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ISSN 2414-3146

trans-Bis(dimethyl sulfoxide-κO)bis(3-nitrobenzohydroxamato-$\kappa^2 O,O'$)zinc(II)

Bruna Lisboa Gonçalves,[a] Samantha Oliveira Monteiro,[a] Roberta Cargnelutti[b] and Juliano Rosa de Menezes Vicenti[a]*

[a]Laboratório de Físico-Química Aplicada e Tecnológica, Escola de Química e Alimentos, Universidade Federal do Rio Grande, Av. Itália km 08, Campus Carreiros, 96203-900, Rio Grande-RS, Brazil, and [b]Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, Av. Roraima, 97105-900, Santa Maria-RS, Brazil. *Correspondence e-mail: julianovicenti@gmail.com

Received 10 July 2019
Accepted 13 July 2019

Edited by M. Weil, Vienna University of Technology, Austria

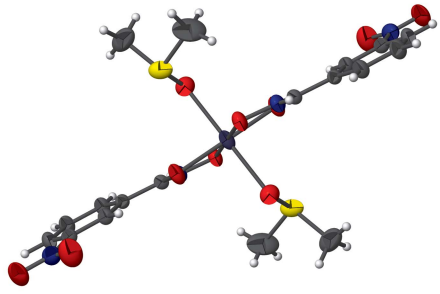
Keywords: crystal structure; hydroxamate; Hirshfeld surface analysis; zinc(II).

CCDC reference: 1940726

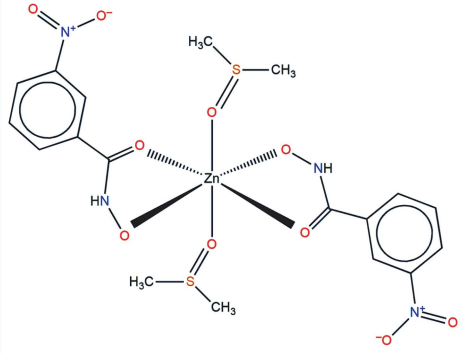
Structural data: full structural data are available from iucrdata.iucr.org

Single crystals of the title complex, $[Zn(C_7H_5N_2O_4)_2(C_2H_6OS)_2]$ or $[Zn(NBZH)_2(DMSO)_2]$, were isolated from a dimethyl sulfoxide (DMSO) solution containing $[Zn(NBZH)_2]\cdot 2H_2O$ (NBZH = 3-nitrobenzohydroxamate anion). The asymmetric unit comprises of one *O*,*O*′-chelating NBZH anion, one O-bound DMSO ligand and one zinc(II) cation localized on an inversion centre. The three-dimensional crystal packing includes N—H···O and C—H···O hydrogen bonding, as well as O···H and H···H contacts identified by Hirshfeld isosurface analysis.

3D view



Chemical scheme



Structure description

Hydroxamic acids, *R*C(=O)–NH–OH (where *R* = alkyl, aryl), play important roles in biology and medicine and have been a source of great interest because they present a wide variety of biological activities (Codd, 2008; Marmion *et al.*, 2004). These are related to the ability to form stable complexes with metal ions, especially iron(III) (Ugwu *et al.*, 2014; Griffith *et al.*, 2008). In addition, this class of compounds provides several sites for hydrogen-bonding interactions with enzyme structures, thus becoming potent and selective inhibitors of a number of enzymes such as matrix metalloproteinase (Muri *et al.*, 2002; Sani *et al.*, 2004), peroxidases (O'Brien *et al.*, 2000; Indiani *et al.*, 2003), histone deacetylases (Richon, 2006; Krennhrubec *et al.*, 2007), or ureases (Xiao *et al.*, 2013; Krajewska, 2009; Shi *et al.*, 2016). In our previous work, we have synthesized, characterized and investigated some physical-chemical properties of zinc(II) aromatic hydroxamates (Gonçalves *et al.*, 2019) and report here the crystal structure of $[Zn(C_7H_5N_2O_4)_2(C_2H_6OS)_2]$ or $[Zn(NBZH)_2(DMSO)_2]$.

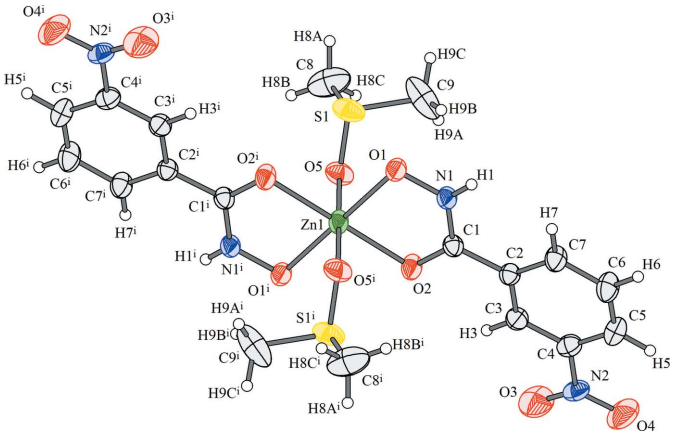


Figure 1
Molecular structure of $[Zn(NBZH)_2(DMSO)_2]$. Ellipsoids are drawn at the 50% probability level [symmetry code: (i) $-x+1, -y+1, -z+2$].

A slightly distorted octahedral environment around the zinc(II) cation (site symmetry $\overline{1}$) is generated by symmetry operation $2-x, -y, -z$, leading to an all-*trans* configuration of the two ligands (Fig. 1). In the molecular structure, the O-bound DMSO molecule has a distance of 2.3473 (12) Å for Zn1—O5, indicating an elongation along the axial position. The *O*,*O*′-chelating NBZH ligand shows shorter distances of 2.0029 (11) Å for Zn1—O1 and 2.0675 (11) Å for Zn1—O2 in the equatorial positions. The nitro group attached to the NBZH ligand is almost planar with the aromatic ring, displaying a dihedral angle of 3.2 (2)°.

In the crystal structure, discrete molecular units of $[Zn(NBZH)_2(DMSO)_2]$ (Fig. 2) are packed along the [010] and [001] directions. The intermolecular interactions collated in Table 1 are suggestive of two weak non-classical C—H···O hydrogen bonds involving dimethylsulfoxide molecules. As shown in Fig. 3, the hydroxamate fragment plays a dominant role in the packing through an N—H···O5 hydrogen bond of medium strength along [100] (Table 1). These structural features generate a three-dimensional supramolecular network that was further investigated by Hirshfeld surface analysis (Fig. 4), as determined with *CrystalExplorer* (Turner *et al.*, 2017). The results indicate a significant contribution by O···H contacts, corresponding to 43.1% of the two-dimensional fingerprint plots. H···H and C···H contacts are also observed, covering 30.1% and 11.6% of the isosurface, respectively, followed by C···C (2.9%), S···H (2.6%) and N···H (1%) interactions.

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8C···O4^{i}	0.96	2.55	3.381 (3)	145
C8—H8A···O1^{ii}	0.96	2.66	3.533 (3)	150
N1—H1···O5^{iii}	0.84 (2)	2.08 (2)	2.916 (1)	175 (2)

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

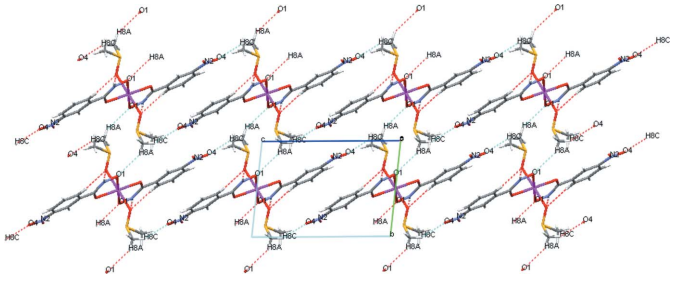


Figure 2
Hydrogen bonding in $[Zn(NBZH)_2(DMSO)_2]$ along the [010] and [001] directions.

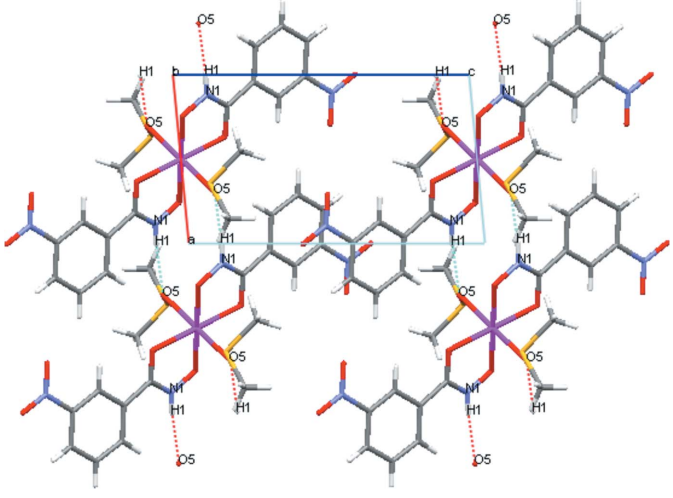


Figure 3
Hydrogen bonding in $[Zn(NBZH)_2(DMSO)_2]$ along the [100] direction.

Synthesis and crystallization

Suitable single crystals of the title compound were obtained within one week from a dimethylsulfoxide solution containing $[Zn(NBZH)_2]\cdot 2H_2O$, previously reported by us (Gonçalves *et al.*, 2019).

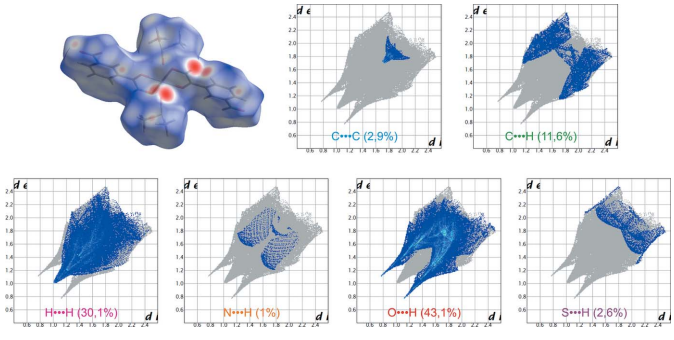


Figure 4
Results of Hirshfeld analysis for $[Zn(NBZH)_2(DMSO)_2]$.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn(C_7H_5N_2O_4)_2(C_2H_6OS)_2]$
M_r	583.91
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	294
a, b, c (Å)	6.4899 (2), 7.8961 (3), 11.4224 (4)
α, β, γ (°)	83.496 (1), 84.591 (1), 89.567 (1)
V (Å^3)	578.98 (3)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.30
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.786, 0.880
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30874, 3558, 2961
R_{int}	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.097, 0.92
No. of reflections	3558
No. of parameters	166
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, −0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2006), *Mercury* (Macrae *et al.*, 2006), *CrystalExplorer17* (Turner *et al.*, 2017) and *publCIF* (Westrip, 2010).

Acknowledgements

The authors acknowledge CT–Infra (FINEP).

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full crystallographic data

IUCrData (2019). **4**, x191005 [https://doi.org/10.1107/S2414314619010058]

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trans-Bis(dimethyl sulfoxide-κO)bis(3-nitrobenzohydroxamato-$\kappa^2 O,O'$)zinc(II)

Crystal data

$[Zn(C_7H_5N_2O_4)_2(C_2H_6OS)_2]$
M_r = 583.91
Triclinic, $P\overline{1}$
a = 6.4899 (2) Å
b = 7.8961 (3) Å
c = 11.4224 (4) Å
α = 83.496 (1)°
β = 84.591 (1)°
γ = 89.567 (1)°
V = 578.98 (3) Å^3
Z = 1
$F(000)$ = 298
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9996 reflections
θ = 3.0–30.3°
μ = 1.30 mm^{-1}
T = 294 K
Block, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.786, T_{max} = 0.880
30874 measured reflections
3558 independent reflections
2961 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 30.6°, θ_{min} = 3.0°
h = −9→9
k = −11→11
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.097
S = 0.92
3558 reflections
166 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.1979P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.500000	0.500000	1.000000	0.03291 (10)
S1	0.35743 (8)	0.88919 (6)	0.91043 (4)	0.04435 (13)
C1	0.8166 (2)	0.47473 (18)	0.82661 (13)	0.0259 (3)
O1	0.75668 (17)	0.64360 (15)	0.98049 (10)	0.0319 (2)
N1	0.88330 (19)	0.58558 (17)	0.89218 (12)	0.0281 (3)
H1	1.006 (3)	0.618 (3)	0.8898 (19)	0.037 (5)*
C3	0.8709 (2)	0.32583 (19)	0.64935 (13)	0.0288 (3)
H3	0.730590	0.299127	0.659747	0.035*
O2	0.63195 (17)	0.41942 (16)	0.84399 (10)	0.0350 (3)
O5	0.30496 (19)	0.70808 (15)	0.89650 (12)	0.0388 (3)
C6	1.2902 (3)	0.3979 (3)	0.61715 (16)	0.0396 (4)
H6	1.431200	0.421972	0.607033	0.048*
O4	1.0035 (3)	0.1408 (2)	0.38495 (13)	0.0596 (4)
C5	1.2036 (3)	0.3072 (2)	0.53664 (15)	0.0386 (4)
H5	1.283893	0.269754	0.472840	0.046*
O3	0.7091 (3)	0.1606 (2)	0.48421 (16)	0.0629 (4)
C4	0.9935 (3)	0.2746 (2)	0.55502 (14)	0.0317 (3)
C2	0.9584 (2)	0.41788 (18)	0.72915 (12)	0.0259 (3)
C8	0.1489 (5)	1.0145 (3)	0.8571 (3)	0.0721 (8)
H8A	0.165888	1.130499	0.872306	0.108*
H8B	0.020259	0.970410	0.896870	0.108*
H8C	0.148280	1.010210	0.773505	0.108*
N2	0.8946 (3)	0.18484 (19)	0.46896 (13)	0.0413 (3)
C7	1.1708 (2)	0.4532 (2)	0.71197 (15)	0.0331 (3)
H7	1.231884	0.514253	0.764663	0.040*
C9	0.5491 (5)	0.9574 (4)	0.7945 (3)	0.0868 (10)
H9A	0.507520	0.927737	0.720948	0.130*
H9B	0.677978	0.902758	0.809873	0.130*
H9C	0.565880	1.078767	0.789709	0.130*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02448 (13)	0.04346 (16)	0.03212 (15)	−0.01039 (10)	0.00407 (9)	−0.01494 (11)
S1	0.0614 (3)	0.0350 (2)	0.0395 (2)	−0.01645 (19)	−0.0177 (2)	−0.00475 (17)
C1	0.0233 (6)	0.0292 (7)	0.0254 (6)	−0.0030 (5)	−0.0023 (5)	−0.0036 (5)
O1	0.0265 (5)	0.0382 (6)	0.0324 (5)	−0.0062 (4)	0.0034 (4)	−0.0145 (4)
N1	0.0212 (5)	0.0331 (6)	0.0303 (6)	−0.0053 (5)	0.0014 (4)	−0.0082 (5)
C3	0.0265 (6)	0.0305 (7)	0.0298 (7)	−0.0011 (5)	−0.0033 (5)	−0.0046 (5)
O2	0.0234 (5)	0.0491 (7)	0.0346 (6)	−0.0105 (4)	0.0028 (4)	−0.0179 (5)
O5	0.0351 (6)	0.0337 (6)	0.0491 (7)	−0.0088 (5)	−0.0093 (5)	−0.0071 (5)
C6	0.0250 (7)	0.0538 (10)	0.0398 (9)	0.0008 (7)	0.0016 (6)	−0.0084 (7)
O4	0.0774 (11)	0.0651 (10)	0.0399 (8)	0.0042 (8)	−0.0002 (7)	−0.0262 (7)
C5	0.0355 (8)	0.0470 (9)	0.0328 (8)	0.0067 (7)	0.0037 (6)	−0.0090 (7)
O3	0.0543 (9)	0.0770 (11)	0.0651 (10)	−0.0103 (8)	−0.0140 (7)	−0.0338 (8)

C4	0.0375 (8)	0.0303 (7)	0.0284 (7)	0.0026 (6)	−0.0055 (6)	−0.0057 (6)
C2	0.0244 (6)	0.0275 (6)	0.0258 (6)	0.0001 (5)	−0.0019 (5)	−0.0032 (5)
C8	0.102 (2)	0.0500 (13)	0.0705 (16)	0.0217 (13)	−0.0284 (15)	−0.0171 (12)
N2	0.0558 (9)	0.0359 (7)	0.0350 (7)	0.0027 (6)	−0.0089 (6)	−0.0124 (6)
C7	0.0250 (7)	0.0431 (8)	0.0323 (7)	−0.0027 (6)	−0.0028 (5)	−0.0092 (6)
C9	0.0757 (18)	0.090 (2)	0.086 (2)	−0.0402 (16)	−0.0005 (15)	0.0262 (17)

Geometric parameters (Å, º)

Zn1—O1^{i}	2.0029 (11)	C6—C7	1.381 (2)
Zn1—O1	2.0029 (11)	C6—C5	1.389 (3)
Zn1—O2^{i}	2.0675 (11)	C6—H6	0.9300
Zn1—O2	2.0675 (11)	O4—N2	1.219 (2)
Zn1—O5	2.3473 (12)	C5—C4	1.381 (3)
Zn1—O5^{i}	2.3474 (12)	C5—H5	0.9300
S1—O5	1.5019 (13)	O3—N2	1.214 (2)
S1—C9	1.769 (3)	C4—N2	1.471 (2)
S1—C8	1.783 (3)	C2—C7	1.400 (2)
C1—O2	1.2686 (17)	C8—H8A	0.9600
C1—N1	1.3153 (19)	C8—H8B	0.9600
C1—C2	1.484 (2)	C8—H8C	0.9600
O1—N1	1.3584 (16)	C7—H7	0.9300
N1—H1	0.84 (2)	C9—H9A	0.9600
C3—C4	1.375 (2)	C9—H9B	0.9600
C3—C2	1.391 (2)	C9—H9C	0.9600
C3—H3	0.9300		
O1^{i}—Zn1—O1	180.0	C7—C6—C5	121.26 (15)
O1^{i}—Zn1—O2^{i}	81.79 (4)	C7—C6—H6	119.4
O1—Zn1—O2^{i}	98.20 (4)	C5—C6—H6	119.4
O1^{i}—Zn1—O2	98.21 (4)	C4—C5—C6	117.40 (15)
O1—Zn1—O2	81.80 (4)	C4—C5—H5	121.3
O2^{i}—Zn1—O2	180.0	C6—C5—H5	121.3
O1^{i}—Zn1—O5	86.04 (4)	C3—C4—C5	122.78 (16)
O1—Zn1—O5	93.96 (4)	C3—C4—N2	118.22 (15)
O2^{i}—Zn1—O5	88.40 (5)	C5—C4—N2	118.98 (15)
O2—Zn1—O5	91.60 (5)	C3—C2—C7	118.73 (14)
O1^{i}—Zn1—O5^{i}	93.96 (4)	C3—C2—C1	116.91 (13)
O1—Zn1—O5^{i}	86.04 (4)	C7—C2—C1	124.35 (13)
O2^{i}—Zn1—O5^{i}	91.60 (5)	S1—C8—H8A	109.5
O2—Zn1—O5^{i}	88.40 (5)	S1—C8—H8B	109.5
O5—Zn1—O5^{i}	180.00 (5)	H8A—C8—H8B	109.5
O5—S1—C9	106.83 (13)	S1—C8—H8C	109.5
O5—S1—C8	105.71 (11)	H8A—C8—H8C	109.5
C9—S1—C8	97.80 (16)	H8B—C8—H8C	109.5
O2—C1—N1	120.85 (13)	O3—N2—O4	123.43 (17)
O2—C1—C2	119.91 (13)	O3—N2—C4	118.52 (15)
N1—C1—C2	119.22 (12)	O4—N2—C4	118.04 (17)

N1—O1—Zn1	106.70 (8)	C6—C7—C2	120.31 (15)
C1—N1—O1	120.95 (12)	C6—C7—H7	119.8
C1—N1—H1	124.8 (15)	C2—C7—H7	119.8
O1—N1—H1	113.9 (15)	S1—C9—H9A	109.5
C4—C3—C2	119.51 (14)	S1—C9—H9B	109.5
C4—C3—H3	120.2	H9A—C9—H9B	109.5
C2—C3—H3	120.2	S1—C9—H9C	109.5
C1—O2—Zn1	107.94 (9)	H9A—C9—H9C	109.5
S1—O5—Zn1	115.22 (7)	H9B—C9—H9C	109.5
O2—C1—N1—O1	0.2 (2)	C4—C3—C2—C1	177.88 (13)
C2—C1—N1—O1	178.50 (12)	O2—C1—C2—C3	9.7 (2)
Zn1—O1—N1—C1	9.65 (16)	N1—C1—C2—C3	−168.60 (14)
N1—C1—O2—Zn1	−9.65 (17)	O2—C1—C2—C7	−171.33 (15)
C2—C1—O2—Zn1	172.04 (10)	N1—C1—C2—C7	10.3 (2)
C9—S1—O5—Zn1	91.19 (13)	C3—C4—N2—O3	0.5 (2)
C8—S1—O5—Zn1	−165.37 (12)	C5—C4—N2—O3	−178.16 (18)
C7—C6—C5—C4	0.1 (3)	C3—C4—N2—O4	179.45 (16)
C2—C3—C4—C5	1.5 (2)	C5—C4—N2—O4	0.8 (2)
C2—C3—C4—N2	−177.04 (13)	C5—C6—C7—C2	0.3 (3)
C6—C5—C4—C3	−1.0 (3)	C3—C2—C7—C6	0.3 (2)
C6—C5—C4—N2	177.56 (15)	C1—C2—C7—C6	−178.66 (15)
C4—C3—C2—C7	−1.1 (2)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*C*···O4^{ii}	0.96	2.55	3.381 (3)	145
C8—H8*A*···O1^{iii}	0.96	2.66	3.533 (3)	150
N1—H1···O5^{iv}	0.84 (2)	2.08 (2)	2.916 (1)	175 (2)

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