metal-organic compounds

Poly[(μ₆-benzene-1,3,5-tricarboxylato-κ⁶O^1:$O^{1'}$:O^3:$O^{3'}$:O^5:$O^{5'}$)tris(N,N-dimethylformamide-κO)tris(μ₃-formato-κ³O:O:O')trizinc(II)]

Jaeung Sim, Taemin Kim and Jin Kuk Yang*

Department of Chemistry, Soongsil University, 369 Sangdo-Ro, Dongjak-Gu, Seoul 156-743, Republic of Korea
Correspondence e-mail: jinkukyang@ssu.ac.kr

The asymmetric unit of the title compound, $[Zn_3(HCO_2)_3$-$(C_9H_3O_6)(C_3H_7NO)_3]_n$, contains one Zn ion, one formate ligand, one N,N-dimethylformamide (DMF) ligand and one-third of a benzene-1,3,5-tricarboxylate (btc) ligand situated on a crystallographic 3 axis. Each Zn^{II} atom is coordinated by one O atom from a DMF ligand, two O atoms from two btc ligands and three O atoms from three formate ligands in a distorted octahedral geometry. The Zn^{II} atoms are connected by the formate and btc ligands, forming hexanuclear cores, which are linked by btc ligands, constructing a two-dimensional layered network along the ab plane.

Related literature

For general background to compounds with metal-organic frameworks, see: Eddaoudi et al. (2000)·The crystal structures of isotypic compounds with Ni^{II} and Mg^{II} were reported by Maniam & Stock (2011) and Yeh et al. (2010), respectively.
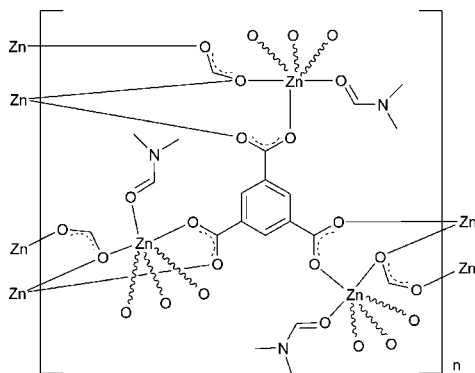
Experimental

Crystal data

$[Zn_3(HCO_2)_3(C_9H_3O_6)(C_3H_7NO)_3]$	Z = 2
M_r = 757.56	Mo Kα radiation
Trigonal, $P\bar{3}$	μ = 2.76 mm⁻¹
a = 13.8594 (17) Å	T = 153 K
c = 8.0100 (14) Å	0.10 × 0.02 × 0.02 mm
V = 1332.5 (4) ų	

Data collection

Bruker SMART APEX CCD diffractometer	7964 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2027 independent reflections
T_{min} = 0.770, T_{max} = 0.947	1563 reflections with I > 2σ(I)
	R_{int} = 0.153

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040	127 parameters
$wR(F^2)$ = 0.089	H-atom parameters constrained
S = 0.81	$\Delta\rho_{max}$ = 0.72 e Å⁻³
2027 reflections	$\Delta\rho_{min}$ = −0.79 e Å⁻³

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (CrystalMaker, 2013); 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: CV5429).

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supporting information

Poly[(*μ*₆-benzene-1,3,5-tricarboxylato-*κ*⁶*O*¹:*O*¹′:*O*³:*O*³′:*O*⁵:*O*⁵′)tris(*N,N*-di-methylformamide-*κO*)tris(*μ*₃-formato-*κ*³*O*:*O*:*O*′)trizinc(II)]

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S1. Comment

Solvothermal reactions between Zn^{II} ion and simple organic ligands such as benzene-1,4-dicarboxylic acid (H_2BDC) and benzene-1,3,5-tricarboxylic acid (H_3BTC) produce prototype metal-organic frameworks known as MOF-2, MOF-3, MOF-4, and MOF-5 (Eddaoudi *et al.*, 2000). Among them, MOF-4 formulated as $[Zn_2(BTC)(NO_3)](C_2H_5OH)_5(H_2O)$ has dinuclear zinc clusters that are held by three carboxylate groups from three distinct BTC ligands. In our trials to make a metal-organic framework composed of Zn^{II} paddle-wheel clusters and BTC, the title compound was obtained as single crystals. During a solvothermal reaction, decomposition of *N,N*-dimethylformamide produced formate which became a component of the title compound.

The title compound, (I) (Fig. 1), is isostructural to the related compounds with Ni^{II} (Maniam & Stock, 2011) and Mg^{II} (Yeh *et al.*, 2010). The crystal packing of (I) is shown in Figs. 2 & 3.

S2. Experimental

The title compound was obtained by a solvothermal reaction between zinc(II) nitrate tetrahydrate (0.157 g, 0.60 mmol) and benzene-1,3,5-tricarboxylic acid (0.084 g, 0.40 mmol) in *N,N*-dimethylformamide (2.0 ml). When a sealed glass tube containing the reaction mixture was heated at 130 °C and for 24 h, the title compound was produced as colorless hexagonal columnar crystals.

S3. Refinement

Hydrogen atoms were placed at calculated positions (C—H = 0.95–0.98 Å) and refined as riding, with $U_{iso}(H) = 1.2$–1.5 $U_{eq}(C)$.
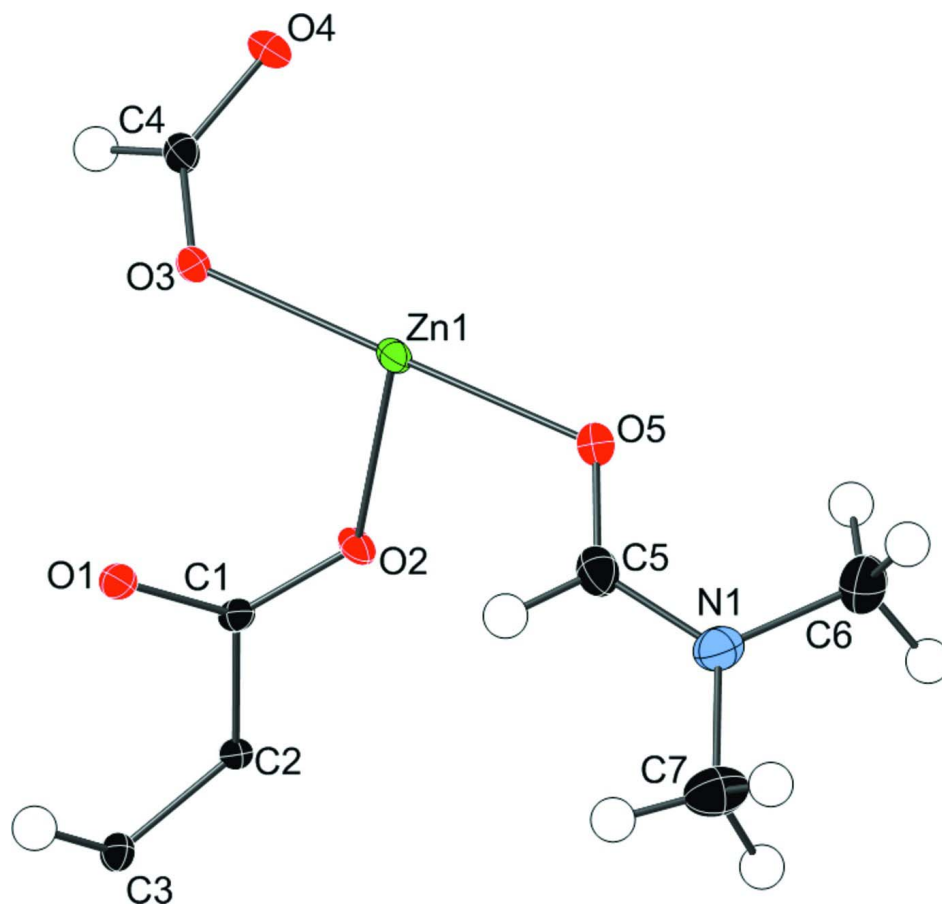
Figure 1

A content of the asymmetric unit of (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented with empty balls without labels.
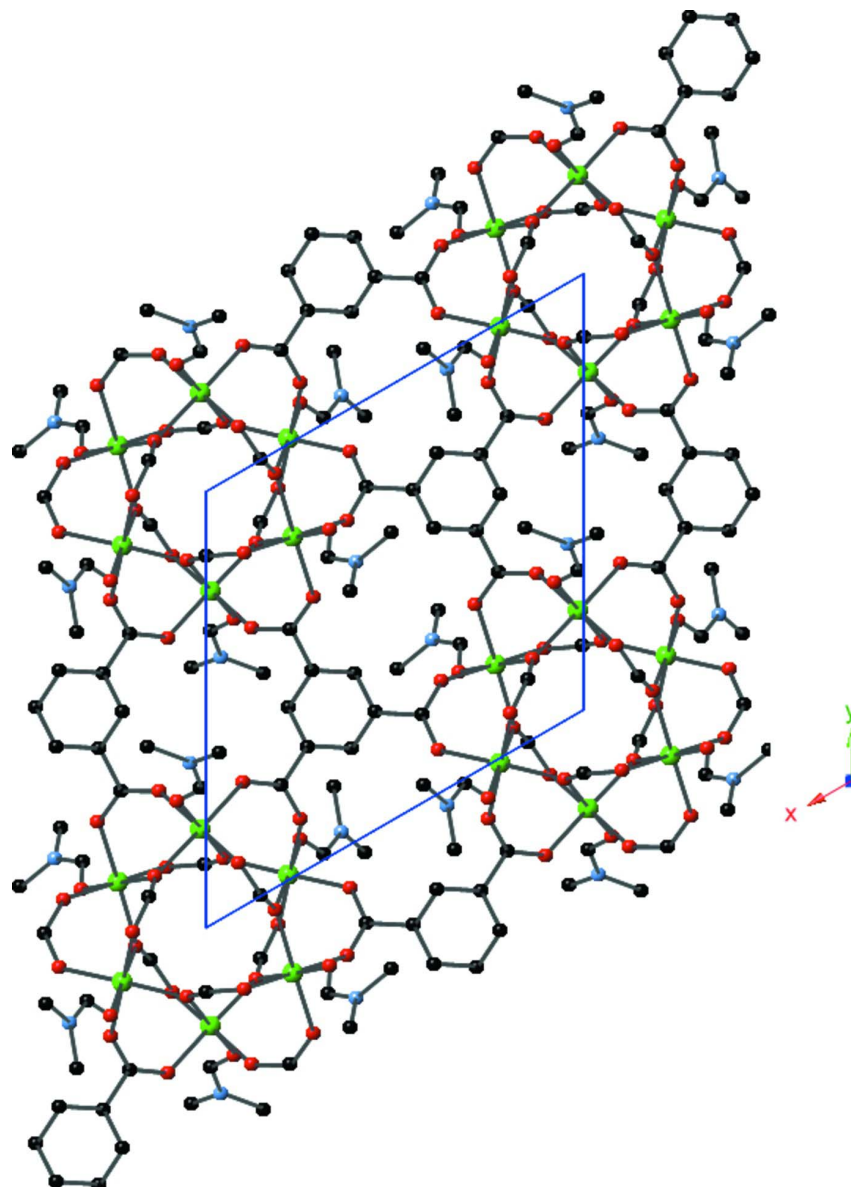
Figure 2
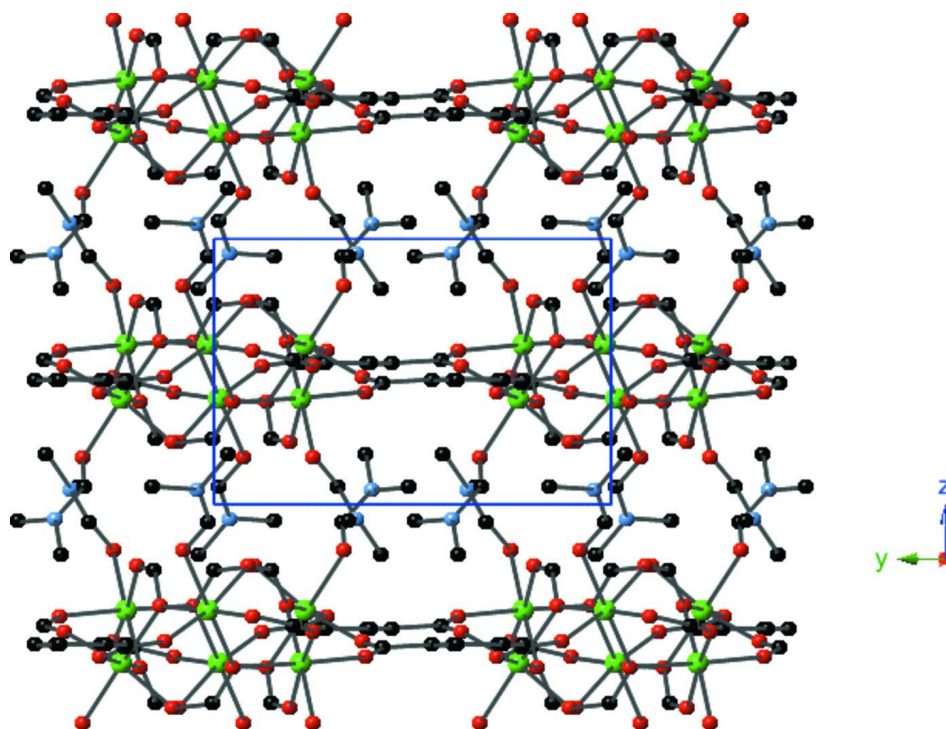A portion of the packing diagram of (I) viewed along the *c* aixs.

Figure 3

A portion of the packing diagram of (I) viewed along the *a* aixs.

Poly[(*μ*₆-benzene-1,3,5-tricarboxylato-*κ*⁶*O*¹:*O*¹′:*O*³:*O*³′:*O*⁵:*O*⁵′)tris(*N,N*-dimethylformamide-*κO*)tris(*μ*₃-formato-*κ*³*O*:*O*:*O*′)trizinc(II)]

Crystal data

[Zn₃(HCO₂)₃(C₉H₃O₆)(C₃H₇NO)₃]	$D_x = 1.888$ Mg m⁻³
$M_r = 757.56$	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Trigonal, $P\bar{3}$	Cell parameters from 2269 reflections
Hall symbol: -P 3	$\theta = 2.4$–28.2°
$a = 13.8594$ (17) Å	$\mu = 2.76$ mm⁻¹
$c = 8.0100$ (14) Å	$T = 153$ K
$V = 1332.5$ (4) Å³	Column, colorless
$Z = 2$	$0.10 \times 0.02 \times 0.02$ mm
$F(000) = 768$	

Data collection

Bruker SMART APEX CCD diffractometer	7964 measured reflections
	2027 independent reflections
Radiation source: fine-focus sealed tube	1563 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.153$
phi and *ω* scans	$\theta_{max} = 27.5°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan	$h = -17 \rightarrow 17$
(*SADABS*; Sheldrick, 2003)	$k = -11 \rightarrow 18$
$T_{min} = 0.770$, $T_{max} = 0.947$	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	0 constraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 0.1686P]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.81$	$(\Delta/\sigma)_{max} < 0.001$
2027 reflections	$\Delta\rho_{max} = 0.72$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.79$ e Å^{-3}
0 restraints	

Special details

Geometry. **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 $F^2 > 2sigma(F^2)$ 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}
Zn1	0.01272 (3)	0.23313 (3)	0.39911 (5)	0.01217 (12)
O1	−0.25265 (17)	0.12229 (17)	0.4805 (3)	0.0160 (5)
O2	−0.10070 (17)	0.28429 (17)	0.4230 (3)	0.0149 (5)
O3	−0.05005 (17)	0.13366 (17)	0.6162 (3)	0.0140 (5)
O4	0.10436 (18)	0.19215 (19)	0.7680 (3)	0.0162 (5)
C1	−0.2019 (3)	0.2249 (2)	0.4582 (4)	0.0115 (6)
C2	−0.2697 (3)	0.2816 (2)	0.4691 (4)	0.0113 (6)
C3	−0.3856 (3)	0.2180 (3)	0.4700 (3)	0.0130 (7)
H3	−0.4213	0.1390	0.4712	0.016*
C4	0.0026 (3)	0.1477 (3)	0.7513 (4)	0.0140 (7)
H4	−0.0408	0.1214	0.8502	0.017*
O5	0.07684 (19)	0.32946 (18)	0.1759 (3)	0.0198 (5)
N1	0.0391 (2)	0.3985 (2)	−0.0540 (3)	0.0204 (6)
C5	0.0119 (3)	0.3253 (3)	0.0664 (4)	0.0203 (8)
H5	−0.0626	0.2651	0.0699	0.024*
C6	0.1529 (3)	0.4921 (3)	−0.0652 (5)	0.0286 (9)
H6A	0.1890	0.5051	0.0442	0.043*
H6B	0.1514	0.5590	−0.1003	0.043*
H6C	0.1948	0.4749	−0.1470	0.043*
C7	−0.0372 (3)	0.3837 (3)	−0.1897 (4)	0.0294 (9)
H7A	−0.1092	0.3163	−0.1697	0.044*
H7B	−0.0061	0.3762	−0.2956	0.044*
H7C	−0.0477	0.4485	−0.1951	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0082 (2)	0.0087 (2)	0.0197 (2)	0.00431 (16)	0.00015 (15)	0.00033 (15)
O1	0.0128 (12)	0.0101 (11)	0.0253 (13)	0.0060 (10)	−0.0020 (10)	0.0021 (10)
O2	0.0088 (11)	0.0097 (11)	0.0276 (12)	0.0056 (9)	0.0017 (10)	−0.0001 (10)
O3	0.0093 (11)	0.0117 (11)	0.0179 (11)	0.0029 (9)	−0.0024 (9)	0.0013 (9)
O4	0.0109 (12)	0.0182 (12)	0.0194 (12)	0.0072 (10)	−0.0014 (10)	−0.0016 (10)
C1	0.0109 (16)	0.0078 (15)	0.0143 (16)	0.0036 (13)	−0.0041 (13)	−0.0021 (13)
C2	0.0106 (15)	0.0107 (15)	0.0129 (15)	0.0056 (13)	−0.0010 (13)	0.0011 (13)
C3	0.0135 (16)	0.0102 (16)	0.0144 (16)	0.0053 (13)	0.0001 (13)	0.0008 (13)
C4	0.0128 (16)	0.0087 (15)	0.0205 (17)	0.0053 (14)	0.0010 (14)	−0.0004 (13)
O5	0.0162 (12)	0.0180 (12)	0.0221 (13)	0.0063 (11)	0.0026 (10)	0.0074 (10)
N1	0.0216 (16)	0.0224 (16)	0.0208 (15)	0.0137 (14)	−0.0002 (13)	0.0020 (13)
C5	0.0178 (18)	0.0160 (18)	0.027 (2)	0.0084 (15)	0.0040 (16)	0.0004 (15)
C6	0.029 (2)	0.028 (2)	0.028 (2)	0.0127 (18)	0.0057 (17)	0.0075 (17)
C7	0.036 (2)	0.038 (2)	0.0217 (19)	0.025 (2)	−0.0024 (18)	−0.0004 (17)

Geometric parameters (Å, º)

Zn1—O1ⁱ	2.028 (2)	C2—C3	1.394 (4)
Zn1—O2	2.031 (2)	C3—C2ⁱᵛ	1.380 (4)
Zn1—O4ⁱⁱ	2.105 (2)	C3—H3	0.9500
Zn1—O3ⁱ	2.108 (2)	C4—H4	0.9500
Zn1—O3	2.117 (2)	O5—C5	1.237 (4)
Zn1—O5	2.140 (2)	N1—C5	1.311 (4)
O1—C1	1.245 (3)	N1—C7	1.458 (4)
O1—Zn1ⁱⁱ	2.028 (2)	N1—C6	1.460 (5)
O2—C1	1.253 (4)	C5—H5	0.9500
O3—C4	1.265 (4)	C6—H6A	0.9800
O3—Zn1ⁱⁱ	2.108 (2)	C6—H6B	0.9800
O4—C4	1.232 (4)	C6—H6C	0.9800
O4—Zn1ⁱ	2.105 (2)	C7—H7A	0.9800
C1—C2	1.499 (4)	C7—H7B	0.9800
C2—C3ⁱⁱⁱ	1.380 (4)	C7—H7C	0.9800
O1ⁱ—Zn1—O2	87.25 (9)	C3—C2—C1	119.7 (3)
O1ⁱ—Zn1—O4ⁱⁱ	168.88 (9)	C2ⁱᵛ—C3—C2	120.1 (3)
O2—Zn1—O4ⁱⁱ	93.23 (9)	C2ⁱᵛ—C3—H3	120.0
O1ⁱ—Zn1—O3ⁱ	90.61 (8)	C2—C3—H3	120.0
O2—Zn1—O3ⁱ	177.54 (9)	O4—C4—O3	126.7 (3)
O4ⁱⁱ—Zn1—O3ⁱ	89.09 (8)	O4—C4—H4	116.6
O1ⁱ—Zn1—O3	96.06 (9)	O3—C4—H4	116.6
O2—Zn1—O3	90.70 (8)	C5—O5—Zn1	119.8 (2)
O4ⁱⁱ—Zn1—O3	95.05 (8)	C5—N1—C7	122.1 (3)
O3ⁱ—Zn1—O3	88.32 (10)	C5—N1—C6	119.8 (3)
O1ⁱ—Zn1—O5	85.20 (9)	C7—N1—C6	117.7 (3)
O2—Zn1—O5	90.77 (9)	O5—C5—N1	124.4 (3)

O4^{ii}—Zn1—O5	83.68 (8)	O5—C5—H5	117.8
O3^{i}—Zn1—O5	90.26 (9)	N1—C5—H5	117.8
O3—Zn1—O5	178.11 (9)	N1—C6—H6A	109.5
C1—O1—Zn1^{ii}	135.5 (2)	N1—C6—H6B	109.5
C1—O2—Zn1	126.83 (19)	H6A—C6—H6B	109.5
C4—O3—Zn1^{ii}	120.2 (2)	N1—C6—H6C	109.5
C4—O3—Zn1	125.8 (2)	H6A—C6—H6C	109.5
Zn1^{ii}—O3—Zn1	113.73 (10)	H6B—C6—H6C	109.5
C4—O4—Zn1^{i}	132.5 (2)	N1—C7—H7A	109.5
O1—C1—O2	126.2 (3)	N1—C7—H7B	109.5
O1—C1—C2	116.5 (3)	H7A—C7—H7B	109.5
O2—C1—C2	117.3 (3)	N1—C7—H7C	109.5
C3^{iii}—C2—C3	119.9 (3)	H7A—C7—H7C	109.5
C3^{iii}—C2—C1	120.3 (3)	H7B—C7—H7C	109.5
Zn1^{ii}—O1—C1—O2	42.6 (5)	C3^{iii}—C2—C3—C2^{iv}	1.0 (6)
Zn1^{ii}—O1—C1—C2	−139.5 (2)	C1—C2—C3—C2^{iv}	−175.8 (2)
Zn1—O2—C1—O1	−2.2 (5)	Zn1^{i}—O4—C4—O3	−21.4 (5)
Zn1—O2—C1—C2	179.99 (19)	Zn1^{ii}—O3—C4—O4	159.8 (3)
O1—C1—C2—C3^{iii}	170.7 (3)	Zn1—O3—C4—O4	−26.7 (4)
O2—C1—C2—C3^{iii}	−11.3 (4)	Zn1—O5—C5—N1	163.2 (2)
O1—C1—C2—C3	−12.5 (4)	C7—N1—C5—O5	173.5 (3)
O2—C1—C2—C3	165.5 (3)	C6—N1—C5—O5	0.5 (5)

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