

An Na–O–Zn–O–Zn bridging complex of Cl-HXTA, where Cl-HXTA is 2,6-bis[[bis(carboxylatomethyl)-amino]methyl]-4-chlorophenolate

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.014$ Å

R factor = 0.097

wR factor = 0.199

Data-to-parameter ratio = 13.2

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

In the structure of heptaaqua- $1\kappa^3\text{O}, 2\kappa^2\text{O}, 3\kappa^2\text{O}-(\mu_3-2,6\text{-bis}\{\{\text{bis}(\text{carboxylatomethyl})\text{amino}\}\text{methyl}\}-4\text{-chlorophenolato-}1\kappa\text{O}; 2\kappa^4\text{O}, \text{O}', \text{N}, \text{O}^1; 3\kappa^4\text{O}^1, \text{N}', \text{O}'', \text{O}''')\text{dizinc(II)sodium(I)pentahydrate}$, $[\text{NaZn}_2(\text{C}_{16}\text{H}_{14}\text{ClN}_2\text{O}_9)(\text{H}_2\text{O})_7]\cdot 5\text{H}_2\text{O}$ or $[\text{Zn}_2(\text{Cl-HXTA})(\text{H}_2\text{O})_4\{\text{Na}(\text{H}_2\text{O})_3\}]\cdot 5\text{H}_2\text{O}$, the trinuclear complex unit consists of two distorted ZnNO_5 octahedra bridged by a phenolate O atom and an NaO_4 tetrahedron linked to one of the Zn octahedra by a carboxylate O atom.

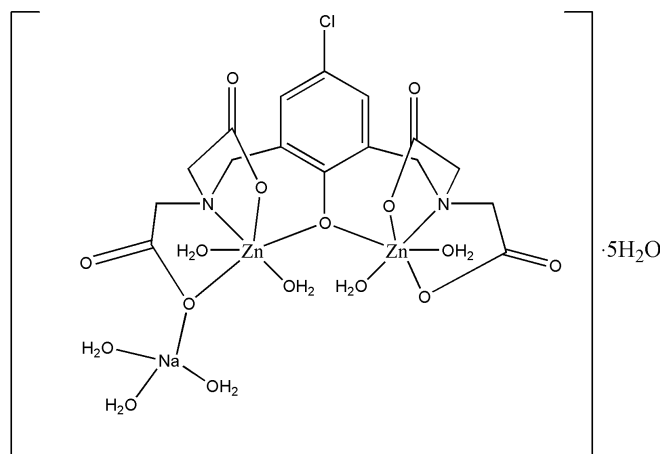
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Comment

2,6-Bis[[bis(carboxylatomethyl)amino]methyl]-4-chlorophenolate (Cl-HXTA) is one of the acyclic dinucleating ligands with a phenolate bridge (Murch *et al.*, 1987). This pentavalent anionic ligand has four methylcarbonyl chelating arms with two sets of donor atoms, *viz.* one N and three O as the coordination sites. One of the advantages of Cl-HXTA is that most of its dinuclear metal complexes are soluble in water. We have reported the crystal structure of a Cl-HXTA–Ni complex containing an Na–O–Ni–O–Ni bridge (Meng *et al.*, 2004). We report here the isostructural Zn trinuclear complex, the title complex, (I).



(I)

In (I), the two Zn^{2+} ions are located in two similar coordination spheres with distorted octahedral geometry; each is composed of two carboxylates, a tertiary N atom, two water molecules and a bridging phenolate O atom (Fig. 1). The average $\text{Zn}-\text{O}(\text{phenolate})$ bond length is 2.052 (6) Å. At each Zn^{2+} centre, the two water molecules and the tertiary N atom as well as the bridging phenolate O atom are almost coplanar. The $\text{Zn1}\cdots\text{Zn2}$ distance is 3.745 (3) Å. Atom O3 from the carboxyl group is coordinated by both the Zn1 and

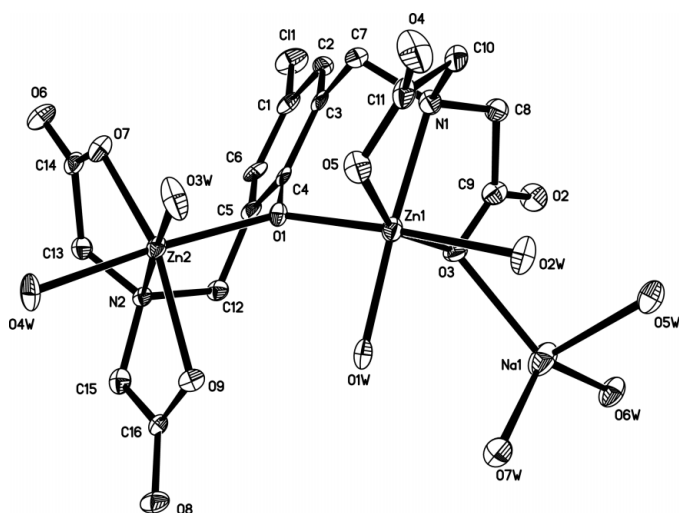


Figure 1
The molecular structure of (I), showing 20% probability displacement ellipsoids. H atoms and water molecules of crystallization have been omitted for clarity.

the Na1 ion, with O3–Na1 and O3–Zn1 distances of 2.315 (7) and 2.041 (6) Å, respectively. These characteristics are very similar to those in the Ni complex reported previously (Meng *et al.*, 2004).

In this Zn complex and the previously reported Ni complex, the coordination geometry around the Na cation is special. Shen & Jing (2002) pointed out that the Na⁺ cation usually forms four- or six-coordinate complexes; five-, seven- and eight-coordinate sodium complexes are relatively rare, but these authors reported a five-coordinate Na complex having trigonal-bipyramidal geometry. In (I), Na1⁺ is coordinated by an O atom of the carboxyl group and three water molecules. The coordination geometry around Na1⁺ is that of an irregular trigonal pyramid with atom O5W at the apical position; atoms O3, O6W and O7W form the basal plane, from which the Na1 atom is shifted by 0.204 (6) Å toward atom O5W. The Cl atom from a neighbouring complex weakly coordinates to Na1⁺ from the opposite side of the trigonal pyramid, with an Na1...Cl distance of 4.001 (5) Å, thus generating an asymmetric trigonal-bipyramidal geometry (Fig. 2). A number of intra- and intermolecular hydrogen bonds (Table 2) stabilize the crystal structure.

Experimental

All chemicals were of reagent grade, were commercially available from the Beijing Chemical Reagents Company of China and were used without further purification. The Cl-HXTA⁵⁻ ligand was synthesized using the procedures reported by Gao *et al.* (2004) and Meng *et al.* (2004). Zn(CH₃COO)₂·4H₂O (0.439 g, 2 mmol) and Na₄H(Cl-HXTA) (0.516 g, 1 mmol) were dissolved in two portions of water (5 ml) and mixed, and the pH was adjusted to 7 using NaOH solution (2 mol l⁻¹); the mixture was stirred at 323 K for 3 h. The resulting colourless solution was filtered and the filtrate was left at room temperature. Colourless crystals of (I) appeared after 10 d, following slow evaporation of the aqueous solvent.

Crystal data

[NaZn₂(C₁₆H₁₄ClN₂O₉)·
(H₂O)₇]·5H₂O
*M*_r = 783.66
Triclinic, *P* $\bar{1}$
a = 10.281 (9) Å
b = 11.733 (10) Å
c = 13.974 (12) Å
 α = 95.781 (11)°
 β = 109.593 (11)°
 γ = 103.043 (11)°
V = 1518 (2) Å³

Z = 2
*D*_x = 1.714 Mg m⁻³
Mo *K*α radiation
Cell parameters from 1639
reflections
 θ = 2.6–22.5°
 μ = 1.77 mm⁻¹
T = 293 (2) K
Block, colourless
0.18 × 0.16 × 0.14 mm

Data collection

SMART 1K CCD area-detector
diffractometer
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2000)
*T*_{min} = 0.741, *T*_{max} = 0.790
7201 measured reflections

5128 independent reflections
3503 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.064
 θ _{max} = 25.0°
h = -7 → 12
k = -13 → 13
l = -16 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.097
wR(*F*²) = 0.199
S = 1.08
5128 reflections
388 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0815*P*)²
+ 1.639*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δσ)_{max} < 0.001
Δρ_{max} = 1.09 e Å⁻³
Δρ_{min} = -0.91 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1–O1W	2.027 (7)	Zn2–O3W	2.035 (6)
Zn1–O3	2.041 (6)	Zn2–O7	2.058 (6)
Zn1–O1	2.055 (6)	Zn2–O4W	2.142 (6)
Zn1–O5	2.077 (6)	Zn2–N2	2.151 (7)
Zn1–N1	2.133 (8)	Zn2–O9	2.176 (6)
Zn1–O2W	2.254 (7)	Zn2–Na1	6.689 (6)
Zn1–Zn2	3.745 (3)	Na1–O6W	2.220 (8)
Zn1–Na1	3.827 (5)	Na1–O5W	2.361 (9)
O1–Zn2	2.049 (6)	Na1–O7W	2.368 (10)
O3–Na1	2.315 (7)		
O1W–Zn1–O3	99.4 (3)	O1–Zn2–O7	98.3 (2)
O1W–Zn1–O1	91.7 (2)	O3W–Zn2–O4W	87.9 (3)
O3–Zn1–O1	95.8 (2)	O1–Zn2–O4W	171.6 (2)
O1W–Zn1–O5	97.7 (3)	O7–Zn2–O4W	88.9 (3)
O3–Zn1–O5	158.6 (3)	O3W–Zn2–N2	177.7 (3)
O1–Zn1–O5	96.6 (2)	O1–Zn2–N2	92.9 (2)
O1W–Zn1–N1	175.1 (3)	O7–Zn2–N2	81.1 (3)
O3–Zn1–N1	81.9 (3)	O4W–Zn2–N2	92.5 (3)
O1–Zn1–N1	92.9 (3)	O3W–Zn2–O9	100.8 (3)
O5–Zn1–N1	80.1 (3)	O1–Zn2–O9	91.7 (2)
O1W–Zn1–O2W	84.9 (3)	O7–Zn2–O9	156.3 (2)
O3–Zn1–O2W	85.0 (2)	O4W–Zn2–O9	83.1 (3)
O1–Zn1–O2W	176.6 (3)	N2–Zn2–O9	77.0 (2)
O5–Zn1–O2W	83.7 (2)	O6W–Na1–O3	133.4 (3)
N1–Zn1–O2W	90.5 (3)	O6W–Na1–O5W	99.5 (3)
Zn2–O1–Zn1	131.7 (3)	O3–Na1–O5W	90.8 (3)
Zn1–O3–Na1	122.8 (3)	O6W–Na1–O7W	126.1 (3)
O3W–Zn2–O1	86.5 (2)	O3–Na1–O7W	98.0 (3)
O3W–Zn2–O7	101.1 (3)	O5W–Na1–O7W	93.8 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H21 \cdots O9	0.89	1.94	2.804 (9)	163
O1W—H22 \cdots O7W	0.89	1.90	2.727 (10)	155
O2W—H23 \cdots O10	0.88	2.00	2.782 (11)	148
O3W—H31 \cdots O8 ⁱ	0.89	1.92	2.786 (9)	164
O3W—H32 \cdots O5	0.89	2.05	2.772 (9)	138
O4W—H41 \cdots O9 ^j	0.88	1.93	2.798 (9)	169
O4W—H42 \cdots O12 ⁱⁱ	0.88	1.87	2.665 (10)	150
O5W—H51 \cdots O2 ⁱⁱⁱ	0.88	1.89	2.710 (10)	155
O5W—H52 \cdots O8W ^{iv}	0.88	1.83	2.701 (11)	170
O6W—H61 \cdots O6 ^v	0.89	1.96	2.800 (10)	155
O6W—H62 \cdots O6 ^{vi}	0.88	1.91	2.744 (9)	156
O7W—H72 \cdots O11 ⁱⁱⁱ	0.88	1.96	2.734 (13)	145
O9W—H91 \cdots O8 ^{vii}	0.89	1.98	2.814 (10)	157
O9W—H92 \cdots O8 ^{viii}	0.88	1.90	2.756 (10)	166
O11—H27 \cdots O4 ^{ix}	0.88	1.82	2.657 (12)	158
O12—H34 \cdots O4	0.88	1.86	2.735 (11)	171

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

H atoms attached to O atoms (water) were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The O—H distances are in the range 0.88–0.91 Å. H atoms attached to C atoms were placed in idealized positions, with C—H = 0.93–0.97 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The residual electron density has a maximum located 1.04 Å from Zn1.

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

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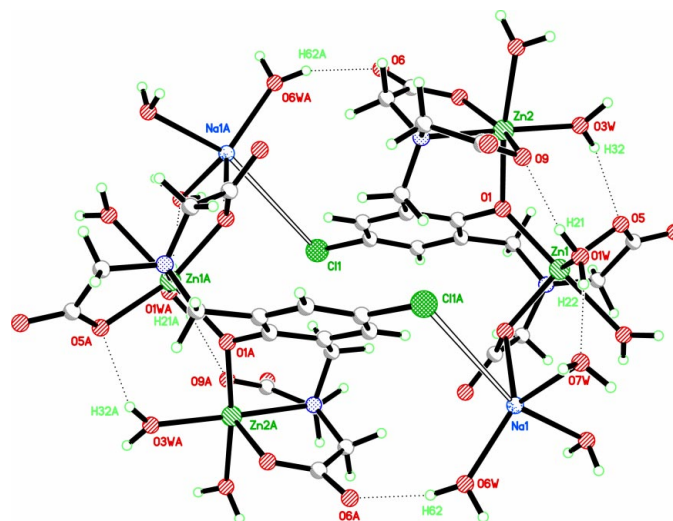


Figure 2
The hydrogen-bond network (dashed lines) and Na \cdots Cl weak interactions (open lines) in the crystal structure of (I). Atoms labelled with the suffix A are at the symmetry position ($2-x, -y, 1-z$).

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