metal-organic compounds

Poly[μ_6-benzene-1,2,4,5-tetracarboxylato-κ^6O^1:O^2:$O^{2'}$:O^4:O^5:$O^{5'}$-bis[diaquazinc(II)]]

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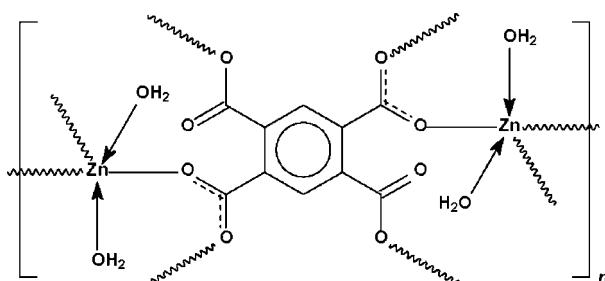
The benzenetetracarboxylate tetraanion in the title compound, $[Zn_2(C_8H_2O_8)(H_2O)_4]_n$, lies on a center of inversion. Two delocalized carboxylate $-CO_2$ groups are each connected to two different diaquazinc units, whereas the other two localized carboxylate $-CO_2$ are each bonded to one different diaquazinc unit. The metal atom is five-coordinate as a consequence of such μ_6-bridging; the water molecules occupy an axial and an equatorial site of the trigonal bipyramid in the three-dimensional network. The architecture is further consolidated by extensive hydrogen bonding in which one water molecule serves as a donor and the other as both a donor and an acceptor.
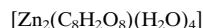
Related literature

For the structure of *catena*-poly[μ_5-1,2,4,5-benzenetetracarboxylato-pentaaquadizinc(II)], which has one Zn atom in a tetrahedral and the other in an octahedral coordination geometry, see: Robl (1987); Wei *et al.* (1991).

Experimental

Crystal data

$[Zn_2(C_8H_2O_8)(H_2O)_4]$	$V = 693.1$ (2) Å³
$M_r = 452.92$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.259$ (1) Å	$\mu = 3.53$ mm⁻¹
$b = 16.342$ (1) Å	$T = 295$ (2) K
$c = 8.143$ (1) Å	$0.29 \times 0.25 \times 0.21$ mm
$\beta = 97.939$ (1)°	

Data collection

Bruker APEX area-detector diffractometer	3774 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1362 independent reflections
	1284 reflections with $I > 2\sigma(I)$
$T_{min} = 0.428$, $T_{max} = 0.524$ (expected range = 0.389–0.477)	$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	5 restraints
$wR(F^2) = 0.066$	All H-atom parameters refined
$S = 1.06$	$\Delta\rho_{max} = 0.41$ e Å⁻³
1362 reflections	$\Delta\rho_{min} = -0.46$ e Å⁻³
130 parameters	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1w—H1$\cdots$O2	0.85 (1)	2.08 (4)	2.745 (2)	134 (5)
O1w—H2$\cdots$O4^i	0.85 (1)	1.96 (1)	2.767 (2)	159 (3)
O2w—H3$\cdots$O1w^{ii}	0.85 (1)	1.91 (1)	2.744 (2)	168 (3)
O2w—H4$\cdots$O4^i	0.85 (1)	1.89 (1)	2.724 (2)	172 (3)

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + 1, y, z$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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supplementary materials

Poly[μ_6-benzene-1,2,4,5-tetracarboxylato-κ^6O^1:O^2:$O^{2'}$:O^4:O^5:$O^{5'}$-bis[diaquazinc(II)]]

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Comment

The are many crystallographic studies of coordination compounds of 1,2,4,5-benzenetetracarboxylic acid (Cambridge Structural Database, Version 5.28, Nov. 2006); a water-coordinated zinc derivative with zinc in both tetrahedral and octahedral geometries has been reported (Robl, 1987; Wei *et al.*, 1991). A slight variation of the synthesis has yielded the title diaquazinc compound, which features a trigonal-bipyramidal zinc coordination environment (Scheme I; Fig. 1).

Experimental

Benzene-1,2,4,5-tetracarboxylic acid (0.05 g, 0.22 mmol), zinc acetate (0.062 g, 0.20 mmol) and sodium hydroxide (0.08 g, 0.20 mmol) were heated in acetonitrile (25 ml) until the reagents dissolved completely. The solution was filtered; diethyl ether was layered over the solution, which was kept in a closed container. Crystals were obtained after a week.

Refinement

All hydrogen atoms were located in difference Fourier maps, and were refined with distance restraints of C–H 0.95±0.01 Å and O–H 0.85±0.01 Å. Their temperature factors were freely refined.

Figures
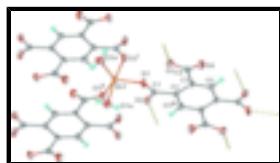
Fig. 1. **Figure 1**. Thermal ellipsoid plot of a portion of the polymeric structure. Displacement ellipsoids are drawn at the 70% probabability level, and H atoms as spheres of arbitrary radii. [Symmetry codes (i): $1/2 + x$, $3/2 - y$, $1/2 + z$; (ii) $x - 1/2$, $3/2 - y$, $1/2 + z$.]

Poly[μ6-benzene-1,2,4,5-tetracarboxylato- κ^6O^1:O^2:$O^{2'}$:O^4:O^5:$O^{5'}$-bis[diaquazinc(II)]]

Crystal data

[Zn$_2$(C$_8$H$_2$O$_8$)(H$_2$O)$_4$]	F_{000} = 452
M_r = 452.92	D_x = 2.170 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2515 reflections
a = 5.259 (1) Å	θ = 2.5–26.1º
b = 16.342 (1) Å	μ = 3.53 mm^{-1}
c = 8.143 (1) Å	T = 295 (2) K
β = 97.939 (1)º	Block, colorless

$V = 693.1\ (2)\ \text{Å}^3$

$Z = 2$

$0.29 \times 0.25 \times 0.21$ mm

Data collection

Bruker APEX area-detector diffractometer	1362 independent reflections
Radiation source: fine-focus sealed tube	1284 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.028$
$T = 295(2)$ K	$\theta_{max} = 26.1°$
φ and ω scans	$\theta_{min} = 2.5°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -6 \rightarrow 5$
$T_{min} = 0.428$, $T_{max} = 0.524$	$k = -19 \rightarrow 16$
3774 measured reflections	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.024$	All H-atom parameters refined
$wR(F^2) = 0.066$	$w = 1/[\sigma^2(F_o{}^2) + (0.0414P)^2 + 0.1318P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
1362 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
130 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
5 restraints	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.030 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Zn1	0.64624 (4)	0.66722 (1)	0.6294 (1)	0.0154 (1)
O1	0.6293 (3)	0.78505 (9)	0.57696 (18)	0.0215 (3)
O2	0.4252 (3)	0.79266 (9)	0.31917 (17)	0.0190 (3)
O3	0.9206 (3)	0.87008 (9)	0.28756 (18)	0.0199 (3)
O4	0.9313 (3)	0.99480 (9)	0.18210 (18)	0.0230 (3)
O1w	0.3378 (3)	0.6354 (1)	0.4158 (2)	0.0230 (3)
O2w	0.8804 (3)	0.5957 (1)	0.5220 (2)	0.0271 (4)
C1	0.5300 (4)	0.8244 (1)	0.4509 (3)	0.0145 (4)
C2	0.5241 (4)	0.9156 (1)	0.4733 (2)	0.0132 (4)
C3	0.6670 (4)	0.9715 (1)	0.3922 (2)	0.0142 (4)
C4	0.8534 (4)	0.9442 (1)	0.2782 (2)	0.0148 (4)
C5	0.6398 (4)	1.0548 (1)	0.4197 (2)	0.0155 (4)
H1	0.308 (11)	0.672 (3)	0.341 (5)	0.15 (3)*

H2	0.372 (5)	0.591 (1)	0.370 (3)	0.04 (1)*
H3	1.008 (4)	0.612 (2)	0.478 (3)	0.04 (1)*
H4	0.795 (5)	0.564 (2)	0.452 (3)	0.04 (1)*
H5	0.748 (4)	1.091 (1)	0.371 (3)	0.03 (1)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0175 (2)	0.0122 (2)	0.0172 (2)	−0.0011 (1)	0.0051 (1)	0.0004 (1)
O1	0.033 (1)	0.012 (1)	0.018 (1)	−0.001 (1)	−0.004 (1)	0.001 (1)
O2	0.024 (1)	0.014 (1)	0.018 (1)	0.001 (1)	−0.003 (1)	−0.003 (1)
O3	0.024 (1)	0.016 (1)	0.022 (1)	0.006 (1)	0.010 (1)	0.000 (1)
O4	0.028 (1)	0.020 (1)	0.024 (1)	0.001 (1)	0.014 (1)	0.004 (1)
O1w	0.026 (1)	0.019 (1)	0.025 (1)	0.002 (1)	0.006 (1)	0.003 (1)
O2w	0.019 (1)	0.031 (1)	0.033 (1)	−0.004 (1)	0.009 (1)	−0.014 (1)
C1	0.014 (1)	0.014 (1)	0.017 (1)	0.001 (1)	0.004 (1)	0.000 (1)
C2	0.015 (1)	0.012 (1)	0.013 (1)	0.002 (1)	0.000 (1)	0.000 (1)
C3	0.016 (1)	0.013 (1)	0.014 (1)	0.002 (1)	0.003 (1)	0.001 (1)
C4	0.014 (1)	0.016 (1)	0.015 (1)	0.000 (1)	0.001 (1)	−0.002 (1)
C5	0.019 (1)	0.014 (1)	0.015 (1)	−0.001 (1)	0.004 (1)	0.001 (1)

Geometric parameters (Å, °)

Zn1—O1	1.972 (2)	O1w—H2	0.85 (1)
Zn1—O2^i	2.084 (1)	O2w—H3	0.85 (1)
Zn1—O3^{ii}	1.965 (1)	O2w—H4	0.85 (1)
Zn1—O1w	2.269 (2)	C1—C2	1.502 (3)
Zn1—O2w	1.986 (2)	C2—C5^{iii}	1.394 (3)
O1—C1	1.262 (3)	C2—C3	1.404 (3)
O2—C1	1.249 (3)	C3—C5	1.390 (3)
O3—C4	1.261 (2)	C3—C4	1.508 (2)
O4—C4	1.246 (2)	C5—C2^{iii}	1.394 (3)
O1w—H1	0.85 (1)	C5—H5	0.94 (1)
O3^{ii}—Zn1—O1	115.55 (6)	Zn1—O2w—H4	110 (2)
O3^{ii}—Zn1—O2w	125.00 (7)	H3—O2w—H4	106 (3)
O1—Zn1—O2w	119.44 (7)	O2—C1—O1	124.8 (2)
O3^{ii}—Zn1—O2^i	92.21 (6)	O2—C1—C2	120.2 (2)
O1—Zn1—O2^i	81.92 (6)	O1—C1—C2	114.9 (2)
O2w—Zn1—O2^i	95.49 (6)	C5^{iii}—C2—C3	119.0 (2)
O3^{ii}—Zn1—O1w	89.93 (6)	C5^{iii}—C2—C1	116.5 (2)
O1—Zn1—O1w	92.96 (6)	C3—C2—C1	124.5 (2)
O2w—Zn1—O1w	87.07 (6)	C5—C3—C2	119.2 (2)
O2^i—Zn1—O1w	174.88 (6)	C5—C3—C4	118.6 (2)
C1—O1—Zn1	132.5 (1)	C2—C3—C4	122.2 (2)
C1—O2—Zn1^{iv}	133.5 (1)	O4—C4—O3	124.2 (2)
C4—O3—Zn1^v	116.6 (1)	O4—C4—C3	119.3 (2)

Zn1—O1w—H1	116 (4)	O3—C4—C3	116.5 (2)
Zn1—O1w—H2	111 (2)	C3—C5—C2^{iii}	121.8 (2)
H1—O1w—H2	109 (4)	C3—C5—H5	118 (2)
Zn1—O2w—H3	126 (2)	C2^{iii}—C5—H5	120 (2)
O3^{ii}—Zn1—O1—C1	−105.7 (2)	C5^{iii}—C2—C3—C5	−0.6 (3)
O2w—Zn1—O1—C1	73.9 (2)	C1—C2—C3—C5	178.2 (2)
O2^{i}—Zn1—O1—C1	165.7 (2)	C5^{iii}—C2—C3—C4	178.4 (2)
O1w—Zn1—O1—C1	−14.4 (2)	C1—C2—C3—C4	−2.9 (3)
Zn1^{iv}—O2—C1—O1	155.2 (2)	Zn1^{v}—O3—C4—O4	−3.8 (3)
Zn1^{iv}—O2—C1—C2	−19.4 (3)	Zn1^{v}—O3—C4—C3	176.3 (1)
Zn1—O1—C1—O2	−4.4 (3)	C5—C3—C4—O4	−16.9 (3)
Zn1—O1—C1—C2	170.4 (1)	C2—C3—C4—O4	164.1 (2)
O2—C1—C2—C5^{iii}	106.5 (2)	C5—C3—C4—O3	163.0 (2)
O1—C1—C2—C5^{iii}	−68.6 (2)	C2—C3—C4—O3	−15.9 (3)
O2—C1—C2—C3	−72.3 (3)	C2—C3—C5—C2^{iii}	0.6 (3)
O1—C1—C2—C3	112.6 (2)	C4—C3—C5—C2^{iii}	−178.4 (2)

Symmetry codes: (i) $x+1/2$, $−y+3/2$, $z+1/2$; (ii) $x−1/2$, $−y+3/2$, $z+1/2$; (iii) $−x+1$, $−y+2$, $−z+1$; (iv) $x−1/2$, $−y+3/2$, $z−1/2$; (v) $x+1/2$, $−y+3/2$, $z−1/2$.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1w—H1⋯O1^{iv}	0.85 (1)	2.33 (3)	3.109 (2)	152 (6)
O1w—H1⋯O2	0.85 (1)	2.08 (4)	2.745 (2)	134 (5)
O1w—H2⋯O4^{vi}	0.85 (1)	1.96 (1)	2.767 (2)	159 (3)
O2w—H3⋯O1w^{vii}	0.85 (1)	1.91 (1)	2.744 (2)	168 (3)
O2w—H4⋯O4^{vi}	0.85 (1)	1.89 (1)	2.724 (2)	172 (3)

Symmetry codes: (iv) $x−1/2$, $−y+3/2$, $z−1/2$; (vi) $−x+3/2$, $y−1/2$, $−z+1/2$; (vii) $x+1$, y, z.

Fig. 1