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[μ -(4*S*,5*S*,15*S*,16*S*)-10,21-Di-*tert*-butyl-4,5,15,16-tetraphenyl-3,6,14,17-tetraazatricyclo[17.3.1.1^{8,12}]tetracos-1(23),8,10,12(24),19,21-hexaene-23,24-diolato- κ^8 N³,N⁶,O²³,O²⁴:N¹⁴N¹⁷,O²³,-O²⁴]bis[acetato- κ O]zinc(II)] ethanol disolvate

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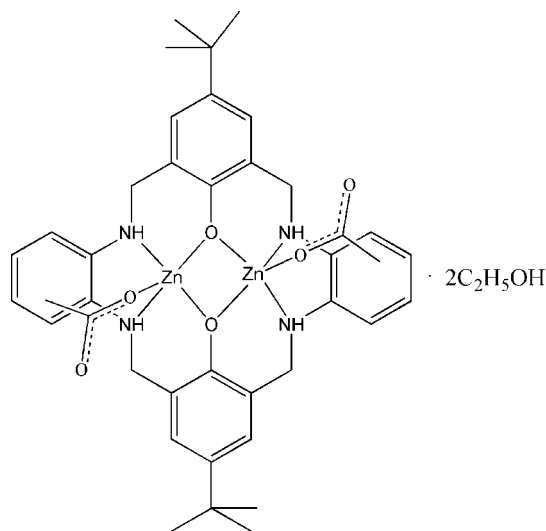
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.010$ Å; disorder in main residue; R factor = 0.077; wR factor = 0.253; data-to-parameter ratio = 22.3.

In the title compound, $[Zn_2(C_{36}H_{42}N_4O_2)(CH_3COO)_2] \cdot 2CH_3CH_2OH$, a centrosymmetric dinuclear zinc macrocyclic complex is accompanied by two half-occupied ethanol solvent molecules resulting in a 1:2 macrocycle–solvent composition. The Zn^{II} atom has a square-pyramidal geometry arising from an N_2O_3 donor set, being coordinated by two N atoms and two O atoms from the macrocyclic ligand in the equatorial sites and one O atom from an acetate anion in the apical site. The two Zn^{II} atoms are linked by two phenolate O atoms, generating a four-membered Zn_2O_2 ring at the centre of the macrocycle. The *tert*-butyl group shows rotational disorder over two sets of sites in a 0.552 (12):0.448 (12) ratio. In the crystal, $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds are seen and a short intramolecular $C-H \cdots O$ contact occurs.

Related literature

For background to the biochemistry of zinc compounds, see: Lipscomb & Straeter (1996); Burley *et al.* (1990); Roderick & Mathews (1993); Bazzicalupi *et al.* (1997). For related structures, see: Dutta *et al.* (2005); Liu *et al.* (2007). For further synthetic details, see: Tian *et al.* (1999).



Experimental

Crystal data

$[Zn_2(C_{36}H_{42}N_4O_2)(C_2H_3O_2)_2] \cdot 2C_2H_5O$
 $M_r = 903.70$
 Triclinic, $P\bar{1}$
 $a = 9.0566$ (3) Å
 $b = 10.8410$ (5) Å
 $c = 14.2828$ (5) Å
 $\alpha = 71.246$ (4)°

$\beta = 86.514$ (3)°
 $\gamma = 78.362$ (3)°
 $V = 1300.56$ (9) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.97$ mm⁻¹
 $T = 293$ K
 0.45 × 0.25 × 0.20 mm

Data collection

Oxford Diffraction Gemini R Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
 $T_{min} = 0.748$, $T_{max} = 0.824$

11846 measured reflections
 6368 independent reflections
 4133 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.253$
 $S = 1.05$
 6368 reflections
 285 parameters
 655 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 1.15$ e Å⁻³
 $\Delta\rho_{min} = -0.77$ e Å⁻³

Table 1

Selected bond lengths (Å).

Zn1–O1	2.025 (5)	Zn1–N2	2.100 (5)
Zn1–O3	2.033 (4)	Zn1–N1	2.104 (5)
Zn1–O3 ⁱ	2.043 (4)		

 Symmetry code: (i) $-x, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4A \cdots O2	0.97	2.45	3.246 (10)	139
N1—H1N \cdots O4	0.86 (7)	2.23 (7)	2.952 (9)	141 (6)
N2—H2N \cdots O5 ⁱⁱ	0.87 (4)	2.13 (4)	2.999 (9)	175 (4)
O4—H4 \cdots O2 ⁱⁱⁱ	0.82	2.06	2.768 (10)	145
O5—H5 \cdots O1 ^{iv}	0.82	1.92	2.700 (9)	159

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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the Fok Ying Tung Education Foundation and the Analysis and Testing Foundation of Northeast Normal University for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2961).

References

- Bazzicalupi, C., Bencini, A., Bianchi, A., Fusi, V., Giorgi, C., Paoletti, P., Valtancoli, B. & Zanchi, D. (1997). *Inorg. Chem.* **36**, 2784–2790.
- Burley, S. K., David, P. R., Taylor, A. & Lipscomb, W. N. (1990). *Proc. Natl Acad. Sci. USA*, **87**, 6878–6882.
- Dutta, B., Bag, P., Flörke, U. & Nag, K. (2005). *Inorg. Chem.* **44**, 147–157.
- Lipscomb, W. N. & Straeter, N. (1996). *Chem. Rev.* **96**, 2375–2434.
- Liu, J., Ma, J.-F., Li, S.-L. & Ping, G.-J. (2007). *Acta Cryst.* **E63**, m1954.
- Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
- Roderick, S. & Mathews, B. W. (1993). *Biochemistry*, **32**, 3907–3912.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tian, Y. Q., Tong, J., Frenzen, G. & Sun, J. Y. (1999). *J. Org. Chem.* **64**, 1442–1446.

supplementary materials

Acta Cryst. (2009). E65, m777-m778 [doi:10.1107/S1600536809021990]

[μ -(4*S*,5*S*,15*S*,16*S*)-10,21-Di-*tert*-butyl-4,5,15,16-tetraphenyl-3,6,14,17-tetraazatricyclo[17.3.1.1^{8,12}]tetracos-1(23),8,10,12(24),19,21-hexaene-23,24-diolato- κ^8 N³,N⁶,O²³,O²⁴:N¹⁴N¹⁷,O²³,O²⁴]bis[(acetato- κ O)zinc(II)] ethanol disolvate

L.-J. jing Fan, J.-F. Ma and J. Liu

Comment

Zinc is an essential element for all forms of life and plays a critical role in various functions, both structural and catalytic, in proteins and enzymes (Lipscomb *et al.*, 1996; Burley *et al.*, 1990; Roderick & Mathews, 1993). In addition, some synthetic dinuclear zinc(II) compounds appears to have functions in dephosphorylation (Bazzicalupi *et al.*, 1997). As part of our studies in this area, the title compound, (I), a new dinuclear zinc(II) compound has been synthesized, and its structure is reported here (Fig. 1).

The complete macrocycle is generated by a crystallographic inversion centre. The coordination environment around zinc is a square-pyramid with two N atoms and two O atoms from the macrocyclic (C₃₆H₄₄N₄O₂) ligand occupying the basal positions and one O atom from an acetate anion occupying the apical position. The two zinc atoms are bridged by two phenolate O atoms to generate a four-membered Zn₂O₂ ring. The Zn—O and Zn—N distances are normal (Dutta *et al.*, 2005).

Experimental

To a stirred methanol (30 ml) suspension of the schiff base C₃₆H₄₀N₄O₂ (0.5 mmol), which was synthesized by the methods reported previously (Tian *et al.*, 1999), was added solid NaBH₄ (0.5 g, 13 mmol) in small portions. Over a period of 0.5 h when the red solid material gradually went into solution, and eventually an amorphous yellow mass precipitated. After 1 h, the formed yellow powder products (H₂L) were filtrated off and washed thoroughly with water and ethanol, and dried in a vacuum (yield 54%).

The title compound was prepared by reaction between the ligand (H₂L) and zinc acetate. A mixture of H₂L (0.108 g, 0.2 mmol) and Zn(OAc)₂·6H₂O (0.117 g, 0.4 mmol) in ethanol (20 ml) was heated with stirring to yield a clear pale yellow solution. Filtration and cooling to room temperature resulted in formation of a crystalline precipitate. Recrystallization by slow evaporation of an ethanol solution of the compound resulted in well-formed yellow blocks of (I) (yield 46%).

Refinement

The N-bonded H atoms were located in a difference map and their positions were freely refined. The other H atoms were placed in calculated positions (O—H = 0.82 Å, C—H = 0.93–0.96 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The methyl entities of the *tert*-butyl group are disordered over two sets of sites in a 0.552 (12):0.448 (12) ratio. The highest difference peak is 1.55 Å from O5 and the deepest difference hole is 0.77 Å from C17'. The anisotropic displacement factors of the disordered atoms were restrained to be nearly isotropic. Additionally, the solvent of ethanol molecule is disordered in two positions (the occupancies were fixed as 0.5:0.5).

Figures

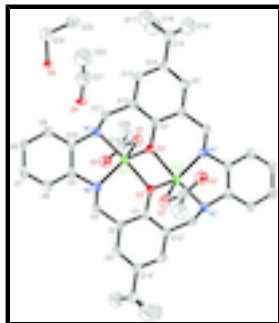


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

[μ -(4*S*,5*S*,15*S*,16*S*)-10,21-Di-*tert*-butyl- 4,5,15,16-tetraphenyl-3,6,14,17-tetraazatricyclo[17.3.1.1^{8,12}]tetracos-1(23),8,10,12 (24),19,21-hexaene-23,24-diolato- κ^8 N³,N⁶,O²³,O²⁴: N¹⁴N¹⁷,O²³,O²⁴]bis[(acetato- κ O)zinc(II)] ethanol disolvate

Crystal data

[Zn₂(C₃₆H₄₂N₄O₂)(C₂H₃O₂)₂] \cdot 2C₂H₆O

M_r = 903.70

Triclinic, $P\bar{1}$

Hall symbol: -P 1

a = 9.0566 (3) Å

b = 10.8410 (5) Å

c = 14.2828 (5) Å

α = 71.246 (4)°

β = 86.514 (3)°

γ = 78.362 (3)°

V = 1300.56 (9) Å³

Z = 1

F_{000} = 476

D_x = 1.154 Mg m⁻³

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 2131 reflections

θ = 3.1–26.5°

μ = 0.97 mm⁻¹

T = 293 K

Block, yellow

0.45 \times 0.25 \times 0.20 mm

Data collection

Oxford Diffraction Gemini R Ultra diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 10.0 pixels mm⁻¹

T = 293 K

ω scans

Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)

T_{\min} = 0.748, T_{\max} = 0.824

11846 measured reflections

6368 independent reflections

4133 reflections with $I > 2\sigma(I)$

R_{int} = 0.035

θ_{max} = 29.8°

θ_{min} = 4.4°

h = -11 \rightarrow 12

k = -14 \rightarrow 14

l = -18 \rightarrow 19

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.077$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.253$	$w = 1/[\sigma^2(F_o^2) + (0.1644P)^2]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
6368 reflections	$(\Delta/\sigma)_{\max} < 0.001$
285 parameters	$\Delta\rho_{\max} = 1.15 \text{ e } \text{\AA}^{-3}$
655 restraints	$\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.05562 (7)	0.12433 (7)	0.50054 (5)	0.0340 (3)	
C1	-0.1270 (7)	-0.0328 (6)	0.6667 (4)	0.0348 (12)	
C2	-0.0490 (7)	-0.0070 (7)	0.7384 (5)	0.0393 (13)	
C3	-0.0831 (8)	-0.0639 (8)	0.8383 (5)	0.0466 (15)	
H3	-0.0290	-0.0493	0.8858	0.056*	
C4	0.0649 (7)	0.0818 (7)	0.7131 (5)	0.0414 (13)	
H4A	0.0126	0.1736	0.6901	0.050*	
H4B	0.1207	0.0693	0.7724	0.050*	
C5	0.3043 (7)	0.1208 (6)	0.6217 (5)	0.0378 (12)	
C6	0.3920 (8)	0.1117 (7)	0.7007 (6)	0.0465 (14)	
H6	0.3657	0.0661	0.7646	0.056*	
C7	0.5162 (8)	0.1685 (8)	0.6863 (6)	0.0509 (15)	
H7	0.5743	0.1609	0.7401	0.061*	
C8	0.5554 (8)	0.2371 (8)	0.5923 (6)	0.0489 (15)	
H8	0.6404	0.2755	0.5821	0.059*	
C9	0.4671 (7)	0.2484 (7)	0.5129 (6)	0.0454 (14)	

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H9	0.4931	0.2953	0.4493	0.055*	
C10	0.3420 (7)	0.1915 (6)	0.5269 (5)	0.0375 (12)	
C11	0.3368 (7)	0.1223 (7)	0.3804 (5)	0.0397 (13)	
H11A	0.3798	0.0336	0.4223	0.048*	
H11B	0.4192	0.1649	0.3484	0.048*	
C12	0.2376 (7)	0.1125 (7)	0.3023 (5)	0.0397 (13)	
C13	0.2679 (8)	0.1641 (8)	0.2016 (5)	0.0513 (15)	
H13	0.3412	0.2163	0.1820	0.062*	
C14	0.1915 (9)	0.1397 (8)	0.1302 (5)	0.0530 (16)	
C15	0.2210 (10)	0.2038 (10)	0.0195 (6)	0.070 (2)	
C16	0.0903 (18)	0.274 (2)	-0.0392 (19)	0.106 (6)*	0.448 (12)
H16A	0.0088	0.2276	-0.0169	0.159*	0.448 (12)
H16B	0.1117	0.2812	-0.1072	0.159*	0.448 (12)
H16C	0.0625	0.3617	-0.0331	0.159*	0.448 (12)
C17	0.3466 (18)	0.269 (2)	-0.0069 (17)	0.078 (5)*	0.448 (12)
H17A	0.4286	0.2207	0.0380	0.117*	0.448 (12)
H17B	0.3183	0.3576	-0.0035	0.117*	0.448 (12)
H17C	0.3774	0.2721	-0.0730	0.117*	0.448 (12)
C18	0.276 (3)	0.084 (2)	-0.022 (2)	0.101 (6)*	0.448 (12)
H18A	0.3649	0.0287	0.0136	0.151*	0.448 (12)
H18B	0.2996	0.1178	-0.0908	0.151*	0.448 (12)
H18C	0.1983	0.0336	-0.0136	0.151*	0.448 (12)
C16'	0.146 (3)	0.3448 (14)	-0.0045 (17)	0.106 (5)*	0.552 (12)
H16D	0.0426	0.3503	0.0157	0.158*	0.552 (12)
H16E	0.1510	0.3878	-0.0745	0.158*	0.552 (12)
H16F	0.1963	0.3879	0.0297	0.158*	0.552 (12)
C17'	0.373 (3)	0.163 (3)	0.0001 (18)	0.106 (5)*	0.552 (12)
H17D	0.3988	0.0676	0.0228	0.160*	0.552 (12)
H17E	0.4347	0.1978	0.0340	0.160*	0.552 (12)
H17F	0.3908	0.1950	-0.0697	0.160*	0.552 (12)
C18'	0.154 (2)	0.1537 (17)	-0.0493 (15)	0.083 (4)*	0.552 (12)
H18D	0.0463	0.1770	-0.0471	0.124*	0.552 (12)
H18E	0.1845	0.0589	-0.0303	0.124*	0.552 (12)
H18F	0.1882	0.1926	-0.1152	0.124*	0.552 (12)
C19	-0.1180 (8)	0.3676 (7)	0.4525 (7)	0.0524 (18)	
C20	-0.2183 (11)	0.4959 (9)	0.3983 (7)	0.074 (3)	
H20A	-0.2489	0.4915	0.3365	0.110*	
H20B	-0.1644	0.5672	0.3861	0.110*	
H20C	-0.3057	0.5112	0.4376	0.110*	
C21	0.192 (3)	0.573 (3)	0.260 (2)	0.107 (7)*	0.50
H21A	0.2097	0.6567	0.2627	0.129*	0.50
H21B	0.0950	0.5895	0.2286	0.129*	0.50
C22	0.308 (3)	0.525 (3)	0.197 (2)	0.117 (7)*	0.50
H22A	0.3097	0.5925	0.1341	0.176*	0.50
H22B	0.2863	0.4467	0.1867	0.176*	0.50
H22C	0.4052	0.5031	0.2281	0.176*	0.50
C23	0.690 (2)	0.287 (2)	0.1224 (14)	0.081 (5)	0.50
H23A	0.7180	0.3421	0.0591	0.121*	0.50
H23B	0.5824	0.3020	0.1279	0.121*	0.50

H23C	0.7284	0.1956	0.1289	0.121*	0.50
C24	0.7513 (19)	0.3194 (16)	0.1974 (12)	0.058 (4)	0.50
H24A	0.7141	0.4124	0.1901	0.070*	0.50
H24B	0.8602	0.3056	0.1912	0.070*	0.50
O1	-0.0909 (5)	0.2773 (5)	0.4110 (4)	0.0537 (13)	
O2	-0.0635 (7)	0.3485 (6)	0.5334 (5)	0.0669 (15)	
O3	-0.1018 (5)	0.0163 (4)	0.5695 (3)	0.0338 (9)	
O4	0.1846 (10)	0.4916 (7)	0.3531 (5)	0.0344 (18)	0.50
H4	0.1170	0.5264	0.3826	0.052*	0.50
O5	0.7114 (8)	0.2386 (7)	0.2940 (5)	0.0252 (15)	0.50
H5	0.7511	0.2567	0.3367	0.038*	0.50
H2N	0.205 (8)	-0.030 (3)	0.652 (5)	0.050 (6)*	
H1N	0.225 (12)	0.271 (6)	0.394 (5)	0.095 (4)*	
N2	0.1736 (6)	0.0556 (5)	0.6353 (4)	0.0366 (11)	
N1	0.2504 (6)	0.2002 (5)	0.4438 (4)	0.0342 (11)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0304 (4)	0.0382 (4)	0.0374 (5)	-0.0082 (3)	0.0014 (3)	-0.0165 (3)
C1	0.031 (3)	0.042 (3)	0.036 (3)	-0.006 (2)	0.003 (2)	-0.019 (2)
C2	0.035 (3)	0.049 (3)	0.041 (3)	-0.009 (2)	0.001 (2)	-0.024 (3)
C3	0.043 (3)	0.065 (4)	0.038 (3)	-0.013 (3)	0.000 (3)	-0.022 (3)
C4	0.040 (3)	0.052 (3)	0.040 (3)	-0.015 (2)	0.003 (2)	-0.022 (2)
C5	0.029 (2)	0.044 (3)	0.047 (3)	-0.009 (2)	-0.001 (2)	-0.023 (2)
C6	0.040 (3)	0.058 (3)	0.049 (3)	-0.012 (3)	-0.002 (3)	-0.026 (3)
C7	0.038 (3)	0.063 (4)	0.061 (4)	-0.011 (3)	-0.009 (3)	-0.030 (3)
C8	0.032 (3)	0.061 (4)	0.060 (4)	-0.016 (3)	-0.005 (3)	-0.024 (3)
C9	0.036 (3)	0.054 (3)	0.053 (3)	-0.015 (3)	0.003 (3)	-0.023 (3)
C10	0.030 (2)	0.041 (3)	0.048 (3)	-0.008 (2)	0.000 (2)	-0.023 (2)
C11	0.032 (3)	0.052 (3)	0.044 (3)	-0.014 (2)	0.006 (2)	-0.024 (2)
C12	0.035 (3)	0.051 (3)	0.040 (3)	-0.015 (2)	0.007 (2)	-0.022 (3)
C13	0.048 (3)	0.067 (4)	0.046 (3)	-0.025 (3)	0.010 (3)	-0.021 (3)
C14	0.055 (3)	0.069 (4)	0.042 (3)	-0.021 (3)	0.009 (3)	-0.024 (3)
C15	0.071 (4)	0.095 (5)	0.050 (4)	-0.035 (4)	0.011 (3)	-0.021 (4)
C19	0.035 (4)	0.041 (4)	0.077 (5)	-0.008 (3)	0.003 (4)	-0.014 (4)
C20	0.077 (6)	0.055 (5)	0.083 (6)	0.014 (4)	-0.017 (5)	-0.027 (5)
C23	0.067 (10)	0.097 (12)	0.058 (9)	-0.011 (9)	0.004 (8)	0.000 (9)
C24	0.060 (9)	0.051 (8)	0.062 (9)	-0.008 (7)	-0.013 (7)	-0.016 (7)
O1	0.042 (3)	0.040 (3)	0.078 (4)	-0.001 (2)	-0.005 (2)	-0.021 (2)
O2	0.067 (4)	0.057 (3)	0.069 (4)	-0.002 (3)	-0.012 (3)	-0.014 (3)
O3	0.033 (2)	0.039 (2)	0.033 (2)	-0.0101 (17)	0.0037 (17)	-0.0157 (18)
O4	0.056 (5)	0.015 (3)	0.024 (4)	-0.001 (3)	0.009 (4)	0.000 (3)
O5	0.026 (4)	0.024 (4)	0.027 (4)	-0.008 (3)	-0.004 (3)	-0.008 (3)
N2	0.034 (3)	0.042 (3)	0.040 (3)	-0.010 (2)	0.000 (2)	-0.019 (2)
N1	0.032 (3)	0.037 (3)	0.037 (3)	-0.005 (2)	0.000 (2)	-0.017 (2)

supplementary materials

Geometric parameters (Å, °)

Zn1—O1	2.025 (5)	C16—H16A	0.9600
Zn1—O3	2.033 (4)	C16—H16B	0.9600
Zn1—O3 ⁱ	2.043 (4)	C16—H16C	0.9600
Zn1—N2	2.100 (5)	C17—H17A	0.9600
Zn1—N1	2.104 (5)	C17—H17B	0.9600
Zn1—Zn1 ⁱ	3.0670 (13)	C17—H17C	0.9600
C1—O3	1.341 (7)	C18—H18A	0.9600
C1—C2	1.407 (8)	C18—H18B	0.9600
C1—C12 ⁱ	1.412 (9)	C18—H18C	0.9600
C2—C3	1.403 (9)	C16 ⁺ —H16D	0.9600
C2—C4	1.501 (9)	C16 ⁺ —H16E	0.9600
C3—C14 ⁱ	1.370 (10)	C16 ⁺ —H16F	0.9600
C3—H3	0.9300	C17 ⁺ —H17D	0.9600
C4—N2	1.496 (8)	C17 ⁺ —H17E	0.9600
C4—H4A	0.9700	C17 ⁺ —H17F	0.9600
C4—H4B	0.9700	C18 ⁺ —H18D	0.9600
C5—C6	1.385 (9)	C18 ⁺ —H18E	0.9600
C5—C10	1.386 (9)	C18 ⁺ —H18F	0.9600
C5—N2	1.470 (8)	C19—O2	1.223 (10)
C6—C7	1.363 (10)	C19—O1	1.276 (9)
C6—H6	0.9300	C19—C20	1.497 (11)
C7—C8	1.374 (11)	C20—H20A	0.9600
C7—H7	0.9300	C20—H20B	0.9600
C8—C9	1.386 (10)	C20—H20C	0.9600
C8—H8	0.9300	C21—O4	1.34 (3)
C9—C10	1.371 (9)	C21—C22	1.47 (3)
C9—H9	0.9300	C21—H21A	0.9700
C10—N1	1.456 (8)	C21—H21B	0.9700
C11—N1	1.511 (7)	C22—H22A	0.9600
C11—C12	1.517 (9)	C22—H22B	0.9600
C11—H11A	0.9700	C22—H22C	0.9600
C11—H11B	0.9700	C23—C24	1.40 (2)
C12—C13	1.398 (10)	C23—H23A	0.9600
C12—C1 ⁱ	1.412 (9)	C23—H23B	0.9600
C13—C14	1.387 (10)	C23—H23C	0.9600
C13—H13	0.9300	C24—O5	1.446 (18)
C14—C3 ⁱ	1.370 (10)	C24—H24A	0.9700
C14—C15	1.540 (11)	C24—H24B	0.9700
C15—C17 ⁺	1.40 (2)	O3—Zn1 ⁱ	2.043 (4)
C15—C16	1.426 (11)	O4—H4	0.8200
C15—C17	1.426 (11)	O5—H5	0.8200
C15—C18 ⁺	1.475 (17)	N2—H2N	0.87 (3)
C15—C16 ⁺	1.479 (11)	N1—H1N	0.86 (3)
C15—C18	1.57 (2)		

O1—Zn1—O3	96.05 (19)	H16A—C16—H16B	109.5
O1—Zn1—O3 ⁱ	105.62 (19)	C15—C16—H16C	109.5
O3—Zn1—O3 ⁱ	82.40 (17)	H16A—C16—H16C	109.5
O1—Zn1—N2	144.5 (2)	H16B—C16—H16C	109.5
O3—Zn1—N2	88.07 (18)	C15—C17—H17A	109.5
O3 ⁱ —Zn1—N2	109.82 (19)	C15—C17—H17B	109.5
O1—Zn1—N1	95.6 (2)	H17A—C17—H17B	109.5
O3—Zn1—N1	168.18 (18)	C15—C17—H17C	109.5
O3 ⁱ —Zn1—N1	92.33 (17)	H17A—C17—H17C	109.5
N2—Zn1—N1	83.8 (2)	H17B—C17—H17C	109.5
O1—Zn1—Zn1 ⁱ	104.44 (14)	C15—C18—H18A	109.5
O3—Zn1—Zn1 ⁱ	41.32 (11)	C15—C18—H18B	109.5
O3 ⁱ —Zn1—Zn1 ⁱ	41.08 (11)	H18A—C18—H18B	109.5
N2—Zn1—Zn1 ⁱ	101.75 (15)	C15—C18—H18C	109.5
N1—Zn1—Zn1 ⁱ	132.53 (13)	H18A—C18—H18C	109.5
O3—C1—C2	122.6 (6)	H18B—C18—H18C	109.5
O3—C1—C12 ⁱ	118.4 (5)	C15—C16 ^a —H16D	109.5
C2—C1—C12 ⁱ	119.0 (6)	C15—C16 ^a —H16E	109.5
C3—C2—C1	118.2 (6)	H16D—C16 ^a —H16E	109.5
C3—C2—C4	118.5 (6)	C15—C16 ^a —H16F	109.5
C1—C2—C4	123.2 (6)	H16D—C16 ^a —H16F	109.5
C14 ⁱ —C3—C2	123.6 (6)	H16E—C16 ^a —H16F	109.5
C14 ⁱ —C3—H3	118.2	C15—C17 ^a —H17D	109.5
C2—C3—H3	118.2	C15—C17 ^a —H17E	109.5
N2—C4—C2	112.9 (5)	H17D—C17 ^a —H17E	109.5
N2—C4—H4A	109.0	C15—C17 ^a —H17F	109.5
C2—C4—H4A	109.0	H17D—C17 ^a —H17F	109.5
N2—C4—H4B	109.0	H17E—C17 ^a —H17F	109.5
C2—C4—H4B	109.0	C15—C18 ^a —H18D	109.5
H4A—C4—H4B	107.8	C15—C18 ^a —H18E	109.5
C6—C5—C10	119.2 (6)	H18D—C18 ^a —H18E	109.5
C6—C5—N2	121.9 (6)	C15—C18 ^a —H18F	109.5
C10—C5—N2	118.9 (5)	H18D—C18 ^a —H18F	109.5
C7—C6—C5	121.1 (7)	H18E—C18 ^a —H18F	109.5
C7—C6—H6	119.5	O2—C19—O1	120.5 (7)
C5—C6—H6	119.5	O2—C19—C20	122.1 (7)
C6—C7—C8	119.9 (7)	O1—C19—C20	117.4 (8)
C6—C7—H7	120.0	C19—C20—H20A	109.5
C8—C7—H7	120.0	C19—C20—H20B	109.5
C7—C8—C9	119.4 (6)	H20A—C20—H20B	109.5
C7—C8—H8	120.3	C19—C20—H20C	109.5
C9—C8—H8	120.3	H20A—C20—H20C	109.5
C10—C9—C8	121.0 (7)	H20B—C20—H20C	109.5
C10—C9—H9	119.5	O4—C21—C22	116 (2)
C8—C9—H9	119.5	O4—C21—H21A	108.2
C9—C10—C5	119.4 (6)	C22—C21—H21A	108.2

supplementary materials

C9—C10—N1	121.4 (6)	O4—C21—H21B	108.2
C5—C10—N1	119.2 (5)	C22—C21—H21B	108.2
N1—C11—C12	112.1 (5)	H21A—C21—H21B	107.4
N1—C11—H11A	109.2	C21—C22—H22A	109.5
C12—C11—H11A	109.2	C21—C22—H22B	109.5
N1—C11—H11B	109.2	H22A—C22—H22B	109.5
C12—C11—H11B	109.2	C21—C22—H22C	109.5
H11A—C11—H11B	107.9	H22A—C22—H22C	109.5
C13—C12—C1 ⁱ	119.9 (6)	H22B—C22—H22C	109.5
C13—C12—C11	121.2 (6)	C24—C23—H23A	109.5
C1 ⁱ —C12—C11	118.3 (6)	C24—C23—H23B	109.5
C14—C13—C12	121.6 (7)	H23A—C23—H23B	109.5
C14—C13—H13	119.2	C24—C23—H23C	109.5
C12—C13—H13	119.2	H23A—C23—H23C	109.5
C3 ⁱ —C14—C13	117.6 (7)	H23B—C23—H23C	109.5
C3 ⁱ —C14—C15	121.7 (7)	C23—C24—O5	111.0 (14)
C13—C14—C15	120.6 (7)	C23—C24—H24A	109.4
C17 ^a —C15—C16	135.3 (16)	O5—C24—H24A	109.4
C17 ^a —C15—C17	45.7 (11)	C23—C24—H24B	109.4
C16—C15—C17	113.1 (11)	O5—C24—H24B	109.4
C17 ^a —C15—C18 ^a	98.4 (13)	H24A—C24—H24B	108.0
C16—C15—C18 ^a	56.2 (11)	C19—O1—Zn1	106.4 (5)
C17—C15—C18 ^a	122.3 (14)	C1—O3—Zn1	128.5 (4)
C17 ^a —C15—C16 ^a	123.3 (15)	C1—O3—Zn1 ⁱ	113.8 (4)
C16—C15—C16 ^a	50.1 (11)	Zn1—O3—Zn1 ⁱ	97.60 (17)
C17—C15—C16 ^a	78.5 (13)	C21—O4—H4	109.5
C18 ^a —C15—C16 ^a	105.0 (10)	C24—O5—H5	109.5
C17 ^a —C15—C14	108.8 (12)	C5—N2—C4	114.9 (5)
C16—C15—C14	115.4 (13)	C5—N2—Zn1	107.9 (4)
C17—C15—C14	118.0 (11)	C4—N2—Zn1	107.6 (4)
C18 ^a —C15—C14	116.1 (10)	C5—N2—H2N	109 (5)
C16 ^a —C15—C14	105.7 (12)	C4—N2—H2N	107 (5)
C17 ^a —C15—C18	58.0 (8)	Zn1—N2—H2N	110 (5)
C16—C15—C18	102.3 (11)	C10—N1—C11	110.9 (5)
C17—C15—C18	99.6 (14)	C10—N1—Zn1	108.1 (4)
C18 ^a —C15—C18	46.8 (10)	C11—N1—Zn1	110.1 (3)
C16 ^a —C15—C18	145.6 (14)	C10—N1—H1N	124 (7)
C14—C15—C18	105.2 (12)	C11—N1—H1N	93 (7)
C15—C16—H16A	109.5	Zn1—N1—H1N	109 (7)
C15—C16—H16B	109.5		

Symmetry codes: (i) $-x, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4A \cdots O2	0.97	2.45	3.246 (10)	139
N1—H1N \cdots O4	0.86 (7)	2.23 (7)	2.952 (9)	141 (6)
N2—H2N \cdots O5 ⁱⁱ	0.87 (4)	2.13 (4)	2.999 (9)	175 (4)

O4—H4···O2 ⁱⁱⁱ	0.82	2.06	2.768 (10)	145
O5—H5···O1 ^{iv}	0.82	1.92	2.700 (9)	159

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

Fig. 1

