

A novel trinuclear zinc(II) cluster with a tetrahedral ZnO_4 core

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The reaction of 0.67 molar equivalents of the O,N,O' -tridentate zwitterionic Schiff base (2*Z*,4*E*)-4-[(2-hydroxyphenyl)iminio]pent-2-en-2-olate (H_2L) with one equivalent of zinc(II) acetate in methanol affords a novel trinuclear Zn^{II} cluster, di- μ -acetato-1:2 $\kappa^2O:O'$:2:3 $\kappa^2O:O'$ -dimethanol-1 κO ,3 κO -bis{ μ -2-[(2*E*,3*Z*)-4-oxido-pent-3-en-2-ylideneamino]phenolato}-1:2 $\kappa^4O^2,N,O^4:O^4$:2:3 $\kappa^4O^4:O^2,N,O^4$ -trizinc(II), [$\text{Zn}_3(\text{C}_{11}\text{H}_{11}\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{CH}_3\text{O})_2$], (I), in which two bridging acetate ligands link the terminal square-based pyramidal Zn^{II} ions to the approximately tetrahedral Zn^{II} ion at the core of the cluster. The ZnO_4 coordination group of the central Zn^{II} ion is established by two bridging phenolate and two bridging acetate O atoms. The remaining four coordination sites of each terminal Zn^{II} ion are occupied by methanol and deprotonated H_2L . Furthermore, the Zn-bound methanol hydroxyl groups are involved in complementary hydrogen bonding with the Zn-bound enolate O atom of a neighbouring molecule, about an inversion centre in each case. The structure of (I) is therefore best described as an extended one-dimensional hydrogen-bonded chain of trinuclear Zn^{II} clusters.

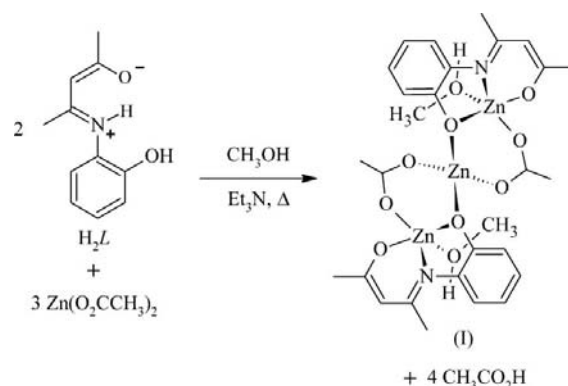
Comment

Schiff base ligands with O,N,O' -donor atom sets may be prepared from several synthons depending on which structural, electronic or steric properties are required. One straightforward strategy for preparing resonance-stabilized nonplanar O,N,O' -tridentate Schiff base ligands based on the structure of (2*Z*,4*E*)-4-[(2-hydroxyphenyl)iminio]pent-2-en-2-olate (H_2L) involves the condensation of pentane-2,4-dione and 2-aminophenol. In this ligand, nonbonded interactions between the aryl ring and closest methyl group distort the system from planarity (Kabak *et al.*, 1998), providing a potentially useful tool for modulating the electronic properties of coordination compounds. There are three reported X-ray structures of the parent ligand system based on 2-aminophenol (Kabak *et al.*, 1998; Chen *et al.*, 1999; Rajnikant *et al.*, 2006). Although there is some debate about the exact struc-

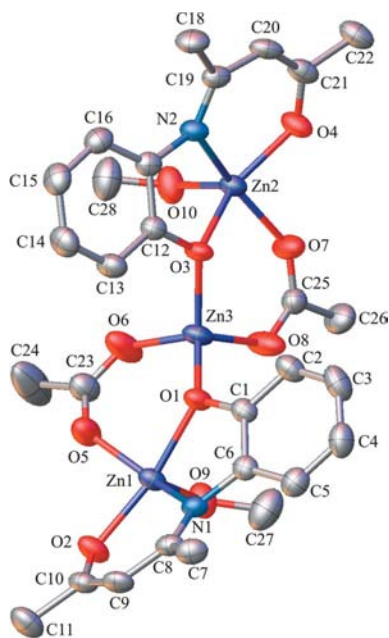
ture or resonance form of the ligand, it is best understood as a resonance hybrid with significant zwitterion character, as depicted in the scheme.

Coordination of H_2L to a metal ion requires the loss of two H atoms to form the tridentate dianion 2-[(2*E*,3*Z*)-4-oxido-pent-3-en-2-ylideneamino]phenolate, L^- . Examples of structurally characterized complexes of L^- include the centrosymmetric tetranuclear Cu^{II} cluster Cu_4L_4 (Barclay & Hoskins, 1965), the dinuclear organometallic complex $\text{Ga}_2(\text{Me})_2\text{L}_2$ (Shen *et al.*, 2004), the unusual square-pyramidal Si^{IV} complexes $\text{Si}(\text{NCO})_2\text{L}_2$ and $\text{Si}(\text{NCS})_2\text{L}_2$ (Seiler *et al.*, 2005), a six-coordinate Si^{IV} complex, SiL_2 (Seiler *et al.*, 2005), a centrosymmetric dinuclear Cu^{II} cluster, $\text{Cu}_2\text{L}'_2$ (utilizing the 4-chloro analogue of L ; Tahir *et al.*, 1996), and the mixed-ligand complexes SiLX , where X is the dianion of 2-hydroxybenzoic acid, (*S*)-lactic acid or 2-hydroxyethanoic acid (Seiler *et al.*, 2007). While these examples illustrate some of the coordination chemistry possible with H_2L , further development and application of this type of ligand in both coordination and supramolecular chemistry are warranted.

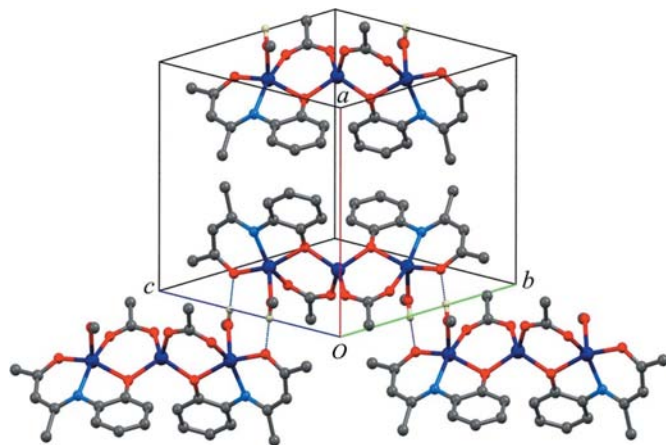
Reaction of H_2L with Zn^{II} in a 1:1 ratio in methanol should, in principle, generate the mononuclear Zn^{II} complexes $\text{ZnL}(\text{OHCH}_3)$ or $\text{ZnL}(\text{OHCH}_3)_2$, due to the preference of Zn^{II} for a four- or five-coordinate geometry, respectively. In this paper, we describe the isolation and structure elucidation of the title novel trinuclear Zn^{II} cluster, (I), generated from this reaction system when Zn^{II} acetate is used for metallation. Since only a few colourless crystals of (I) were located in the bulk pale-yellow polycrystalline product, we surmise that (I) is a stable yet minor component of the product mixture resulting from a 2:3 ligand–metal reaction stoichiometry.



The structure of (I) has a central ZnO_4 group with approximate tetrahedral (td) geometry forming the core of a trinuclear Zn^{II} cluster (Fig. 1). The central Zn^{II} ion is linked *via* bridging ligands (two acetate ions and two phenoxide O atoms) to two terminal Zn^{II} ions with square-based pyramidal (sbp) coordination. The five-coordinate geometry of each terminal Zn^{II} ion is brought about by ligation of the metal by a solvent-derived methanol molecule as the fifth ligand. The trinuclear cluster has approximate C_2 symmetry by virtue of a pseudo-twofold rotation axis passing through the central ZnO_4 core. The chemically equivalent pairs of $\text{Zn}(\text{sbp})\text{—N}$

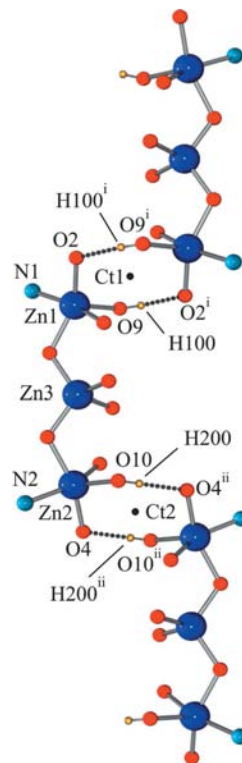
**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

**Figure 2**

Ball-and-tube representation of part of the unit-cell contents of (I). All H atoms, except those involved in hydrogen bonding (dashed lines), have been omitted for clarity. Linkage of the trinuclear Zn^{II} clusters to form a corrugated extended one-dimensional hydrogen-bonded chain is depicted for the lower molecule in the unit cell.

and $\text{Zn}(\text{sbp})\text{--O}(\text{enolate})$ bonds average 2.054 (1) and 1.982 (14) Å, respectively. The $\text{Zn}\text{--O}$ bonds involving the bridging phenoxide and acetate O atoms are shorter to the central Zn^{II} ion and longer to the terminal Zn^{II} ions, consistent with the lower coordination number for td Zn3 and the geometric constraints imposed by each tridentate Schiff base chelate in (I). More specifically, the $\text{Zn}(\text{sbp})\text{--O}(\text{phenoxide})$ bonds average 2.050 (5) Å within the five-membered chelate ring in contrast to the mean $\text{Zn}(\text{td})\text{--O}(\text{phenoxide})$ bonds involving the central Zn^{II} ion, which are markedly shorter at 1.947 (6) Å. The $\text{Zn}(\text{sbp})\text{--O}(\text{acetate})$ and $\text{Zn}(\text{td})\text{--O}(\text{ace-})$

**Figure 3**

Partially labelled illustration of the inorganic core of three hydrogen-bonded molecules of (I). Displacement ellipsoids are drawn at the 40% probability level. H and C atoms have been omitted for clarity. Ct1 and Ct2 are the inversion centres, with coordinates $(0, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$, respectively. O atoms involved in complementary hydrogen bonding are linked by dashed bonds. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y + 1, -z$.]

tate) bonds are also distinct, averaging 2.032 (11) and 1.938 (2) Å, respectively. Collectively, the ZnO_4 coordination group at the centre of the trinuclear cluster exhibits a mean $\text{Zn}(\text{td})\text{--O}$ distance of 1.942 (7) Å. The bonds to the axial methanol solvent molecules, *viz.* $\text{Zn}(\text{sbp})\text{--O}(\text{methanol})$, average a fairly typical 2.021 (8) Å (Orpen *et al.*, 1989).

Structurally characterized trinuclear Zn^{II} clusters stabilized by bridging acetate ligands are well known in the literature. In most cases, anionic O-atom donors surround the central Zn^{II} ion to give a six-coordinate nominally octahedral ZnO_6 coordination group, as is the case when two tridentate pyridine-imine-enolate ligands (de Hoog *et al.*, 2004; Majumder *et al.*, 2006) or two tridentate phenolate-imine-phenolate ligands (Gembicky *et al.*, 2000) serve as the capping groups for the cluster. Interestingly, even tetradentate salen-type ligands [H_2salen is bis(salicylidene)ethylenediamine], when metalated with Zn^{II} acetate, form trinuclear μ_2 -acetate-bridged clusters with square-pyramidal terminal Zn^{II} ions and a central ZnO_6 core (Ülkü *et al.*, 2001). Trinuclear Zn^{II} cluster formation is evidently favoured in the presence of acetate ions. What distinguishes compound (I) from previously described trinuclear Zn^{II} clusters is the fact that it is the first compound to be based upon a nominally tetrahedral ZnO_4 core.

Returning to the structure of (I), it is worth noting that the tridentate imine-enolate ligands are nonplanar by virtue of

the steric repulsion between the adjacent benzene and methyl groups in the structure. The dihedral angles between the benzene rings and imine-enolate moieties are 32.3 (3) and 28.3 (3)° for the ligands containing atoms N1 and N2, respectively. This dihedral angle is 32.9 (3)° in the free ligand (Kabak *et al.*, 1998), suggesting that complexation of Zn^{II} does not lead to any measurable distortion of the tridentate chelate. The terminal square-pyramidal Zn^{II} ions Zn1 and Zn2 are displaced towards their axial methanol ligands from the four-atom mean planes passing through their equatorial ligand donor-atom sets by 0.423 (1) and 0.409 (1) Å, respectively. Furthermore, the angle between these latter two planes is 86.6 (3)°. The approximately orthogonal relative orientation of these two coordination group planes is a geometric manifestation of having two *cis* O-atom donors in each plane as bridging groups, and thus *cis* ligands, to the central tetrahedral ZnO₄ core of the cluster.

Finally, the unit cell for (I) comprises two trinuclear clusters in general positions (Fig. 2). More interesting, however, is the fact that each molecule is a member of an extended one-dimensional hydrogen-bonded chain with a corrugated architecture that is enabled by complementary hydrogen-bond formation between Zn-bound methanol molecules belonging to neighbouring trinuclear clusters in the crystalline solid state (Table 2 and Fig. 3). Each trinuclear cluster is therefore related to its immediate neighbour in the chain by an inversion centre. The metal-bound methanol molecules evidently direct the extended structure of (I) in the crystal structure. One other trinuclear Zn^{II} cluster has been described with hydrogen bonding between metal-bound methanol molecules and neighbouring clusters and, consequently, extended chain formation in the crystalline solid state (Akine *et al.*, 2007). The elegance and simplicity of the complementary hydrogen-bonding interactions displayed by (I) are, however, currently unmatched, at least for trinuclear clusters of the type presented here.

Experimental

Compound (I) was prepared essentially as described in the literature (Kabak *et al.*, 1998). Zinc acetate (1.000 g, 4.6 mmol) and H₂L (0.871 g, 4.6 mmol) were weighed into a round-bottomed flask and dissolved in a minimum of methanol. The solution went bright yellow as it came to reflux. Triethylamine (0.920 g, 9.2 mmol) was added and the solution was left to reflux for 2 h. A yellow precipitate was filtered off and allowed to dry in the air. A crystal of (I) suitable for X-ray diffraction was grown by slow evaporation from the methanol solution. This crystal was a large colourless rectangular rhomb amidst the bulk polycrystalline material (pale yellow).

Crystal data

$[\text{Zn}_3(\text{C}_{11}\text{H}_{11}\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot(\text{CH}_4\text{O})_2]$	$\beta = 79.582 (2)^\circ$
$M_r = 756.70$	$\gamma = 76.594 (2)^\circ$
Triclinic, $P\bar{1}$	$V = 1591.11 (7) \text{ \AA}^3$
$a = 10.5348 (2) \text{ \AA}$	$Z = 2$
$b = 11.6175 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 13.5918 (4) \text{ \AA}$	$\mu = 2.30 \text{ mm}^{-1}$
$\alpha = 88.768 (2)^\circ$	$T = 295 \text{ K}$
	$0.50 \times 0.40 \times 0.30 \text{ mm}$

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	2.075 (2)	Zn2—O7	2.040 (3)
Zn1—O2	1.992 (2)	Zn2—O10	2.027 (3)
Zn1—O5	2.024 (2)	Zn2—N2	2.054 (2)
Zn1—O9	2.015 (3)	Zn3—O1	1.943 (2)
Zn1—N1	2.053 (2)	Zn3—O3	1.951 (2)
Zn2—O3	2.046 (2)	Zn3—O6	1.936 (3)
Zn2—O4	1.972 (2)	Zn3—O8	1.939 (3)
O1—Zn1—O2	160.21 (9)	O4—Zn2—O7	85.31 (10)
O1—Zn1—O5	91.74 (9)	O4—Zn2—O10	107.35 (10)
O1—Zn1—O9	97.88 (10)	O4—Zn2—N2	93.50 (10)
O1—Zn1—N1	79.38 (9)	O7—Zn2—O10	93.45 (13)
O2—Zn1—O5	87.33 (9)	O7—Zn2—N2	162.31 (11)
O2—Zn1—O9	101.87 (10)	O10—Zn2—N2	103.71 (11)
O2—Zn1—N1	91.97 (9)	O1—Zn3—O3	115.38 (9)
O5—Zn1—O9	96.62 (13)	O1—Zn3—O6	105.92 (11)
O5—Zn1—N1	151.03 (11)	O1—Zn3—O8	111.55 (10)
O9—Zn1—N1	111.82 (11)	O3—Zn3—O6	109.10 (12)
O3—Zn2—O4	150.52 (9)	O3—Zn3—O8	108.13 (10)
O3—Zn2—O7	92.03 (9)	O6—Zn3—O8	106.37 (13)
O3—Zn2—O10	102.11 (10)	Zn1—O1—Zn3	115.71 (11)
O3—Zn2—N2	80.33 (9)	Zn2—O3—Zn3	116.30 (11)

Table 2

Hydrogen-bond geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O9—H100 \cdots O2 ⁱ	0.81 (2)	1.83 (2)	2.633 (2)	176 (1)
O10—H200 \cdots O4 ⁱⁱ	0.81 (2)	1.82 (2)	2.627 (2)	176 (1)

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y + 1, -z$.

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer	17802 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	6772 independent reflections
$T_{\min} = 0.372, T_{\max} = 0.500$	4756 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.096$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
6772 reflections	
404 parameters	
2 restraints	

The H atoms attached to methanol atoms O9 and O10 were located by difference Fourier synthesis and refined isotropically, with an O—H distance constraint of 0.82 (2) Å. The remaining H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine H atoms, C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. For methyl H atoms, the torsion angle was optimized to fit the electron density.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 1999) and

OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3029). Services for accessing these data are described at the back of the journal.

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