sup>	0.73 (3)	2.09 (3)	2.818 (2)	176 (3)
O2W—H2WA···O3W <sup>ii</sup>	0.82 (3)	1.89 (3)	2.690 (3)	167 (2)
O1W—H1WB···O5 <sup>iii</sup>	0.74 (3)	1.98 (3)	2.713 (2)	173 (3)
O1W—H1WA···O4 <sup>iv</sup>	0.77 (3)	1.97 (3)	2.732 (2)	173 (3)

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

H atoms attached to C atoms were added at their expected positions (C–H = 0.97 Å) and not refined, but these atoms were allowed to ride. H atoms pertaining to the water molecules were found in the final difference Fourier map and refined with isotropic displacement parameters.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINTE-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2000); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

We acknowledge Fundación Andes (grant No. C13575) and CONICYT-FONDAP (grant No. 11980002) for the purchase of the CCD detector, and the Spanish Research Council (CSIC) for providing us with a free-of-charge licence to the Cambridge Structural Database (Allen, 2002). MP is a member of CONICET.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1002). Services for accessing these data are described at the back of the journal.

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