Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

A novel O–Zn bridging polymer complex of 2,6-bis[bis(carboxylatomethyl)aminomethyl]-4-methylphenolate

Yuan-Yuan Zhang,[a] Fang-Jun Huo[b] and Fei Gao[a]*

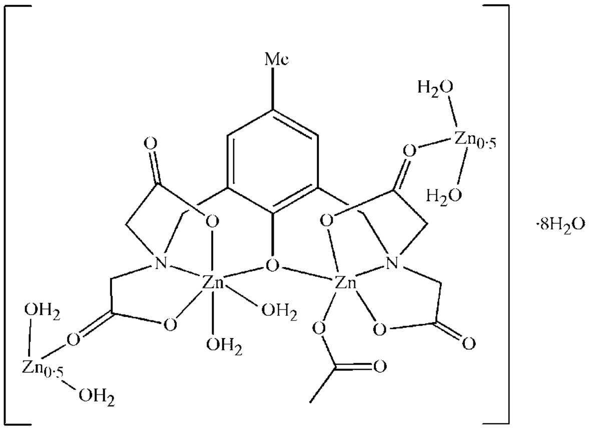
[a]Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China, and [b]Research Institute of Applied Chemistry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China
Correspondence e-mail: feigao@sxu.edu.cn

Received 22 July 2007
Accepted 26 September 2007
Online 14 December 2007

A new one-dimensional coordination polymer, *catena*-poly[[acetatohexaaqua{μ_4-2,6-bis[bis(carboxylatomethyl)aminomethyl]-4-methylphenolato}trizinc(II)] octahydrate], $[Zn_3(C_{17}H_{17}N_2O_9)(C_2H_3O_2)(H_2O)_6]\cdot 8H_2O$, is a trinuclear complex consisting of three zinc centers joined by a phenolate bridge and $Zn(H_2O)_4$ units. In each complex polymer unit, the three Zn atoms have different coordination modes. Of the two phenolate-bridged Zn ions, one adopts a distorted octahedral coordination composed of two carboxylate ligands, one tertiary N atom, two water molecules and the bridging phenolate ligand, while the other adopts a pyramidal geometry composed of two carboxylate ligands, one tertiary N atom from another coordination arm, one acetate anion as the counter-anion and the bridging phenolate ligand. The third type of Zn centre is represented by two independent Zn atoms lying on inversion centres. They both have an octahedral coordination consisting of four O atoms from four water molecules and two acetate carbonyl O atoms from the ligand. The latter Zn atoms join the above-mentioned binuclear complex units through O atoms of the carboxylate groups into an infinite chain. Neighboring aromatic rings are distributed above and below the chain in an alternating manner. Between the coordination chains, the Zn$\cdots$Zn separations are 5.750 (4) and 6.806 (4) Å. The whole structure is stabilized by hydrogen bonds formed mainly by solvent water molecules.

Comment

Zinc enzymes often use coordinated water molecules or internal alcoholic hydroxy residues as nucleophiles to react with electrophilic substrates (Kim & Wyckoff, 1991). The role of zinc centers in these enzymes is to orientate and activate the substrates (Hegg & Burstyn, 1998; Krämer, 1999; Lipscomb & Sträer, 1996). The preparation and development of new metallic model compounds to mimic the activity of nucleases in hydrolytic cleavage of DNA is an important and prosperous field in bioinorganic chemistry. Previously, we reported a few binuclear metal complexes, including Ni_2 (Meng *et al.*, 2004) and Mg_2 (Gao, Meng & Wei, 2004) complexes of Cl-HXTA (5-chloro-2-hydroxy-1,3-xylene-α,α-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid), which are able to scissor DNA hydrolytically. Cl-HXTA is an acyclic dinucleating ligand with a phenolate bridge (Murch *et al.*, 1987). As a pentavalent anionic ligand, it has four methoxycarbonyl chelating arms with two sets of donor atoms, *i.e.* one N and three O atoms, as the coordination sites. One of the advantages of Cl-HXTA is that most of its dinuclear metal complexes are highly soluble in water.



(I)

As a continuation of the aforementioned study, we report here a newly synthesized binuclear zinc complex with CH_3-HXTA (5-methyl-2-hydroxy-1,3-xylene-α,α-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid), (I). CH_3-HXTA is very similar to Cl-HXTA in structure, with the Cl atom in the latter replaced by a methyl group in the former.

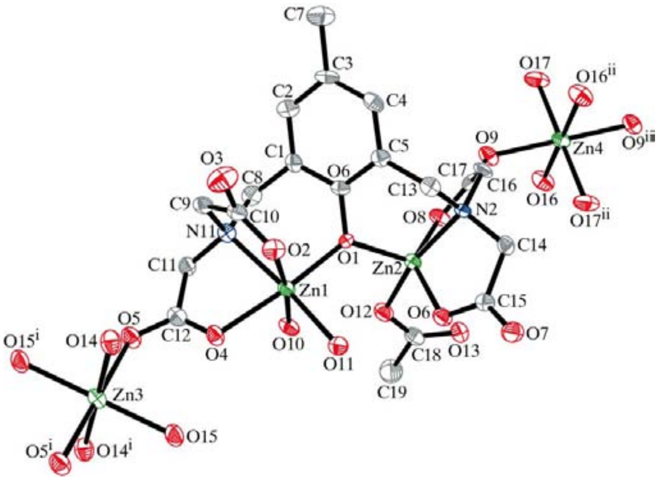


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level. All H atoms and solvent water molecules have been omitted for clarity. [Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y+1, -z+2$.]

DOI: 10.1107/S0108270107047282

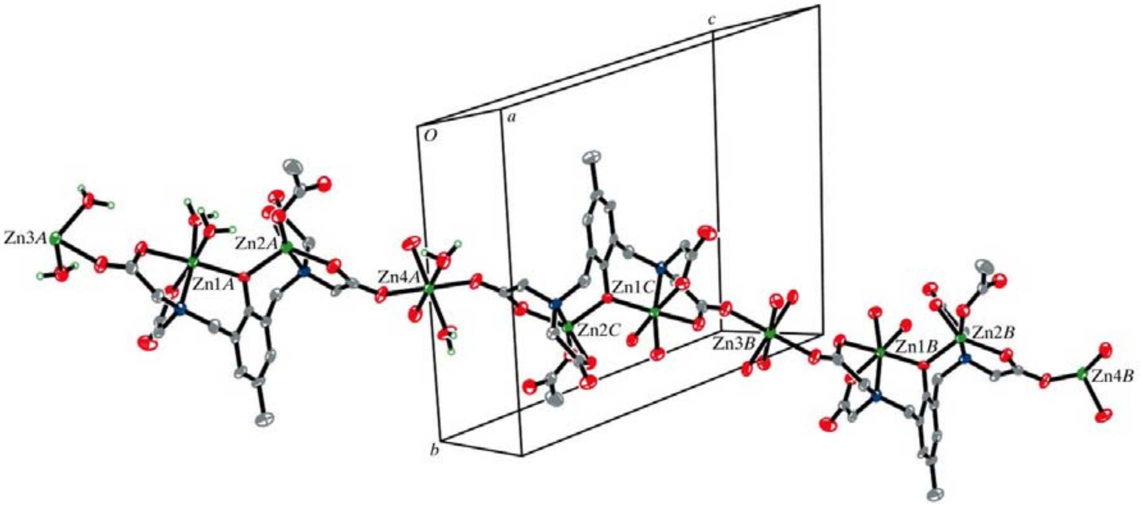


Figure 2
Part of the coordination polymer chains, viewed along a favorable direction close to the *c* axis. Selected atoms are labeled (suffixes *A*, *B* and *C* indicate different molecular units in the polymer chain). Free water molecules and all H atoms that are not involved in hydrogen bonds have been omitted for clarity.

Selected geometric parameters of the title compound are listed in Table 1, while the molecular configuration and crystal packing are illustrated in Figs. 1 and 2, respectively. Fig. 1 shows that the coordination environments of the two oxo-bridged Zn ions are different in geometry and donor atoms, and differ from those in a related Zn complex (Gao, Meng & Zhu, 2004), where the two Zn atoms have similar coordination environments with distorted octahedral geometry. More specifically, atom Zn1 adopts a distorted octahedral coordination composed of two carboxylate groups, one tertiary N atom, two water molecules and the bridging phenolate ligand (atom O1), while atom Zn2 adopts a five-coordinate pyramidal geometry composed of two carboxylate groups, one tertiary N atom from another coordination arm, one acetate anion as the counter-anion and the bridging phenolate ligand (O1). The Zn1···Zn2 separation of 3.630 (4) Å, which is shorter than the value of 3.745 (3) Å reported by Gao, Meng & Zhu (2004), suggests no obvious metal–metal bond formation. The Zn1—O1 distance is 2.036 (4) Å, while the Zn2—O1 distance is 1.990 (4) Å, indicating that the bridging O atom is similar but not equivalent for both Zn1 and Zn2. The Zn1—O1—Zn2 angle is 128.74 (19)°, which is less than that found by Gao, Meng & Zhu (2004) [131.7 (3)°]. In spite of this slight difference, the only oxo bridge is similar to those in the structures reported previously [Zn—O—Zn (Gao, Meng & Zhu, 2004), Ni—O—Ni (Meng *et al.*, 2004) and Mg—O—Mg (Gao, Meng & Wei, 2004)]. The average Zn—O bond length in the phenolate bridge is 2.014 Å, in accordance with that of the metal–phenolate bonds in other reported dinulear complexes, such as [$Fe_2(sal)_3(trien)(OMe)]Cl_2$ (Chiari *et al.*, 1982) and [$Fe_2(sal)_3(trien)(OH)]Cl_2$ (sal and trien are salicylic aldehyde and triethylenetetramine, respectively; Chiari *et al.*, 1983). The complex anion as a whole has a pseudo-C_2 axis passing through atoms C7, C3, C6 and O1, as has been reported previously (Sakiyama *et al.*, 1999). The least-squares plane of the benzene ring of CH_3-HXTA and the Zn1/O1/Zn2 plane are twisted with a dihedral angle of 52.75 (4)°. Zn3 and Zn4 atoms lie on inversion centres and join binuclear complex units containing Zn1 and Zn2 through carboxylate O atoms of the CH_3-HXTA ligand into an infinite chain (Fig. 2). Zn3 and Zn4 have equal octahedral environments consisting of four O atoms from four water molecules and two acetate carbonyl O atoms from the CH_3-HXTA ligand. Thus, an infinite one-dimensional coordination polymer is constructed (Fig. 2). In this chain, the Zn1···Zn3 separation is 5.345 (4) Å and the Zn2···Zn4 separation is 5.775 (4) Å. Along the chain, neighboring aromatic rings are distributed alternately above and below the chain. This chain extends infinitely with a repeat unit (*e.g.* Zn3*A*···Zn3*B*) of 29.0 (4) Å (Fig. 2). Between the coordination chains, the shortest Zn···Zn separations are 5.750 (4) and 6.806 (4) Å. The whole structure is stabilized by a hydrogen-bond net, which is formed mainly by solvent water molecules, as shown in Fig. 2. Their geometric parameters are also listed in Table 2.

In summary, we have described a novel coordination polymer structure constructed by Zn—O—Zn bridges and $Zn(H_2O)_4$ units. The bioactivity of this compound, for example as a DNA cleavage agent, is under investigation in our laboratory.

Experimental

All chemicals were of reagent grade, were obtained commercially from the Beijing Chemical Reagents Company of China and were used without further purification. The CH_3-HXTA ligand was synthesized according to a published procedure (Branum *et al.*, 2001). $Zn(CH_3COO)_2·2H_2O$ (0.4390 g, 2 mmol) and $Na_4(CH_3$-HXTA) (0.486 g, 1 mmol) were dissolved in water (5 ml) and mixed with stirring at 323 K for 3 h. The resulting colorless solution was filtered and the filtrate was left to stand at room temperature. Colorless crystals of (I) appeared after half a month as a result of slow evaporation of the aqueous solvent.

Crystal data

$[Zn_3(C_{17}H_{17}N_2O_9)(C_2H_3O_2)(H_2O)_6]\cdot 8H_2O$
$M_r = 900.70$
Triclinic, $P\overline{1}$
$a = 10.0095\ (18)$ Å
$b = 13.293\ (2)$ Å
$c = 14.052\ (3)$ Å
$\alpha = 93.573\ (3)^\circ$
$\beta = 99.225\ (3)^\circ$
$\gamma = 110.134\ (2)^\circ$
$V = 1718.7\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.17$ mm^{-1}
$T = 213\ (2)$ K
$0.40 \times 0.30 \times 0.30$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.477$, $T_{max} = 0.562$ (expected range = 0.442–0.521)
8459 measured reflections
5932 independent reflections
4769 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.131$
$S = 1.18$
5932 reflections
446 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.88$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.036 (4)	Zn2—O6	2.094 (4)
Zn1—O11	2.078 (4)	Zn2—N2	2.143 (5)
Zn1—O2	2.106 (4)	Zn3—O15^{i}	2.061 (4)
Zn1—O4	2.113 (4)	Zn3—O15	2.061 (4)
Zn1—O10	2.126 (4)	Zn3—O5	2.091 (4)
Zn1—N1	2.134 (5)	Zn3—O14	2.164 (4)
Zn2—O12	1.984 (4)	Zn4—O17	2.057 (4)
Zn2—O1	1.990 (4)	Zn4—O9	2.088 (4)
Zn2—O8	2.036 (4)	Zn4—O16	2.092 (4)

O1—Zn1—O11	94.90 (16)	O12—Zn2—O8	94.54 (17)
O1—Zn1—O2	97.25 (16)	O1—Zn2—O8	119.23 (17)
O11—Zn1—O2	89.60 (16)	O12—Zn2—O6	95.87 (16)
O1—Zn1—O4	167.44 (16)	O1—Zn2—O6	99.32 (17)
O11—Zn1—O4	94.77 (16)	O8—Zn2—O6	138.07 (18)
O2—Zn1—O4	90.82 (17)	O12—Zn2—N2	167.19 (19)
O1—Zn1—O10	88.64 (16)	O1—Zn2—N2	94.66 (18)
O11—Zn1—O10	92.99 (16)	O8—Zn2—N2	81.15 (17)
O2—Zn1—O10	173.35 (17)	O6—Zn2—N2	79.83 (17)
O4—Zn1—O10	82.86 (16)	O15—Zn3—O5	91.93 (16)
O1—Zn1—N1	92.85 (17)	O15—Zn3—O14	91.63 (16)
O11—Zn1—N1	168.87 (18)	O5—Zn3—O14	88.70 (16)
O2—Zn1—N1	81.49 (17)	O17—Zn4—O9	90.33 (17)
O4—Zn1—N1	78.80 (17)	O17—Zn4—O16	89.86 (17)
O10—Zn1—N1	95.18 (17)	O9—Zn4—O16	84.85 (17)
O12—Zn2—O1	97.96 (17)		

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

H atoms attached to C atoms were placed in geometrically idealized positions [Csp^3—H = 0.97 Å (methyl), Csp^3—H = 0.98 Å (methylene) and Csp^2—H = 0.94 Å] and constrained to ride on their parent atoms [U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C)]. H atoms attached to O atoms (in water molecules) were located in difference Fourier maps and constrained to ride on their parent atoms [U_{iso}(H) = $1.5U_{eq}$(O)].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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

D—H···A	D—H	H···A	D···A	D—H···A
O10—H10A···O7^{ii}	0.85	1.92	2.741 (5)	163
O10—H10B···O12	0.85	1.87	2.691 (6)	162
O11—H11C···O6	0.85	2.08	2.867 (6)	154
O11—H11D···O6^{ii}	0.85	1.95	2.793 (5)	168
O14—H14C···O20	0.85	1.91	2.752 (6)	173
O14—H14D···O24^{iii}	0.85	1.89	2.728 (6)	171
O15—H15A···O4	0.85	2.02	2.678 (5)	133
O15—H15B···O23^{ii}	0.85	1.94	2.737 (6)	155
O16—H16C···O22^{iv}	0.85	1.82	2.667 (7)	175
O16—H16D···O25^{v}	0.85	2.14	2.964 (6)	164
O17—H17A···O23^{vi}	0.85	1.91	2.734 (6)	165
O17—H17B···O21^{iv}	0.85	1.86	2.707 (6)	174
O18—H18A···O24^{ii}	0.85	2.07	2.893 (7)	162
O19—H19D···O3	0.85	1.85	2.687 (7)	166
O19—H19E···O21^{vii}	0.85	2.42	3.182 (6)	150
O20—H20A···O13^{ii}	0.85	1.87	2.710 (6)	172
O20—H20B···O2	0.85	2.04	2.887 (6)	177
O21—H21A···O14^{vii}	0.85	2.08	2.910 (6)	165
O21—H21B···O19	0.85	2.04	2.786 (6)	146
O22—H22A···O3	0.85	1.96	2.772 (6)	160
O23—H23A···O18^{viii}	0.85	1.93	2.772 (7)	169
O23—H23B···O13	0.85	2.09	2.818 (7)	144
O24—H24A···O25	0.85	1.94	2.790 (6)	172
O24—H24B···O7	0.85	1.96	2.803 (6)	173
O25—H25A···O8^{ix}	0.85	1.99	2.835 (6)	173
O25—H25B···O19^{x}	0.85	1.99	2.789 (6)	157

Symmetry codes: (ii) $-x+1, -y, -z+1$; (iii) $x, y, z-1$; (iv) $x+1, y, z+1$; (v) $x+1, y, z+1$; (vi) $-x+2, -y+1, -z+2$; (vii) $-x+1, -y+1, -z$; (viii) $x, y, z+1$; (ix) $x-1, y, z$; (x) $-x+1, -y+1, -z+1$.

The authors thank the Provincial Natural Science Foundation of Shanxi for financial support (grant No. 2006011018 for FG).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3103). Services for accessing these data are described at the back of the journal.

References

Branum, M. E., Tipton, A. K., Zhu, S. & Que, L. Jr (2001). *J. Am. Chem. Soc.* **123**, 1898–1904.
Bruker (2000). *SMART* (Version 5.0) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Chiari, B., Piovesana, O., Tarantelli, T. & Zanazzi, P. F. (1982). *Inorg. Chem.* **21**, 2444–2448.
Chiari, B., Piovesana, O., Tarantelli, T. & Zanazzi, P. F. (1983). *Inorg. Chem.* **22**, 2781–2784.
Gao, F., Meng, B.-H. & Wei, Y.-B. (2004). *Acta Cryst.* C**60**, m360–m362.
Gao, F., Meng, B.-H. & Zhu, M.-L. (2004). *Acta Cryst.* E**60**, m1225–m1227.
Hegg, E. L. & Burstyn, J. N. (1998). *Coord. Chem. Rev.* **173**, 133–165.
Kim, E. E. & Wyckoff, H. W. (1991). *J. Mol. Biol.* **218**, 449–464.
Krämer, R. (1999). *Coord. Chem. Rev.* **182**, 243–261.
Lipscomb, W. N. & Sträer, N. (1996). *Chem. Rev.* **96**, 2375–2433.
Meng, B.-H., Gao, F. & Zhu, M.-L. (2004). *Acta Cryst.* C**60**, m308–m310.
Murch, B. P., Bradley, F. C., Boyle, P. D., Papaefthymiou, V. & Que, L. Jr (1987). *J. Am. Chem. Soc.* **109**, 7993–8003.
Sakiyama, H., Mochizuki, R., Sugawara, A., Sakamoto, M., Nishida, Y. & Yamasaki, M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 997–1000.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.