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catena-Poly[[bis(*N*,*N*-dimethylformamide-κO)zinc]-μ_2-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$]

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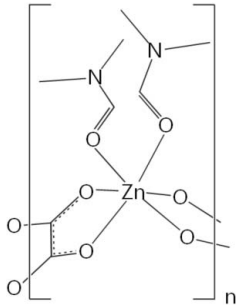
Key indicators: single-crystal synchrotron study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.058; wR factor = 0.169; data-to-parameter ratio = 10.4.

In the crystal structure of the title compound, $[Zn(C_2O_4)(C_3H_7NO)_2]_n$, the Zn^{II} ion is situated on a twofold rotation axis and has a distorted octahedral coordination geometry defined by the O atoms of two dimethylformamide molecules and four O atoms of two bidentate oxalate ligands. The oxalate anion is located on an inversion centre and bridges two metal ions, resulting in a polymeric structure with infinite zigzag chains extending parallel to [010].

Related literature

For related structures, see: Yao *et al.* (2007); van Albada *et al.* (2004); Ghosh *et al.* (2004); Evans & Lin (2001). For a general review on compounds with metal-organic framework structures, see: Czaja *et al.* (2009). For the synthesis of the ligand, see: Yoneda *et al.* (1978).



Experimental

Crystal data

$[Zn(C_2O_4)(C_3H_7NO)_2]$
M_r = 299.58
Orthorhombic, *Pbna*
a = 7.795 (1) Å
b = 9.809 (1) Å
c = 15.421 (1) Å
V = 1179.1 (2) Å^3
Z = 4
Synchrotron radiation
λ = 0.90000 Å
μ = 2.10 mm^{-1}
T = 298 K
0.14 × 0.10 × 0.09 mm

Data collection

ADSC Quantum210 diffractometer
Absorption correction: multi-scan (*HKL-2000 SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.757, T_{max} = 0.833
839 measured reflections
839 independent reflections
778 reflections with $I > 2\sigma(I)$
θ_{max} = 30.4°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.169
S = 1.09
839 reflections
81 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.80 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O2	2.101 (2)	Zn1—O3	2.134 (2)
Zn1—O1	2.104 (2)		

Data collection: *ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (CrystalMaker, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2511).

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catena-Poly[[bis(*N*,*N*-dimethylformamide-κO)zinc]-μ_2-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$]

Ju Eun Lee and Hong-In Lee

S1. Comment

Metal-organic frameworks (MOFs) have been widely investigated for their potential and/or practical applications in catalysis, gas storage, and many others fields (Czaja *et al.*, 2009). We aimed at constructing a new functional MOF material using a conducting organic molecule, *viz* tetrathiafulvalene (TTF) functionalized with carboxylate groups, by the hydro(solvo)thermal method. During synthesis, we unexpectedly discovered a Zn^{II}-oxalate coordination polymer, (I), forming an infinite one-dimensional zigzag chain. We are currently studying the detailed formation mechanism of the compound.

In the structure of compound (I), the Zn^{II} ion lies on a 2-fold axis and is coordinated by four oxygen atoms of the two bridging oxalate groups and two oxygen atoms of DMF solvent molecules, resulting in a distorted octahedral geometry (Fig. 1). The Zn—O_{ox} bond lengths are in the range of 2.101 (2) - 2.104 (2) Å and the Zn—O_{DMF} bond length is 2.134 (2) Å. The bond angles about the Zn^{II} ion range between 78.62 (8) and 98.81 (9)° for *cis* and between 163.08 (9) and 176.23 (11)° for the *trans* ligands (Table 1). The bond angle of O_{ox}—Zn—O_{ox} (78.62 (8)°) is smaller than that of O_{DMF}—Zn—O_{DMF} (86.53 (13)°) due to the five-membered chelate ring strain. The Zn—O bond lengths and the bond angles about Zn^{II} are comparable to those of other reported Zn-oxalate coordination polymers (Yao *et al.*, 2007; van Albada *et al.*, 2004; Ghosh *et al.*, 2004; Evans & Lin, 2001). The Zn-oxalate backbone has a zigzag shape with a Zn—Zn—Zn angle of 126.47 (2)° and a Zn—Zn distance of 5.493 (1) Å. The resulting one-dimensional zigzag chains run parallel to [010] and pack effectively through the inter-wedges of the coordinated DMF ligands (Fig. 2).

S2. Experimental

This experiment was originally intended for synthesis of compounds with metal-organic frameworks, consisting of Zn^{II} ions and tetrathiafulvalene (TTF) functionalized with carboxylate groups [= bis(4-carboxy-1,3-dithiolidene) = 2COOH-TTF]. Bis(4-carboxy-1,3-dithiolidene) was prepared according to literature (Yoneda *et al.* 1978). 2COOH-TTF (0.050 g, 0.17 mmol) and 4,4-bipyridine (0.013 g, 0.098 mmol) were added to 12 ml DMF:H_2O (5:1, *v*/*v*) solution of $[Zn(NO_3)_2]\cdot 6H_2O$ (0.051 g, 0.17 mmol) to be stirred for 10 min. The mixture was sealed in a Pyrex test tube and stored at 358 K for 3 days. After cooled down to room temperature, the mixture was filtered and washed with ethanol. Colorless crystals suitable for X-ray analysis were obtained and were dried in air.

S3. Refinement

All C-bound H atoms were placed in geometrically idealized positions and refined using a riding model with $U_{iso} = 1.5U_{eq}$ and C–H = 0.96 Å for CH_3, and $U_{iso} = 1.2U_{eq}$ and C–H = 0.93 Å for CH.

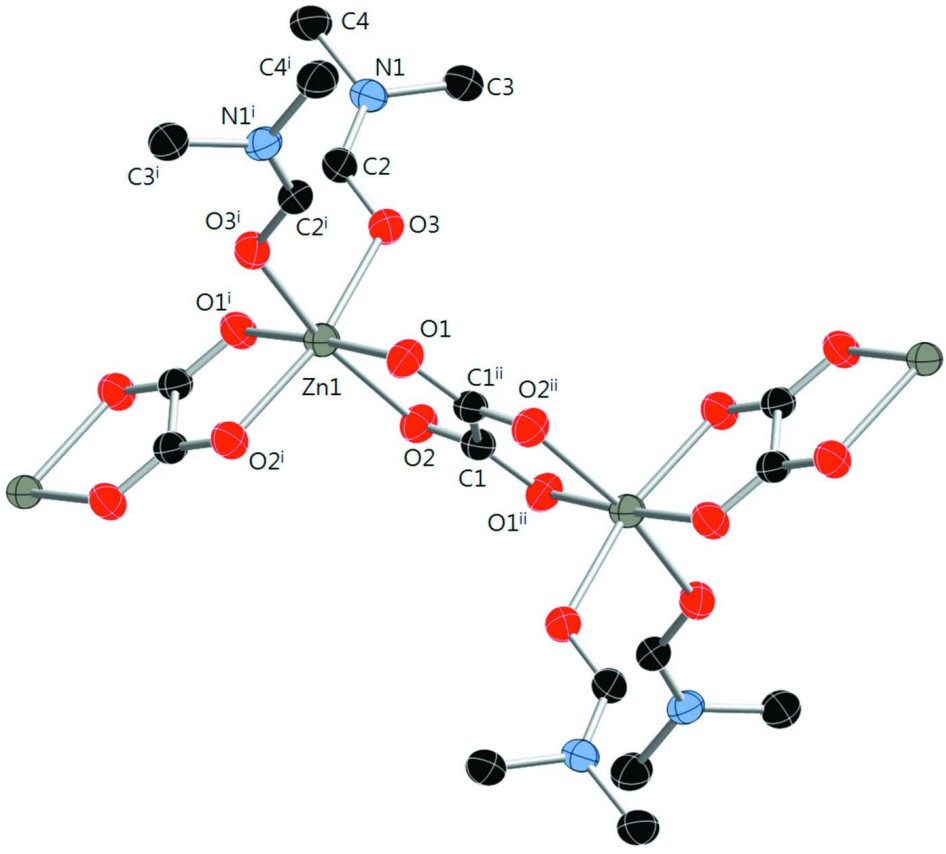

Figure 1

Partial structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. All H atoms are omitted for clarity. Symmetry codes: (i) *x*, -*y* + 3/2, -*z*. (ii) -*x*, -*y* + 1, -*z*.

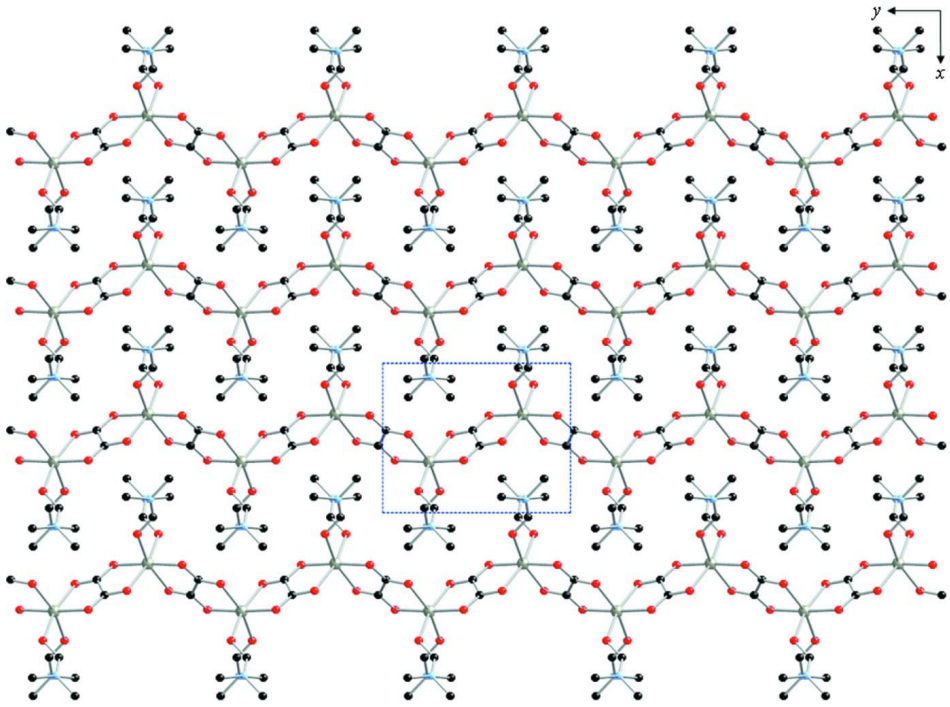

Figure 2

two-dimensional packing structure of the one-dimensional zigzag chains of the title compound viewing along the crystal *z*-direction (gray, Zn; black, C; red, O; blue, N) Dotted box represents the *xy*-plane of the unit cell and *x*-, *y*- directions are denoted by arrows at upper right corner.

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$M_r = 299.58$
Orthorhombic, *Pbna*
Hall symbol: -P 2ac 2b
$a = 7.795$ (1) Å
$b = 9.809$ (1) Å
$c = 15.421$ (1) Å
$V = 1179.1$ (2) Å^3
$Z = 4$
$F(000) = 616$
$D_x = 1.688$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.90000$ Å
Cell parameters from 839 reflections
$\theta = 5.4$–$30.4°$
$\mu = 2.10$ mm^{-1}
$T = 298$ K
Block, colourless
0.14 × 0.10 × 0.09 mm

Data collection

ADSC Quantum210 diffractometer
Radiation source: 6BIMX-I synchroton beamlin PLS, KOREA
Si111 double crystal monochromator
φ scans
Absorption correction: multi-scan (*HKL-2000 SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.757$, $T_{max} = 0.833$
839 measured reflections
839 independent reflections
778 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 30.4°$, $\theta_{min} = 5.4°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.169$
$S = 1.09$
839 reflections
81 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
$w = 1/[\sigma^2(F_o^2) + (0.1443P)^2 + 0.1456P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.034 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.15869 (6)	0.7500	0.0000	0.0503 (6)
O1	0.1498 (3)	0.5678 (2)	0.07184 (15)	0.0600 (8)
O2	−0.0220 (3)	0.6367 (2)	−0.07091 (14)	0.0592 (8)
O3	0.3580 (3)	0.6927 (3)	−0.08757 (15)	0.0599 (8)
N1	0.5920 (4)	0.7617 (2)	−0.1613 (2)	0.0541 (9)
C1	−0.0497 (4)	0.5204 (3)	−0.0417 (2)	0.0498 (9)
C2	0.4708 (5)	0.7774 (4)	−0.1043 (3)	0.0559 (10)
H2	0.4686	0.8590	−0.0737	0.067*
C3	0.6058 (5)	0.6357 (4)	−0.2119 (2)	0.0687 (11)
H3A	0.6896	0.5769	−0.1858	0.103*
H3B	0.6403	0.6571	−0.2701	0.103*
H3C	0.4966	0.5905	−0.2130	0.103*
C4	0.7261 (5)	0.8631 (4)	−0.1751 (3)	0.0741 (11)
H4A	0.7063	0.9400	−0.1379	0.111*
H4B	0.7244	0.8924	−0.2345	0.111*
H4C	0.8358	0.8237	−0.1620	0.111*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0436 (8)	0.0500 (8)	0.0573 (8)	0.000	0.000	0.00088 (15)
O1	0.0572 (14)	0.0566 (14)	0.0661 (16)	−0.0077 (9)	−0.0120 (9)	0.0045 (10)
O2	0.0611 (15)	0.0539 (14)	0.0626 (15)	−0.0058 (9)	−0.0082 (9)	0.0082 (9)

O3	0.0538 (16)	0.0587 (17)	0.0672 (16)	−0.0041 (10)	0.0109 (9)	−0.0060 (12)
N1	0.0432 (19)	0.0546 (18)	0.065 (2)	0.0040 (10)	0.0055 (18)	0.0000 (10)
C1	0.0438 (14)	0.0507 (17)	0.055 (2)	0.0013 (12)	0.0012 (15)	0.0008 (13)
C2	0.051 (2)	0.0531 (17)	0.063 (2)	0.0038 (16)	−0.0031 (17)	−0.0021 (16)
C3	0.060 (2)	0.074 (2)	0.072 (2)	0.0038 (16)	0.0104 (18)	−0.0101 (17)
C4	0.057 (2)	0.065 (2)	0.101 (3)	−0.0029 (15)	0.014 (2)	0.0077 (18)

Geometric parameters (Å, º)

Zn1—O2	2.101 (2)	N1—C3	1.466 (4)
Zn1—O2^{i}	2.101 (2)	C1—O1^{ii}	1.254 (4)
Zn1—O1	2.104 (2)	C1—C1^{ii}	1.554 (6)
Zn1—O1^{i}	2.104 (2)	C2—H2	0.9300
Zn1—O3^{i}	2.134 (2)	C3—H3A	0.9600
Zn1—O3	2.134 (2)	C3—H3B	0.9600
O1—C1^{ii}	1.254 (4)	C3—H3C	0.9600
O2—C1	1.246 (3)	C4—H4A	0.9600
O3—C2	1.237 (5)	C4—H4B	0.9600
N1—C2	1.299 (5)	C4—H4C	0.9600
N1—C4	1.458 (5)		
O2—Zn1—O2^{i}	95.82 (14)	C4—N1—C3	116.4 (3)
O2—Zn1—O1	78.62 (8)	O2—C1—O1^{ii}	127.3 (3)
O2^{i}—Zn1—O1	98.81 (9)	O2—C1—C1^{ii}	116.7 (3)
O2—Zn1—O1^{i}	98.81 (9)	O1^{ii}—C1—C1^{ii}	116.1 (3)
O2^{i}—Zn1—O1^{i}	78.62 (8)	O3—C2—N1	125.3 (4)
O1—Zn1—O1^{i}	176.23 (11)	O3—C2—H2	117.3
O2—Zn1—O3^{i}	163.08 (9)	N1—C2—H2	117.3
O2^{i}—Zn1—O3^{i}	91.12 (9)	N1—C3—H3A	109.5
O1—Zn1—O3^{i}	85.09 (9)	N1—C3—H3B	109.5
O1^{i}—Zn1—O3^{i}	97.67 (9)	H3A—C3—H3B	109.5
O2—Zn1—O3	91.12 (9)	N1—C3—H3C	109.5
O2^{i}—Zn1—O3	163.08 (9)	H3A—C3—H3C	109.5
O1—Zn1—O3	97.67 (9)	H3B—C3—H3C	109.5
O1^{i}—Zn1—O3	85.09 (9)	N1—C4—H4A	109.5
O3^{i}—Zn1—O3	86.53 (13)	N1—C4—H4B	109.5
C1^{ii}—O1—Zn1	114.3 (2)	H4A—C4—H4B	109.5
C1—O2—Zn1	114.36 (19)	N1—C4—H4C	109.5
C2—O3—Zn1	118.2 (2)	H4A—C4—H4C	109.5
C2—N1—C4	122.6 (3)	H4B—C4—H4C	109.5
C2—N1—C3	120.9 (3)		
O2—Zn1—O1—C1^{ii}	0.7 (2)	O2^{i}—Zn1—O3—C2	29.7 (5)
O2^{i}—Zn1—O1—C1^{ii}	94.9 (2)	O1—Zn1—O3—C2	−137.2 (3)
O3^{i}—Zn1—O1—C1^{ii}	−174.7 (2)	O1^{i}—Zn1—O3—C2	45.3 (3)
O3—Zn1—O1—C1^{ii}	−88.9 (2)	O3^{i}—Zn1—O3—C2	−52.7 (2)
O2^{i}—Zn1—O2—C1	−98.8 (2)	Zn1—O2—C1—O1^{ii}	−179.4 (3)
O1—Zn1—O2—C1	−0.9 (2)	Zn1—O2—C1—C1^{ii}	0.9 (4)

O1^{i}—Zn1—O2—C1	−178.1 (2)	Zn1—O3—C2—N1	−174.2 (3)
O3^{i}—Zn1—O2—C1	15.0 (4)	C4—N1—C2—O3	−177.0 (4)
O3—Zn1—O2—C1	96.7 (2)	C3—N1—C2—O3	−0.6 (6)
O2—Zn1—O3—C2	144.1 (3)		

Symmetry codes: (i) x, $-y+3/2$, $-z$; (ii) $-x$, $-y+1$, $-z$.