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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 σ(C–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-1κ^3O,2κ^2O,3κ^2O-(μ_3-2,6-bis{[bis(carboxylatomethyl)amino]methyl}-4-chlorophenolato-1κO;2κ^4O,O',N,O^1;3κ^4O^1,N',O'',O''')dizinc(II)sodium(I) pentahydrate, $[NaZn_2(C_{16}H_{14}ClN_2O_9)(H_2O)_7]\cdot 5H_2O$ or $[Zn_2(Cl\text{-}HXTA)(H_2O)_4\{Na(H_2O)_3\}]\cdot 5H_2O$, 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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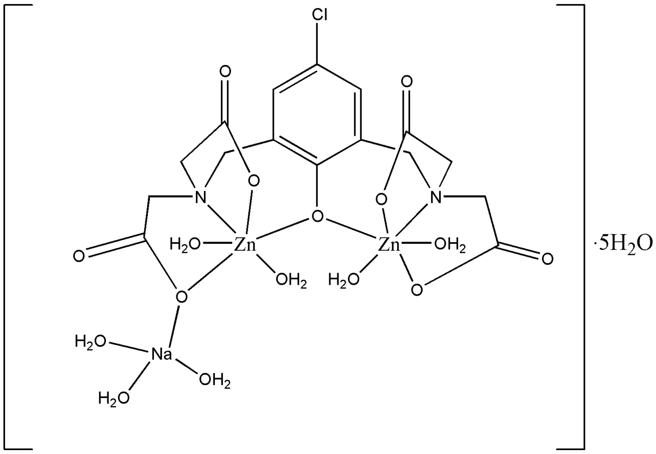
Comment

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 Zn—O(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 Zn1···Zn2 distance is 3.745 (3) Å. Atom O3 from the carboxyl group is coordinated by both the Zn1 and

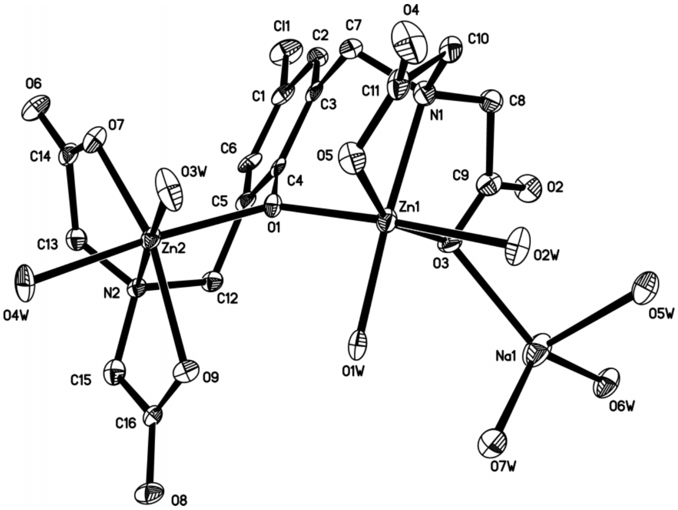


Figure 1
The molecular structure of (I), showing 20% probability displacement ellipsoids. H atoms and water molecules of crystallization have been omitted for clarity.

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 O5*W* at the apical position; atoms O3, O6*W* and O7*W* form the basal plane, from which the Na1 atom is shifted by 0.204 (6) Å toward atom O5*W*. 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-HXTA^{5-} ligand was synthesized using the procedures reported by Gao *et al.* (2004) and Meng *et al.* (2004). $Zn(CH_3COO)_2\cdot 4H_2O$ (0.439 g, 2 mmol) and $Na_4H(\text{Cl-HXTA})$ (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 moll^{-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

$[NaZn_2(C_{16}H_{14}ClN_2O_9)(H_2O)_7]\cdot 5H_2O$
$M_r = 783.66$
Triclinic, $P\bar{1}$
$a = 10.281$ (9) Å
$b = 11.733$ (10) Å
$c = 13.974$ (12) Å
$\alpha = 95.781$ (11)°
$\beta = 109.593$ (11)°
$\gamma = 103.043$ (11)°
$V = 1518$ (2) $Å^3$
$Z = 2$
$D_x = 1.714$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1639 reflections
$\theta = 2.6$–22.5°
$\mu = 1.77$ 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 $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.097$
$wR(F^2) = 0.199$
$S = 1.08$
5128 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0815P)^2 + 1.639P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.09$ e $Å^{-3}$
$\Delta\rho_{min} = -0.91$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Zn1—O1*W*	2.027 (7)	Zn2—O3*W*	2.035 (6)
Zn1—O3	2.041 (6)	Zn2—O7	2.058 (6)
Zn1—O1	2.055 (6)	Zn2—O4*W*	2.142 (6)
Zn1—O5	2.077 (6)	Zn2—N2	2.151 (7)
Zn1—N1	2.133 (8)	Zn2—O9	2.176 (6)
Zn1—O2*W*	2.254 (7)	Zn2—Na1	6.689 (6)
Zn1—Zn2	3.745 (3)	Na1—O6*W*	2.220 (8)
Zn1—Na1	3.827 (5)	Na1—O5*W*	2.361 (9)
O1—Zn2	2.049 (6)	Na1—O7*W*	2.368 (10)
O3—Na1	2.315 (7)		
O1*W*—Zn1—O3	99.4 (3)	O1—Zn2—O7	98.3 (2)
O1*W*—Zn1—O1	91.7 (2)	O3*W*—Zn2—O4W	87.9 (3)
O3—Zn1—O1	95.8 (2)	O1—Zn2—O4*W*	171.6 (2)
O1*W*—Zn1—O5	97.7 (3)	O7—Zn2—O4*W*	88.9 (3)
O3—Zn1—O5	158.6 (3)	O3*W*—Zn2—N2	177.7 (3)
O1—Zn1—O5	96.6 (2)	O1—Zn2—N2	92.9 (2)
O1*W*—Zn1—N1	175.1 (3)	O7—Zn2—N2	81.1 (3)
O3—Zn1—N1	81.9 (3)	O4*W*—Zn2—N2	92.5 (3)
O1—Zn1—N1	92.9 (3)	O3*W*—Zn2—O9	100.8 (3)
O5—Zn1—N1	80.1 (3)	O1—Zn2—O9	91.7 (2)
O1*W*—Zn1—O2*W*	84.9 (3)	O7—Zn2—O9	156.3 (2)
O3—Zn1—O2*W*	85.0 (2)	O4*W*—Zn2—O9	83.1 (3)
O1—Zn1—O2*W*	176.6 (3)	N2—Zn2—O9	77.0 (2)
O5—Zn1—O2*W*	83.7 (2)	O6*W*—Na1—O3	133.4 (3)
N1—Zn1—O2*W*	90.5 (3)	O6*W*—Na1—O5*W*	99.5 (3)
Zn2—O1—Zn1	131.7 (3)	O3—Na1—O5*W*	90.8 (3)
Zn1—O3—Na1	122.8 (3)	O6*W*—Na1—O7*W*	126.1 (3)
O3*W*—Zn2—O1	86.5 (2)	O3—Na1—O7*W*	98.0 (3)
O3*W*—Zn2—O7	101.1 (3)	O5*W*—Na1—O7*W*	93.8 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H21···O9	0.89	1.94	2.804 (9)	163
O1W—H22···O7W	0.89	1.90	2.727 (10)	155
O2W—H23···O10	0.88	2.00	2.782 (11)	148
O3W—H31···O8$^{\rm i}$	0.89	1.92	2.786 (9)	164
O3W—H32···O5	0.89	2.05	2.772 (9)	138
O4W—H41···O9$^{\rm i}$	0.88	1.93	2.798 (9)	169
O4W—H42···O12$^{\rm ii}$	0.88	1.87	2.665 (10)	150
O5W—H51···O2$^{\rm iii}$	0.88	1.89	2.710 (10)	155
O5W—H52···O8$W^{\rm iv}$	0.88	1.83	2.701 (11)	170
O6W—H61···O6$^{\rm v}$	0.89	1.96	2.800 (10)	155
O6W—H62···O6$^{\rm vi}$	0.88	1.91	2.744 (9)	156
O7W—H72···O11$^{\rm iii}$	0.88	1.96	2.734 (13)	145
O9W—H91···O8$^{\rm vii}$	0.89	1.98	2.814 (10)	157
O9W—H92···O8$^{\rm viii}$	0.88	1.90	2.756 (10)	166
O11—H27···O4$^{\rm ix}$	0.88	1.82	2.657 (12)	158
O12—H34···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 $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(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 $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(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: *SHELXS*97 (Sheldrick, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2000); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

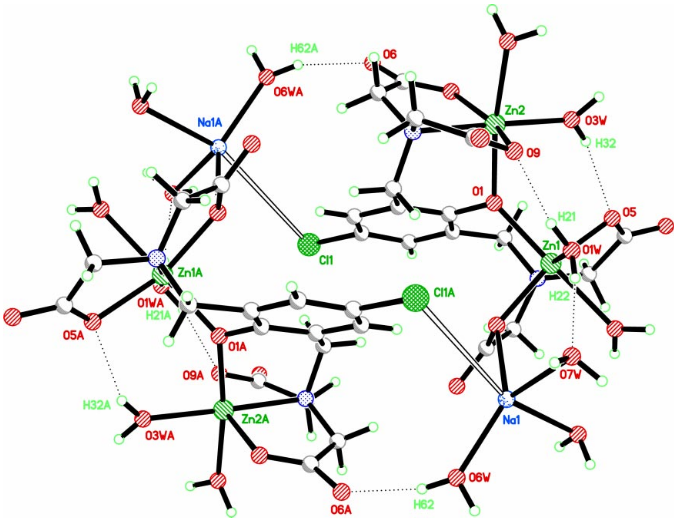

Figure 2
The hydrogen-bond network (dashed lines) and Na···Cl weak interactions (open lines) in the crystal structure of (I). Atoms labelled with the suffix A are at the symmetry position ($2-x$, $-y$, $1-z$).

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