

Hydrothermal synthesis and extended structure of poly[aqua(μ_5 -ethylenediaminetetraacetato)dizinc(II)]

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In the extended structure of the title compound, $[\text{Zn}_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)(\text{H}_2\text{O})]$, prepared under hydrothermal conditions, there are two distinct Zn^{II} sites. The first, with octahedral geometry, bonds to two N and three O atoms from one ethylenediaminetetraacetate tetraanion (EDTA) and one water molecule. The second, with tetrahedral geometry, coordinates to O atoms from four different EDTA ligands. The EDTA ligand almost encapsulates the octahedral Zn^{II} ion and binds to four symmetry-related tetrahedral Zn^{II} ions, hence generating the extended structure. One noncoordinated O-atom site on the EDTA ligand connects to the water molecule by hydrogen bonding. Structural comparisons are made with other compounds containing zinc, EDTA and water.

Comment

For the hydrothermal synthesis of sparingly soluble materials, it is essential to utilize a mineralizer or coordinating agent to aid in maintaining optimum concentrations of metal ions for more controlled crystal growth (Rabenau, 1985). In this study, the ethylenediaminetetraacetate tetraanion (EDTA) has been successfully used in our efforts to improve the synthetic reproducibility and increase the size of ZnO crystals grown under subcritical hydrothermal conditions of approximately 473 K and 15 atm (1 atm = 101325 Pa) (DiLeo *et al.*, 2004). Crystals of $[\text{Zn}_2(\text{EDTA})(\text{H}_2\text{O})]_n$ (I), were grown under acidic conditions, unusual in this research and corresponding to a thermodynamic phase space where ZnO is less likely to precipitate. Thus, the water-insoluble title compound was discovered.

The asymmetric unit of (I), along with the coordination around the distorted Zn^{II} tetrahedron, is shown in Fig. 1, and selected bond distances and angles are included in Table 1. There are two distinct Zn^{II} sites in this structure. Atom Zn1 is connected to one EDTA tetraanion and the water molecule in

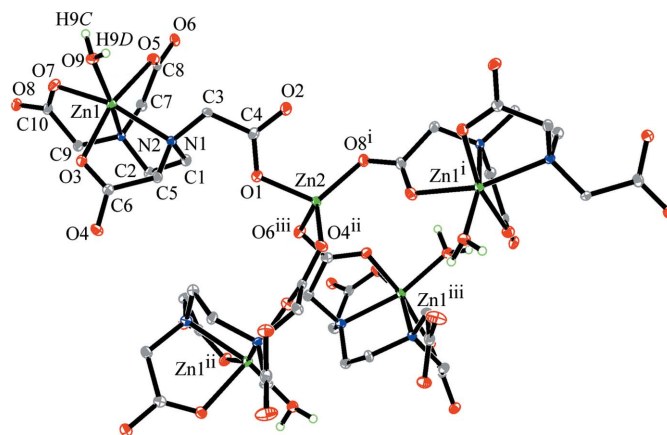


Figure 1

The asymmetric unit and connectivity for (I), highlighting the Zn-centered tetrahedron and four associated Zn–EDTA species. Only H atoms of the water molecule are shown. Displacement ellipsoids are drawn at the 50% probability level. The symmetry codes are as in Table 1.

a distorted octahedral environment. Atom N2, and the two acetate groups bonded to it *via* atoms O5 and O7, bonds to Zn1. The other N atom, N1, and one of its acetate groups coordinate to atom Zn1 *via* atom O3. The sixth bond to atom Zn1 involves atom O9 of the water molecule. The Zn–O bond distances at the octahedral atom Zn1 are in the range 1.9989 (16)–2.1322 (17) Å, and the lower value corresponds to water coordination. Four of the remaining five EDTA O atoms (O1, O4ⁱⁱ, O6ⁱⁱⁱ and O8ⁱ; see Table 1 for symmetry codes), from four different EDTA ligands, bond in a distorted tetrahedral coordination to atom Zn2. The Zn–O bond distances at tetrahedral atom Zn2 are in the range 1.9476 (16)–1.9947 (15) Å. At octahedral atom Zn1, the *trans* and *cis* angles are in the ranges 160.85 (6)–165.78 (6) and 77.50 (7)–110.60 (7)°, respectively, while at tetrahedral atom Zn2, the range is 95.82 (7)–120.87 (7)°.

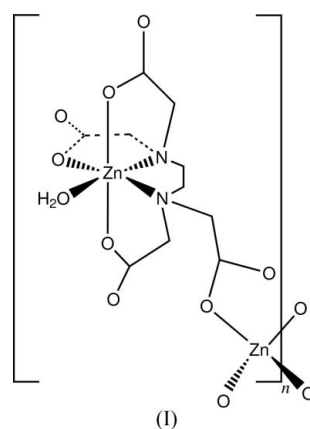
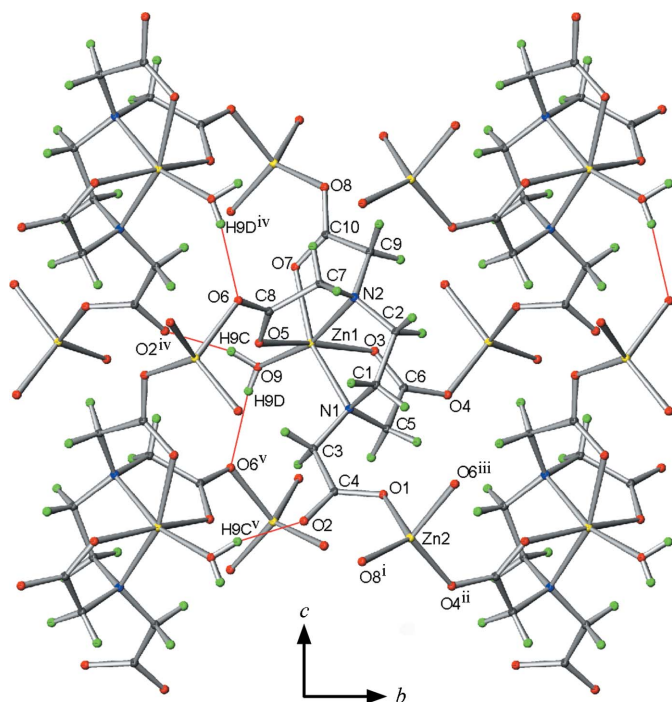


Fig. 2 illustrates the hydrogen bonding. Atom O2 is the only EDTA O atom that is not coordinated to Zn^{II} and it is within hydrogen-bonding distance of water atom H9C. Atom O6, which bonds to Zn2, is within hydrogen-bonding distance of H9D, the second water H atom. Upon inspection of the

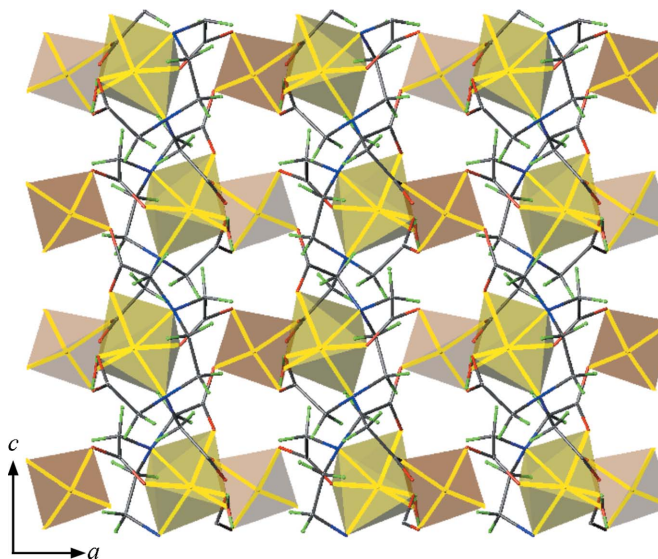

Figure 2

The partial structure of (I), viewed along [100], with hydrogen bonds shown as thin lines. The Zn-centered octahedron is in the center and connections to other polyhedra are illustrated *via* EDTA and hydrogen bonding. Atoms H9C and H9D of the water molecule are closest to atoms O2 and O6, respectively. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z - 1$; (ii) $-x + 1, -y + 2, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + 1, -y + 1, z - \frac{1}{2}$; (v) $-x + 1, -y + 1, z - \frac{1}{2}$.]

displacement parameters, it is clear that U_{11} for O2 is roughly twice that of other atoms in the structure. Because it is the only uncoordinated EDTA O atom, it is reasonable to expect that it would have a higher displacement.

The polyhedral arrangement along b is illustrated in Fig. 3. Both polyhedra form zigzag chains along b and c , and the tetrahedra form AB -like layers along b and c . Within the structure, there are open channels of 2–3 Å along b , approximated using *ATOMS* (Dowty, 2006).

Two other related compounds are $[\text{Zn}_3(\text{HEDTA})_2(\text{H}_2\text{O})_6]$ (Sadikov *et al.*, 2004) and $[\text{Zn}_2(\text{EDTA})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (Pozhidaev *et al.*, 1973; Escrivá *et al.*, 1984). Both contain only octahedrally coordinated zinc. In $[\text{Zn}_3(\text{HEDTA})_2(\text{H}_2\text{O})_6]$, two of the zinc sites coordinate to five O-atom sites on single HEDTA ions and one H_2O molecule. The remaining O-atom site on each of these HEDTA ions coordinates to the third Zn atom, sandwiched in between the other two Zn atoms and coordinating additionally to four H_2O molecules. For $[\text{Zn}_2(\text{EDTA})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, one Zn atom is coordinated entirely by a single EDTA ligand, and the other Zn atom by two H_2O molecules and two O atoms from two distinct EDTA ions; two solvent water molecules connect to the structure by hydrogen bonding. Similarly to the title compound, both of these related structures are extended such that some of the EDTA carboxylate groups serve to bridge Zn^{II} ions throughout the structure.


Figure 3

The unit-cell and polyhedral arrangements in (I), viewed along [010], illustrating the zigzag chains of octahedra and tetrahedra, and the open channels between tetrahedra.

With fewer water molecules per Zn atom ($\text{H}_2\text{O}:\text{Zn}$ ratio of 1:2, compared with 1:1 and 2:1 for the related structures), the title compound represents a denser version of other extended compounds containing zinc, EDTA and water. The previously reported trinuclear and dinuclear compounds have densities of 1.90 and 1.91 Mg m^{-3} , respectively, whereas $[\text{Zn}_2(\text{EDTA})(\text{H}_2\text{O})]$ has a calculated density of 2.15 Mg m^{-3} .

Experimental

Several samples were prepared to ensure reproducibility. Zinc chloride, ZnCl_2 (approximately 0.116 g; Aldrich, 98+%), was dissolved in distilled water (10.0 g). To this mixture, disodium dihydrogen ethylenediaminetetraacetate dihydrate, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (0.27 g; Aldrich, 99+%), was added with stirring. Finally, 1.000 M potassium hydroxide, KOH (1.2 g; Riedel-deHaën Fixanal solution), was added and the entire mixture was allowed to dissolve while stirring. After measuring a pH of 3.0–3.4, the colorless solution was placed in a Parr acid-digestion vessel, with a Teflon liner capacity of 25 ml. The autoclave was closed and placed in a 473 K mechanical convection oven for 7 d. The syntheses produced between one and several crystals, ranging in size from approximately 1 to 5 mm along the longest edge. The density of the crystals was measured at ambient temperature using the technique of neutral buoyancy. The sample was placed in a known mass of bromoform (Aldrich, 99+%) and to that chloroform (Aldrich, 99.8%) was added until the crystals were suspended in the liquid mixture. The density of the bromoform–chloroform mixture was found to be 2.07 (3) Mg m^{-3} , reasonably close to the calculated value from the X-ray structure but differing from that value by an amount that equates to approximately one water molecule. The bulk of the crystals were cloudy except near the edges, which may indicate that water disassociates from the crystal center, producing a lower bulk density compared with the transparent edges. The sample of (I) used for X-ray diffraction was taken from the transparent portion of one of the larger crystals.

Table 1
Selected geometric parameters (Å, °).

Zn1—O9	1.9989 (16)	Zn1—N1	2.209 (2)
Zn1—O3	2.0967 (15)	Zn2—O8 ⁱ	1.9476 (16)
Zn1—O5	2.1098 (15)	Zn2—O4 ⁱⁱ	1.9563 (16)
Zn1—O7	2.1322 (17)	Zn2—O1	1.9660 (16)
Zn1—N2	2.177 (2)	Zn2—O6 ⁱⁱⁱ	1.9947 (15)
O9—Zn1—O3	97.88 (6)	O3—Zn1—N1	79.52 (6)
O9—Zn1—O5	92.64 (6)	O5—Zn1—N1	87.85 (7)
O3—Zn1—O5	165.78 (6)	O7—Zn1—N1	160.85 (6)
O9—Zn1—O7	88.00 (6)	N2—Zn1—N1	84.72 (7)
O3—Zn1—O7	93.83 (6)	O8 ⁱ —Zn2—O4 ⁱⁱ	120.87 (7)
O5—Zn1—O7	96.09 (7)	O8 ⁱ —Zn2—O1	116.76 (6)
O9—Zn1—N2	163.10 (7)	O4 ⁱⁱ —Zn2—O1	101.01 (7)
O3—Zn1—N2	91.77 (7)	O8 ⁱ —Zn2—O6 ⁱⁱⁱ	109.23 (7)
O5—Zn1—N2	80.49 (7)	O4 ⁱⁱ —Zn2—O6 ⁱⁱⁱ	110.19 (7)
O7—Zn1—N2	77.50 (7)	O1—Zn2—O6 ⁱⁱⁱ	95.82 (7)
O9—Zn1—N1	110.60 (7)		

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

Crystal data

$[\text{Zn}_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)(\text{H}_2\text{O})]$	$V = 1350.50 (15) \text{ \AA}^3$
$M_r = 436.97$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 12.7099 (8) \text{ \AA}$	$\mu = 3.61 \text{ mm}^{-1}$
$b = 11.2854 (7) \text{ \AA}$	$T = 100 \text{ K}$
$c = 9.4153 (6) \text{ \AA}$	$0.13 \times 0.10 \times 0.03 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	17189 measured reflections
Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2003)	4275 independent reflections
$T_{\min} = 0.336, T_{\max} = 0.434$	4049 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.83 \text{ e \AA}^{-3}$
4275 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
215 parameters	Absolute structure: Flack (1983), with 1897 Friedel pairs
4 restraints	Flack parameter: 0.498 (9)

Reflection data for two twin components related by an arbitrary twofold crystal intergrowth axis were processed in the standard two-component way by use of *SAINTE-Plus* and *TWINABS* (Bruker, 2003), but the lesser component was eventually omitted because its intensities were more than one order of magnitude less than those of the main component. The refinement of the Flack parameter (Flack & Bernardinelli, 1999) to 0.498 (9) indicated inversion twinning in

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9C \cdots O2 ^{iv}	0.84 (1)	1.80 (1)	2.619 (2)	163 (2)
O9—H9D \cdots O6 ^v	0.84 (1)	1.92 (1)	2.750 (2)	172 (3)

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

addition to the twinning mentioned above. In the space-group assignment, centrosymmetric *Pnam* and noncentrosymmetric *Pna2₁* were investigated, but *Pnam* did not result in an ordered structure. This result is consistent with the estimated $|E^2 - 1| = 0.766$ within *XPREP* (*SHELXTL*; Sheldrick, 2008), which suggested a noncentrosymmetric space group. The two H atoms (H9C and H9D) bonded to atom O9 were then identified in a difference Fourier map. Bond distances O9—H9C and O9—H9D were restrained to 0.84 (1) Å, and the H9C \cdots H9D separation restrained to 1.38 (1) Å. The CH₂ H atoms were constrained to idealized geometry, with C—H = 0.99 Å. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINTE-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3034). Services for accessing these data are described at the back of the journal.

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