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Poly[bis(1,3-dimethyl-1,3-diazinan-2-one)(2,5-dioxidoterephthalato)-zirconium(IV)]

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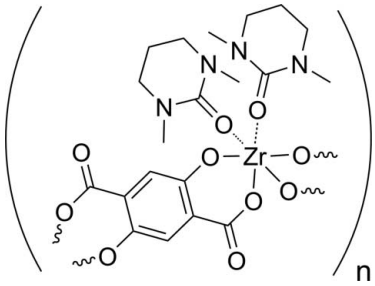
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.038; wR factor = 0.096; data-to-parameter ratio = 18.2.

In the title coordination polymer, $[Zr(C_8H_2O_6)(C_6H_{12}N_2O)_2]_n$, the Zr^{IV} atom, which lies on a crystallographic twofold rotation axis, is coordinated by two O,O'-bidentate 2,5-dioxidoterephthalate ($DHTP^{4-}$) ligands and two O-bonded 1,3-dimethyl-1,3-diazinan-2-one (DMPU) ligands (the latter in a *cis* orientation) in a distorted ZrO_6 octahedral geometry. The deprotonated hydroxy and carboxy O atoms of the $DHTP^{4-}$ ligand chelate the Zr^{IV} ion *via* a six-membered ring; the dihedral angle between the carboxylate group and the aromatic ring is 19.94 (11)°. The $DHTP^{4-}$ ligand is completed by crystallographic inversion symmetry and coordinates to two Zr^{IV} atoms, thereby forming polymeric zigzag chains propagating in the c-axis direction.

Related literature

For examples of DHTP-containing MOFs, see: Dietzel *et al.* (2005, 2006). For examples of zirconium MOFs, see: Chavan *et al.* (2012). For a related structure, see: Maercz *et al.* (2013).



Experimental

Crystal data

$[Zr(C_8H_2O_6)(C_6H_{12}N_2O)_2]$
M_r = 541.67
Monoclinic, $C2/c$
a = 18.761 (2) Å
b = 8.4049 (10) Å
c = 14.8816 (17) Å
β = 102.239 (1)°
V = 2293.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.53 mm^{-1}
T = 293 K
0.10 × 0.08 × 0.06 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.949, T_{max} = 0.969
8477 measured reflections
2730 independent reflections
2437 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.07
2730 reflections
150 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zr1—O1	2.0955 (18)	Zr3—O3	2.0203 (17)
Zr2—O2	2.0723 (18)		

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7026).

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supporting information

Acta Cryst. (2013). E**69**, m153 [doi:10.1107/S1600536813003437]

Poly[bis(1,3-dimethyl-1,3-diazinan-2-one)(2,5-dioxidoterephthalato)zirconium(IV)]

Matthias Maercz, David Stephen Wragg, Pascal Daniel Croumbie Dietzel and Helmer Fjellvåg

S1. Comment

The title compound was synthesized as a part of a larger project (see also Maercz *et al.*, 2013), in which the possibility to form new zirconium containing metal organic frameworks (MOFs) using the linker 2,5-dihydroxyterephthalic acid (DHTP) was investigated. Zirconium containing MOFs (Chavan *et al.*, 2012) using terephthalic acid have shown extraordinary thermal stability whereas DHTP containing MOFs (Dietzel *et al.*, 2005, 2006) have shown remarkable sorption properties.

S2. Experimental

Zirconium(IV) chloride (0.047 g, 0.2 mmol) and 2,5-dihydroxyterephthalic acid (0.040 g, 0.2 mmol) were dissolved in 5 ml *N,N′*-dimethylpropylene urea (DMPU) in a Teflon liner of 23 ml volume under inert atmosphere in a glovebox. The teflon liner was sealed and put into a steel autoclave. The mixture was reacted for 3 d at 160°C. Reaction yielded a brown substance consisting of block shaped crystals and a white impurity. The product was collected by filtration, washed with DMPU and dried over night at room temperature in ambient atmosphere.

S3. Refinement

Hydrogen atoms were placed geometrically in ideal positions and refined using a riding model, the U_{iso} set to 1.5 times the thermal parameter of the carbon atom to which they are attached for methyl groups and 1.2 times for other hydrogen atoms.

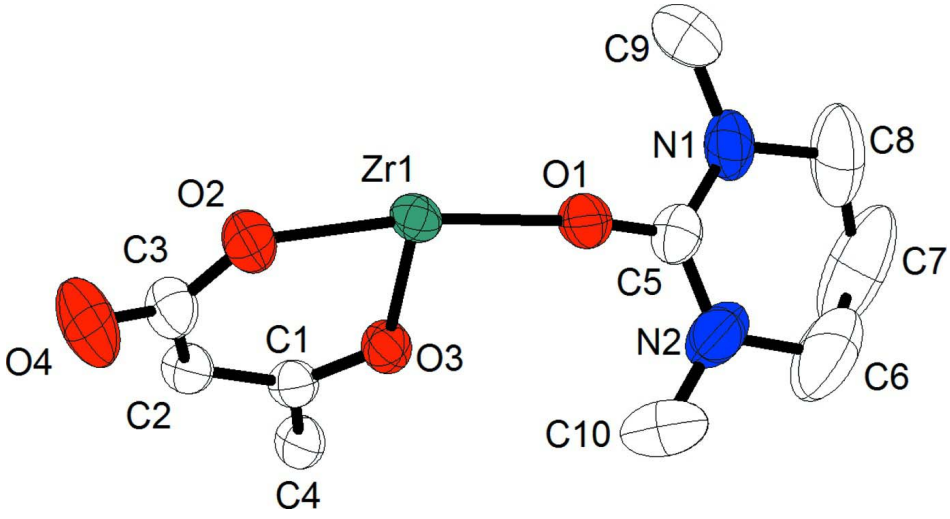

Figure 1

The asymmetric unit of the title compound with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

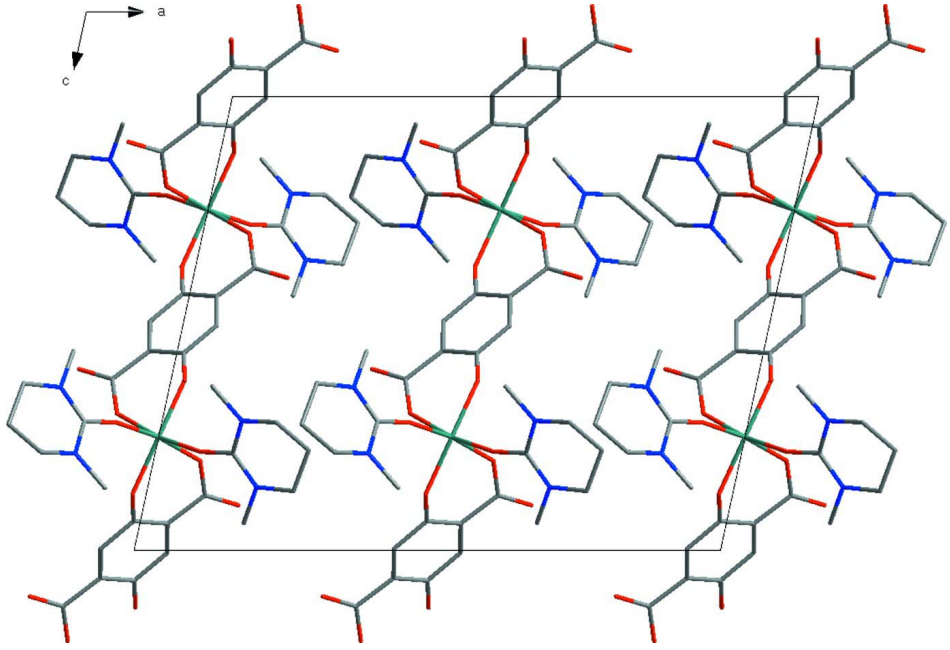

Figure 2

Packing diagram of the title compound viewed along the *b* axis. Hydrogen atoms are omitted for clarity.

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c = 14.8816 (17) Å
β = 102.239 (1)°
V = 2293.3 (5) Å^3
Z = 4
F(000) = 1112
D_x = 1.569 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 2840 reflections
θ = 2.8–24.3°
μ = 0.53 mm^{-1}
T = 293 K
Block, colourless
0.10 × 0.08 × 0.06 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.949, T_{max} = 0.969
8477 measured reflections
2730 independent reflections
2437 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.8°, θ_{min} = 2.2°
h = −24→25
k = −10→10
l = −19→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.07
2730 reflections
150 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 2.0694P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.01168 (12)	0.8750 (3)	0.06523 (15)	0.0370 (5)
C2	−0.04708 (11)	0.9809 (3)	0.06010 (16)	0.0389 (5)
C3	−0.10053 (13)	0.9651 (4)	0.12208 (19)	0.0494 (6)
C4	0.05755 (12)	0.8979 (3)	0.00446 (16)	0.0409 (5)
H4	0.0968	0.8292	0.0072	0.049*
C5	0.13245 (14)	0.4514 (3)	0.28509 (18)	0.0460 (6)
C6	0.1951 (3)	0.2463 (6)	0.2172 (4)	0.1152 (19)
H6A	0.1811	0.1438	0.2380	0.138*
H6B	0.2043	0.2328	0.1559	0.138*
C7	0.2608 (3)	0.3007 (6)	0.2785 (6)	0.137 (3)
H7A	0.2813	0.3874	0.2491	0.164*
H7B	0.2961	0.2146	0.2880	0.164*
C8	0.25001 (19)	0.3551 (5)	0.3685 (4)	0.0998 (15)

H8A	0.2447	0.2635	0.4061	0.120*
H8B	0.2927	0.4139	0.3993	0.120*
C9	0.1770 (2)	0.5490 (5)	0.4385 (2)	0.0860 (12)
H9A	0.2201	0.5396	0.4862	0.129*
H9B	0.1357	0.5104	0.4607	0.129*
H9C	0.1694	0.6587	0.4211	0.129*
C10	0.0730 (3)	0.3413 (7)	0.1388 (3)	0.1198 (18)
H10A	0.0849	0.2712	0.0932	0.180*
H10B	0.0594	0.4435	0.1117	0.180*
H10C	0.0331	0.2977	0.1617	0.180*
N1	0.18563 (12)	0.4566 (3)	0.35990 (19)	0.0583 (6)
N2	0.13613 (17)	0.3589 (3)	0.2142 (2)	0.0732 (8)
O1	0.07673 (10)	0.5374 (2)	0.28218 (12)	0.0532 (5)
O2	−0.07967 (9)	0.8873 (2)	0.19808 (13)	0.0519 (5)
O3	0.02342 (9)	0.7526 (2)	0.12481 (12)	0.0424 (4)
O4	−0.16069 (11)	1.0250 (4)	0.10048 (17)	0.0870 (9)
Zr1	0.0000	0.72101 (4)	0.2500	0.03776 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0321 (10)	0.0424 (14)	0.0359 (11)	0.0017 (9)	0.0060 (8)	−0.0032 (9)
C2	0.0295 (10)	0.0489 (15)	0.0387 (12)	0.0026 (10)	0.0086 (9)	−0.0011 (10)
C3	0.0397 (13)	0.0587 (17)	0.0531 (15)	0.0122 (12)	0.0173 (11)	0.0085 (12)
C4	0.0306 (10)	0.0495 (15)	0.0432 (12)	0.0076 (10)	0.0095 (9)	0.0001 (10)
C5	0.0470 (13)	0.0399 (14)	0.0542 (15)	0.0022 (11)	0.0176 (11)	0.0035 (11)
C6	0.145 (5)	0.082 (3)	0.140 (5)	0.039 (3)	0.078 (4)	−0.006 (3)
C7	0.083 (3)	0.077 (3)	0.277 (9)	0.013 (2)	0.098 (5)	−0.021 (4)
C8	0.0489 (19)	0.069 (3)	0.169 (5)	0.0175 (18)	−0.004 (2)	0.017 (3)
C9	0.086 (2)	0.094 (3)	0.062 (2)	0.013 (2)	−0.0200 (18)	−0.0037 (19)
C10	0.172 (5)	0.107 (4)	0.069 (3)	0.012 (4)	0.001 (3)	−0.037 (3)
N1	0.0422 (12)	0.0490 (15)	0.0787 (17)	0.0082 (10)	0.0014 (11)	0.0044 (12)
N2	0.097 (2)	0.0551 (17)	0.0735 (18)	0.0136 (16)	0.0320 (16)	−0.0102 (14)
O1	0.0458 (10)	0.0629 (13)	0.0478 (10)	0.0151 (9)	0.0028 (8)	−0.0043 (9)
O2	0.0445 (9)	0.0666 (13)	0.0492 (10)	0.0150 (9)	0.0205 (8)	0.0134 (9)
O3	0.0408 (9)	0.0467 (11)	0.0410 (9)	0.0073 (7)	0.0117 (7)	0.0035 (7)
O4	0.0529 (12)	0.134 (2)	0.0840 (16)	0.0459 (14)	0.0373 (11)	0.0487 (16)
Zr1	0.03075 (17)	0.0470 (2)	0.03504 (18)	0.000	0.00586 (12)	0.000

Geometric parameters (Å, º)

C1—O3	1.346 (3)	C7—H7B	0.9700
C1—C4	1.388 (3)	C8—N1	1.462 (4)
C1—C2	1.406 (3)	C8—H8A	0.9700
C2—C4^{i}	1.386 (3)	C8—H8B	0.9700
C2—C3	1.505 (3)	C9—N1	1.442 (4)
C3—O4	1.215 (3)	C9—H9A	0.9600
C3—O2	1.293 (3)	C9—H9B	0.9600

C4—C2^{i}	1.386 (3)	C9—H9C	0.9600
C4—H4	0.9300	C10—N2	1.456 (5)
C5—O1	1.264 (3)	C10—H10A	0.9600
C5—N2	1.325 (4)	C10—H10B	0.9600
C5—N1	1.329 (3)	C10—H10C	0.9600
C6—C7	1.443 (8)	Zr1—O1	2.0955 (18)
C6—N2	1.449 (5)	Zr2—O2	2.0723 (18)
C6—H6A	0.9700	Zr3—O3	2.0203 (17)
C6—H6B	0.9700	Zr1—O3^{ii}	2.0203 (17)
C7—C8	1.470 (8)	Zr1—O2^{ii}	2.0723 (18)
C7—H7A	0.9700	Zr1—O1^{ii}	2.0955 (18)

O3—C1—C4	119.9 (2)	H9A—C9—H9B	109.5
O3—C1—C2	122.5 (2)	N1—C9—H9C	109.5
C4—C1—C2	117.7 (2)	H9A—C9—H9C	109.5
C4^{i}—C2—C1	119.8 (2)	H9B—C9—H9C	109.5
C4^{i}—C2—C3	118.3 (2)	N2—C10—H10A	109.5
C1—C2—C3	121.8 (2)	N2—C10—H10B	109.5
O4—C3—O2	122.2 (2)	H10A—C10—H10B	109.5
O4—C3—C2	120.2 (2)	N2—C10—H10C	109.5
O2—C3—C2	117.6 (2)	H10A—C10—H10C	109.5
C2^{i}—C4—C1	122.5 (2)	H10B—C10—H10C	109.5
C2^{i}—C4—H4	118.7	C5—N1—C9	120.3 (2)
C1—C4—H4	118.7	C5—N1—C8	120.9 (3)
O1—C5—N2	119.4 (3)	C9—N1—C8	118.4 (3)
O1—C5—N1	118.6 (2)	C5—N2—C6	121.8 (4)
N2—C5—N1	122.0 (3)	C5—N2—C10	120.2 (3)
C7—C6—N2	110.9 (4)	C6—N2—C10	116.7 (4)
C7—C6—H6A	109.5	C5—O1—Zr1	162.17 (19)
N2—C6—H6A	109.5	C3—O2—Zr1	136.71 (16)
C7—C6—H6B	109.5	C1—O3—Zr1	132.13 (15)
N2—C6—H6B	109.5	O3—Zr1—O3^{ii}	164.90 (10)
H6A—C6—H6B	108.0	O3—Zr1—O2^{ii}	88.54 (7)
C6—C7—C8	114.2 (4)	O3^{ii}—Zr1—O2^{ii}	81.27 (7)
C6—C7—H7A	108.7	O3—Zr1—O2	81.27 (7)
C8—C7—H7A	108.7	O3^{ii}—Zr1—O2	88.54 (7)
C6—C7—H7B	108.7	O2^{ii}—Zr1—O2	95.19 (12)
C8—C7—H7B	108.7	O3—Zr1—O1^{ii}	99.16 (7)
H7A—C7—H7B	107.6	O3^{ii}—Zr1—O1^{ii}	91.97 (7)
N1—C8—C7	111.9 (4)	O2^{ii}—Zr1—O1^{ii}	171.16 (7)
N1—C8—H8A	109.2	O2—Zr1—O1^{ii}	90.30 (8)
C7—C8—H8A	109.2	O3—Zr1—O1	91.97 (7)
N1—C8—H8B	109.2	O3^{ii}—Zr1—O1	99.16 (7)
C7—C8—H8B	109.2	O2^{ii}—Zr1—O1	90.30 (8)
H8A—C8—H8B	107.9	O2—Zr1—O1	171.16 (7)
N1—C9—H9A	109.5	O1^{ii}—Zr1—O1	85.13 (11)
N1—C9—H9B	109.5		

O3—C1—C2—C4^{i}	−178.2 (2)	C7—C6—N2—C10	164.6 (5)
C4—C1—C2—C4^{i}	0.3 (4)	N2—C5—O1—Zr1	−75.3 (7)
O3—C1—C2—C3	0.7 (4)	N1—C5—O1—Zr1	104.9 (6)
C4—C1—C2—C3	179.2 (2)	O4—C3—O2—Zr1	160.2 (3)
C4^{i}—C2—C3—O4	20.1 (4)	C2—C3—O2—Zr1	−20.1 (4)
C1—C2—C3—O4	−158.8 (3)	C4—C1—O3—Zr1	152.68 (18)
C4^{i}—C2—C3—O2	−159.5 (3)	C2—C1—O3—Zr1	−28.8 (3)
C1—C2—C3—O2	21.6 (4)	C1—O3—Zr1—O3^{ii}	−23.03 (19)
O3—C1—C4—C2^{i}	178.2 (2)	C1—O3—Zr1—O2^{ii}	−70.4 (2)
C2—C1—C4—C2^{i}	−0.3 (4)	C1—O3—Zr1—O2	25.1 (2)
N2—C6—C7—C8	47.7 (6)	C1—O3—Zr1—O1^{ii}	114.0 (2)
C6—C7—C8—N1	−44.6 (6)	C1—O3—Zr1—O1	−160.7 (2)
O1—C5—N1—C9	4.8 (4)	C3—O2—Zr1—O3	0.6 (3)
N2—C5—N1—C9	−175.0 (3)	C3—O2—Zr1—O3^{ii}	169.4 (3)
O1—C5—N1—C8	177.6 (3)	C3—O2—Zr1—O2^{ii}	88.3 (3)
N2—C5—N1—C8	−2.2 (5)	C3—O2—Zr1—O1^{ii}	−98.6 (3)
C7—C8—N1—C5	21.3 (5)	C3—O2—Zr1—O1	−39.9 (6)
C7—C8—N1—C9	−165.7 (4)	C5—O1—Zr1—O3	29.7 (6)
O1—C5—N2—C6	−173.7 (3)	C5—O1—Zr1—O3^{ii}	−140.1 (6)
N1—C5—N2—C6	6.0 (5)	C5—O1—Zr1—O2^{ii}	−58.9 (6)
O1—C5—N2—C10	−7.7 (5)	C5—O1—Zr1—O2	69.6 (9)
N1—C5—N2—C10	172.1 (4)	C5—O1—Zr1—O1^{ii}	128.7 (6)
C7—C6—N2—C5	−28.8 (6)		

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, *y*, −*z*+1/2.