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Tetrahedral and octahedral coordination for zinc in polymeric tris(μ_3-4-carboxyphenoxyacetato)di-μ_3-hydroxo-bis(μ_2-4,4′-bipyridine)tetrazinc(IV) dihydrate

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Key indicators

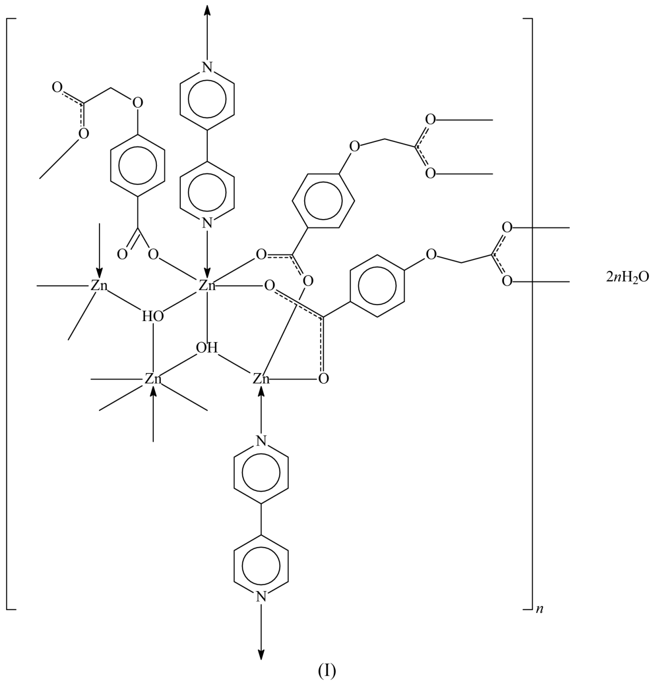
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.051
wR factor = 0.128
Data-to-parameter ratio = 14.9

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

The hydroxide group in the centrosymmetric title complex, $\{[Zn_4(C_9H_6O_5)_3(OH)_2(C_{10}H_8N_2)_2]\cdot 2H_2O\}_n$, which adopts a three-dimensional network structure, bridges three Zn atoms. One of the symmetry-independent dicarboxylate groups chelates to a Zn—OH—Zn unit through the carboxyl group on the aromatic ring, while its other oxyacetate arm uses only one O atom for binding. The other dicarboxylate dianion is disordered over a center of inversion and functions as a chelating ligand to two Zn—OH—Zn units. The modes of coordination by the hydroxide, heterocycle and dicarboxylate ligands give rise to tetrahedral coordination for one Zn atom and octahedral coordination for the other.

Comment

A small number of metal salts of 4-carboxyphenoxyacetic acid have been described in the literature, the most recent being the magnesium derivative (Gao *et al.*, 2004). On the other hand, there is a vast literature on 4,4′-bipyridine, a spacer heterocycle that connects metal atoms in chains, squares and network motifs; the number of zinc dicarboxylate complexes is correspondingly also large. Examples include the succinate (Tao *et al.*, 2001) and the terephthalate (Tao *et al.*, 2000) adducts. The present study extends the list of such complexes to the title compound, a mixed zinc hydroxide/carboxylate complex, (I) (Fig. 1).



(I)

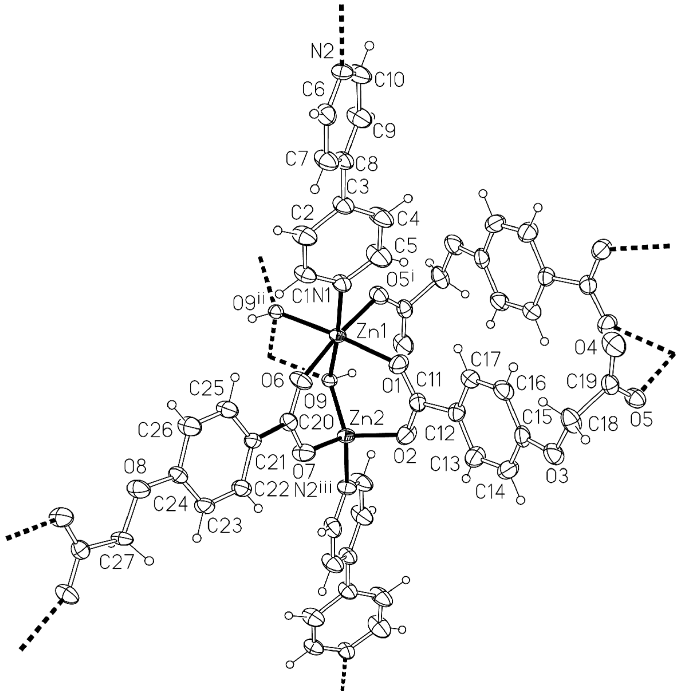


Figure 1
An *ORTEP*II (Johnson, 1976) plot of a fragment of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii. Symmetry codes are as given in Table 1.

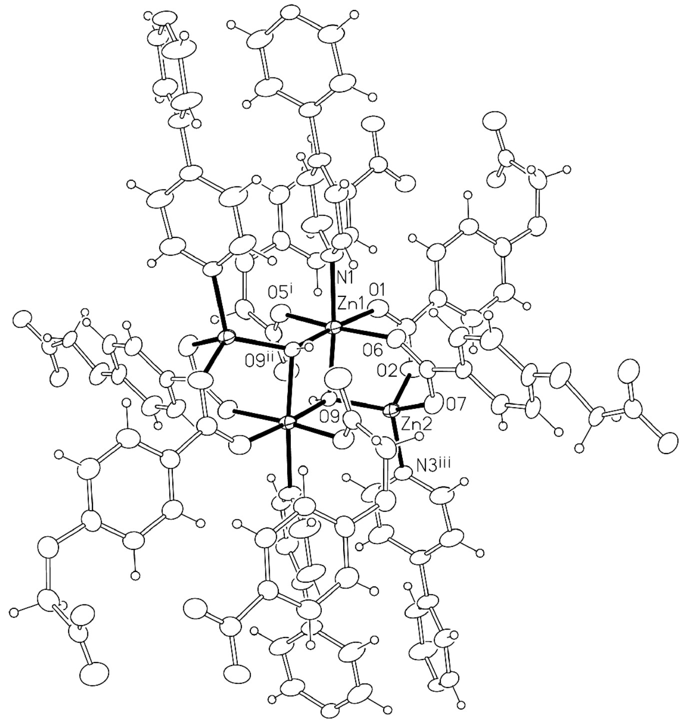


Figure 2
A view of the tetrahedral and octahedral geometries of the Zn atoms in (I).

The unit cell of (I) contains four Zn atoms, two hydroxide groups, two bipyridyl connectors and three dicarboxylate dianions along with two solvent water molecules. The hydroxide group acts as a bridge to link three Zn atoms together. The hydroxide group probably results from the dissociation of water under the conditions of the synthesis. A hydroxide group binding to zinc in the μ_3 mode has been noted in the DMSO-coordinated terephthalate derivative (Wang *et al.*, 2001). In the title compound, one of the symmetry-independent dicarboxylate groups chelates to a Zn—OH—Zn unit to form a six-membered ring through the carboxyl group on the aromatic ring, while its other oxyacetate arm uses only one O atom to bind with a Zn atom. The other dicarboxylate group, which is disordered, functions as a chelating ligand to two Zn—OH—Zn units through both carboxyl ends (Fig. 2). The bipyridine spacer, the hydroxide and dianion give rise to tetrahedral coordination for one of the zinc atoms in the asymmetric unit of the centrosymmetric structure and to octahedral coordination for the the other (Fig. 2). The hydrogen bonds in the structure (Table 2) are relatively unimportant as the three-dimensional architecture is already sufficiently rigid.

Experimental

Stoichiometric amounts of zinc diacetate dihydrate (0.22 g, 1 mmol), 4-carboxyphenoxyacetic acid (0.20 g, 1 mmol) and 4,4′-bipyridine (0.16 g, 1 mmol) were mixed together in water. The pH was adjusted to 6 by adding 0.2 *M* sodium hydroxide. The mixture was then sealed in a 50 ml Teflon-lined stainless-steel bomb. The bomb was heated to 423 K for 120 h and crystals were isolated. Analysis calculated for $C_{47}H_{40}N_4O_{19}Zn_4$: C 46.03, H 3.29, N 4.57%; found C 46.12, H 3.37, N 4.53%.

Crystal data

$[Zn_4(C_9H_6O_5)_3(OH)_2(C_{10}H_8N_2)_2]\cdot 2H_2O$
$M_r = 1226.31$
Triclinic, $P\overline{1}$
$a = 10.679\ (4)$ Å
$b = 10.913\ (4)$ Å
$c = 12.140\ (4)$ Å
$\alpha = 112.43\ (3)^\circ$
$\beta = 104.07\ (3)^\circ$
$\gamma = 100.10\ (3)^\circ$
$V = 1210.4\ (8)$ Å^3
$Z = 1$
$D_x = 1.682$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12424 reflections
$\theta = 3.3$–27.5°
$\mu = 2.04$ mm^{-1}
$T = 295\ (2)$ K
Prism, colourless
0.39 × 0.27 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.545$, $T_{max} = 0.696$
11901 measured reflections
5503 independent reflections
4737 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 27.5^\circ$
$h = -13 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.128$
$S = 1.12$
5503 reflections
370 parameters
H atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 3.5764P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.116 (3)	Zn1—N1	2.141 (3)
Zn1—O5$^{\rm i}$	2.094 (3)	Zn2—O2	1.946 (3)
Zn1—O6	2.149 (3)	Zn2—O7	1.941 (3)
Zn1—O9	2.134 (3)	Zn2—O9	1.917 (3)
Zn1—O9$^{\rm ii}$	2.091 (3)	Zn2—N2$^{\rm iii}$	2.022 (3)
O1—Zn1—O5$^{\rm i}$	86.4 (1)	O9—Zn1—O9$^{\rm ii}$	81.5 (1)
O1—Zn1—O6	87.0 (1)	O9—Zn1—N1	174.1 (1)
O1—Zn1—O9	97.2 (1)	O9$^{\rm ii}$—Zn1—N1	93.1 (1)
O1—Zn1—O9$^{\rm ii}$	175.8 (1)	N1—Zn1—O6	90.4 (1)
O1—Zn1—N1	88.4 (1)	O2—Zn2—O7	106.9 (2)
O5$^{\rm i}$—Zn1—O6	173.3 (1)	O2—Zn2—O9	112.9 (1)
O5$^{\rm i}$—Zn1—O9	90.0 (1)	O2—Zn2—N2$^{\rm iii}$	105.3 (1)
O5$^{\rm i}$—Zn1—O9$^{\rm ii}$	97.6 (1)	O7—Zn2—O9	110.5 (1)
O5$^{\rm i}$—Zn1—N1	88.4 (1)	O7—Zn2—N2$^{\rm iii}$	105.8 (1)
O6—Zn1—O9	91.9 (1)	O9—Zn2—N2$^{\rm iii}$	114.9 (1)
O6—Zn1—O9$^{\rm ii}$	89.1 (1)		

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $1 + x, y, 1 + z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9o···O4$^{\rm i}$	0.98	1.83	2.701 (4)	147
O1w—H1w1···O4	0.88	1.92	2.798 (9)	176
O1w—H1w2···O4$^{\rm iv}$	0.88	2.02	2.902 (9)	176

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

The bipyridine unit is found to be disordered; both the pyridyl rings have two orientations, each with an occupancy of 0.5. The disorder involves the *ortho* and *meta* C atoms but not the N or the *para* C atoms (*i.e.* the two N and two *para* C atoms have full occupancy). The eight N—C distances were restrained to be within ±0.01 Å of each other; the C—C distances in the rings were restrained to 1.39 (1) Å. The anisotropic displacement parameters of the disordered C atoms were set equal to each other. In addition, the pyridyl rings were restrained to be approximately planar. One of the carboxyphenoxyacetate units is disordered across a centre of inversion; the inversion centre is midway between the atoms C23 and C24. For this unit, the carboxyl group (O6/O7/C20) has full site occupancy whereas the other atoms have half occupancies. The aromatic ring of each of the dicarboxylate units was refined as a rigid hexagon (C—C = 1.39 Å). Owing to the degree of disorder, all C atoms were restrained to vibrate in an approximately isotropic manner. The H atoms were placed in calculated positions [aromatic C—H = 0.93 Å, aliphatic C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)], and were included in the refinement in the riding model approximation. The solvent water molecule is probably disordered, but the disorder could not be modelled. Instead, the vibration was treated as being nearly isotropic. The water H atoms could not be located, and were instead placed in chemically sensible positions with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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