

Chlorido(8-hydroxyquinoline- κ^2N,O)- (quinolin-8-olato- κ^2N,O)zinc methanol monosolvate

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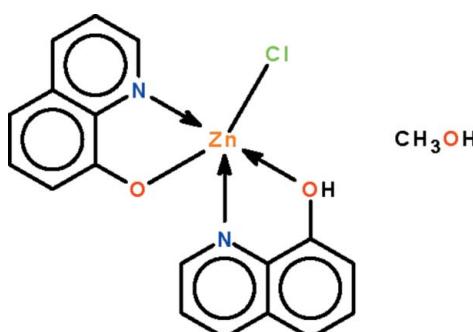
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.003$ Å;
 R factor = 0.034; wR factor = 0.082; data-to-parameter ratio = 15.6.

In the title compound, $[Zn(C_9H_6NO)Cl(C_9H_7NO)] \cdot CH_3OH$, the Zn^{II} ion is N,O -chelated by both a neutral and a deprotonated quinolin-8-ol ligand, with a chloride ligand in the apical site completing the square-pyramidal coordination geometry. The Zn^{II} ion is displaced by 0.586 Å in the direction of the chloride ligand from the atoms forming the square plane. In the crystal, the components are linked by intermolecular O–H···O hydrogen bonds, generating chains along the b axis.

Related literature

For the crystal structure of 8-hydroxy-2-methylquinolinium dichlorido(2-methylquinolin-8-olato- κ^2N,O)zincate(II) acetonitrile disolvate, see: Najafi *et al.* (2011).



Experimental

Crystal data

$[Zn(C_9H_6NO)Cl(C_9H_7NO)] \cdot CH_3OH$	$\gamma = 110.549 (5)^\circ$
$M_r = 422.17$	$V = 859.58 (7) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.4110 (4)$ Å	Mo $K\alpha$ radiation
$b = 8.4692 (4)$ Å	$\mu = 1.61 \text{ mm}^{-1}$
$c = 13.2667 (7)$ Å	$T = 100$ K
$\alpha = 99.905 (4)^\circ$	$0.15 \times 0.15 \times 0.15$ mm
$\beta = 95.341 (4)^\circ$	

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector	6878 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2010)	3806 independent reflections
$T_{\min} = 0.795$, $T_{\max} = 0.795$	3258 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$
3806 reflections	
244 parameters	
2 restraints	

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2–H2···O3	0.84 (1)	1.71 (1)	2.547 (2)	170 (3)
O3–H3···O1 ⁱ	0.84 (1)	1.76 (1)	2.592 (2)	176 (3)

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

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); 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: LH5311).

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Acta Cryst. (2011). E67, m1283 [doi:10.1107/S160053681103337X]

Chlorido(8-hydroxyquinoline- κ^2N,O)(quinolin-8-olato- κ^2N,O)zinc methanol monosolvate

E. Najafi, M. M. Amini and S. W. Ng

Comment

We have previously determined the structure of 8-Hydroxy-2-methylquinolinium dichlorido(2-methylquinolin-8-olato- κ^2N,O)zincate(II) acetonitrile disolvate (Najafi *et al.*, 2011). In the present study, the corresponding reaction of zinc chloride and the parent 8-hydroxyquinoline homolog in methanol yielded a neutral mono-solvated compound. The Zn^{II} atom in $ZnCl(C_9H_6NO)(C_9H_7NO)]CH_3OH$ is *N,O*-chelated by a neutral as well as by a deprotonated 8-hydroxyquinoline ligand and it exists in a square-pyramidal geometry (Fig. 1). Adjacent molecules are linked by O—H···O hydrogen bonds through the solvent molecule to generate a linear chain running along the *b*-axis of the triclinic unit cell (Fig. 2).

Experimental

Zinc chloride (0.13 g, 1 mmol) and 8-hydroxyquinoline (0.29 g, 2 mmol) were loaded into a convection tube and the tube was filled with methanol and kept at 333 K. Yellow crystals were collected from the side arm after several days.

Refinement

Carbon-bound H-atoms were placed in calculated positions [C—H 0.95 to 0.98 Å, $U_{iso}(H)$ 1.2 to 1.5 $U_{eq}(C)$] and were included in the refinement in the riding model approximation.

The hydroxy H-atoms were located in a difference Fourier map, and were refined with a distance restraint O—H 0.84±0.01 Å; their temperature factors were refined.

Figures

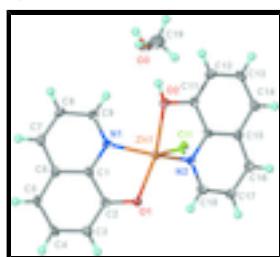


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $ZnCl(C_9H_6NO)(C_9H_7NO)]CH_3OH$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

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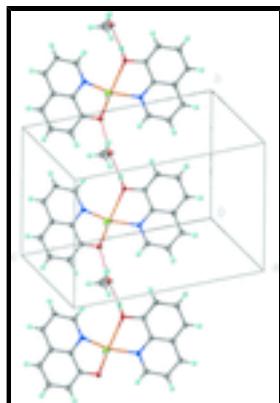


Fig. 2. Part of the crystal structure with hydrogen bonds shown as dashed lines.

Chlorido(8-hydroxyquinoline- κ^2N,O)(quinolin-8-olato- κ^2N,O)zincate methanol monosolvate

Crystal data

[Zn(C ₉ H ₆ NO)Cl(C ₉ H ₇ NO)]·CH ₄ O	Z = 2
M _r = 422.17	F(000) = 432
Triclinic, P $\bar{1}$	D _x = 1.631 Mg m ⁻³
Hall symbol: -P 1	Mo K α radiation, λ = 0.71073 Å
a = 8.4110 (4) Å	Cell parameters from 3680 reflections
b = 8.4692 (4) Å	θ = 2.6–29.3°
c = 13.2667 (7) Å	μ = 1.61 mm ⁻¹
α = 99.905 (4)°	T = 100 K
β = 95.341 (4)°	Cuboid, yellow
γ = 110.549 (5)°	0.15 × 0.15 × 0.15 mm
V = 859.58 (7) Å ³	

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector	3806 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	3258 reflections with $I > 2\sigma(I)$
Mirror	$R_{\text{int}} = 0.045$
Detector resolution: 10.4041 pixels mm ⁻¹	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.6^\circ$
ω scans	$h = -8 \rightarrow 10$
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2010)	$k = -10 \rightarrow 10$
$T_{\text{min}} = 0.795$, $T_{\text{max}} = 0.795$	$l = -17 \rightarrow 17$
6878 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.082$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.2331P]$
3806 reflections	where $P = (F_o^2 + 2F_c^2)/3$
244 parameters	$(\Delta/\sigma)_{\max} = 0.001$
2 restraints	$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
	$\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.64683 (4)	0.45465 (3)	0.717891 (19)	0.01236 (9)
Cl1	0.91659 (8)	0.57790 (8)	0.80776 (4)	0.01774 (14)
O1	0.5263 (2)	0.2082 (2)	0.73472 (12)	0.0148 (4)
O2	0.6496 (2)	0.6842 (2)	0.64293 (12)	0.0156 (4)
O3	0.6795 (2)	0.9898 (2)	0.72616 (12)	0.0196 (4)
N1	0.4816 (3)	0.5009 (2)	0.81134 (14)	0.0121 (4)
N2	0.6744 (3)	0.3866 (2)	0.56612 (14)	0.0121 (4)
C1	0.3948 (3)	0.3574 (3)	0.84634 (16)	0.0118 (5)
C2	0.4213 (3)	0.2018 (3)	0.80397 (16)	0.0123 (5)
C3	0.3344 (3)	0.0553 (3)	0.83838 (17)	0.0153 (5)
H3A	0.3474	-0.0499	0.8109	0.018*
C4	0.2270 (3)	0.0585 (3)	0.91326 (17)	0.0163 (5)
H4	0.1689	-0.0450	0.9350	0.020*
C5	0.2039 (3)	0.2065 (3)	0.95567 (17)	0.0157 (5)
H5	0.1328	0.2064	1.0073	0.019*
C6	0.2873 (3)	0.3594 (3)	0.92149 (17)	0.0131 (5)
C7	0.2700 (3)	0.5192 (3)	0.95927 (17)	0.0143 (5)
H7	0.1977	0.5269	1.0093	0.017*
C8	0.3578 (3)	0.6616 (3)	0.92317 (17)	0.0149 (5)
H8	0.3470	0.7689	0.9481	0.018*
C9	0.4638 (3)	0.6488 (3)	0.84925 (17)	0.0142 (5)
H9	0.5250	0.7490	0.8253	0.017*
C10	0.7339 (3)	0.5164 (3)	0.51453 (16)	0.0121 (5)
C11	0.7243 (3)	0.6787 (3)	0.55646 (17)	0.0131 (5)
C12	0.7850 (3)	0.8125 (3)	0.50826 (18)	0.0159 (5)
H12	0.7808	0.9216	0.5368	0.019*
C13	0.8537 (3)	0.7903 (3)	0.41679 (18)	0.0163 (5)
H13	0.8946	0.8849	0.3841	0.020*
C14	0.8633 (3)	0.6356 (3)	0.37360 (17)	0.0149 (5)
H14	0.9110	0.6233	0.3119	0.018*
C15	0.8012 (3)	0.4946 (3)	0.42191 (17)	0.0130 (5)
C16	0.7985 (3)	0.3275 (3)	0.38085 (17)	0.0150 (5)
H16	0.8439	0.3067	0.3192	0.018*
C17	0.7302 (3)	0.1966 (3)	0.43052 (17)	0.0167 (5)
H17	0.7224	0.0829	0.4017	0.020*

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C18	0.6719 (3)	0.2314 (3)	0.52412 (17)	0.0146 (5)
H18	0.6287	0.1402	0.5591	0.018*
C19	0.8321 (4)	1.0712 (3)	0.8018 (2)	0.0255 (6)
H19A	0.8904	1.1906	0.7952	0.038*
H19B	0.9090	1.0079	0.7907	0.038*
H19C	0.8020	1.0711	0.8714	0.038*
H2	0.653 (4)	0.785 (2)	0.664 (2)	0.033 (9)*
H3	0.626 (4)	1.056 (4)	0.727 (2)	0.040 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01352 (17)	0.01182 (15)	0.01295 (15)	0.00472 (12)	0.00608 (11)	0.00385 (11)
Cl1	0.0132 (3)	0.0223 (3)	0.0164 (3)	0.0050 (3)	0.0049 (2)	0.0030 (2)
O1	0.0179 (10)	0.0128 (8)	0.0163 (8)	0.0067 (7)	0.0085 (7)	0.0049 (7)
O2	0.0220 (10)	0.0138 (9)	0.0148 (8)	0.0091 (8)	0.0096 (7)	0.0039 (7)
O3	0.0210 (11)	0.0166 (9)	0.0222 (9)	0.0101 (8)	0.0017 (8)	0.0016 (7)
N1	0.0120 (11)	0.0112 (9)	0.0134 (9)	0.0046 (8)	0.0023 (8)	0.0029 (8)
N2	0.0129 (11)	0.0119 (9)	0.0136 (9)	0.0057 (9)	0.0040 (8)	0.0049 (8)
C1	0.0091 (12)	0.0139 (11)	0.0117 (10)	0.0029 (10)	0.0005 (9)	0.0046 (9)
C2	0.0127 (12)	0.0127 (11)	0.0114 (11)	0.0046 (10)	0.0023 (9)	0.0031 (9)
C3	0.0161 (13)	0.0126 (11)	0.0159 (12)	0.0042 (10)	0.0034 (10)	0.0023 (9)
C4	0.0154 (13)	0.0160 (12)	0.0156 (12)	0.0016 (10)	0.0028 (10)	0.0072 (10)
C5	0.0120 (13)	0.0191 (12)	0.0155 (11)	0.0038 (10)	0.0055 (9)	0.0049 (10)
C6	0.0092 (12)	0.0158 (12)	0.0130 (11)	0.0032 (10)	0.0015 (9)	0.0033 (9)
C7	0.0147 (13)	0.0186 (12)	0.0121 (11)	0.0079 (11)	0.0053 (9)	0.0044 (9)
C8	0.0174 (14)	0.0145 (12)	0.0158 (11)	0.0094 (11)	0.0044 (10)	0.0025 (9)
C9	0.0148 (13)	0.0136 (11)	0.0153 (11)	0.0057 (10)	0.0031 (10)	0.0048 (9)
C10	0.0125 (13)	0.0101 (11)	0.0132 (11)	0.0033 (10)	0.0015 (9)	0.0037 (9)
C11	0.0110 (12)	0.0148 (11)	0.0154 (11)	0.0058 (10)	0.0037 (9)	0.0049 (9)
C12	0.0158 (13)	0.0128 (12)	0.0193 (12)	0.0063 (10)	0.0030 (10)	0.0022 (10)
C13	0.0164 (14)	0.0152 (12)	0.0180 (12)	0.0038 (11)	0.0049 (10)	0.0089 (10)
C14	0.0153 (13)	0.0180 (12)	0.0119 (11)	0.0050 (11)	0.0042 (9)	0.0061 (9)
C15	0.0112 (12)	0.0145 (11)	0.0120 (11)	0.0039 (10)	0.0006 (9)	0.0025 (9)
C16	0.0167 (13)	0.0166 (12)	0.0118 (11)	0.0061 (11)	0.0040 (9)	0.0028 (9)
C17	0.0203 (14)	0.0120 (11)	0.0174 (12)	0.0070 (11)	0.0049 (10)	-0.0008 (9)
C18	0.0157 (13)	0.0122 (11)	0.0153 (11)	0.0038 (10)	0.0037 (9)	0.0038 (9)
C19	0.0260 (16)	0.0225 (14)	0.0262 (14)	0.0086 (13)	0.0004 (12)	0.0042 (11)

Geometric parameters (\AA , $^\circ$)

Zn1—O1	2.0377 (16)	C7—C8	1.367 (3)
Zn1—N1	2.0392 (18)	C7—H7	0.9500
Zn1—N2	2.0547 (17)	C8—C9	1.401 (3)
Zn1—Cl1	2.2505 (7)	C8—H8	0.9500
Zn1—O2	2.3257 (16)	C9—H9	0.9500
O1—C2	1.327 (3)	C10—C15	1.410 (3)
O2—C11	1.360 (3)	C10—C11	1.424 (3)
O2—H2	0.842 (10)	C11—C12	1.363 (3)

O3—C19	1.425 (3)	C12—C13	1.404 (3)
O3—H3	0.836 (10)	C12—H12	0.9500
N1—C9	1.332 (3)	C13—C14	1.369 (3)
N1—C1	1.364 (3)	C13—H13	0.9500
N2—C18	1.328 (3)	C14—C15	1.414 (3)
N2—C10	1.366 (3)	C14—H14	0.9500
C1—C6	1.409 (3)	C15—C16	1.417 (3)
C1—C2	1.441 (3)	C16—C17	1.367 (3)
C2—C3	1.379 (3)	C16—H16	0.9500
C3—C4	1.407 (3)	C17—C18	1.399 (3)
C3—H3A	0.9500	C17—H17	0.9500
C4—C5	1.369 (3)	C18—H18	0.9500
C4—H4	0.9500	C19—H19A	0.9800
C5—C6	1.414 (3)	C19—H19B	0.9800
C5—H5	0.9500	C19—H19C	0.9800
C6—C7	1.422 (3)		
O1—Zn1—N1	82.18 (7)	C6—C7—H7	120.2
O1—Zn1—N2	95.64 (7)	C7—C8—C9	119.7 (2)
N1—Zn1—N2	143.92 (8)	C7—C8—H8	120.1
O1—Zn1—Cl1	112.11 (5)	C9—C8—H8	120.1
N1—Zn1—Cl1	108.81 (6)	N1—C9—C8	122.2 (2)
N2—Zn1—Cl1	105.34 (6)	N1—C9—H9	118.9
O1—Zn1—O2	150.43 (7)	C8—C9—H9	118.9
N1—Zn1—O2	90.44 (6)	N2—C10—C15	122.63 (19)
N2—Zn1—O2	73.80 (6)	N2—C10—C11	117.76 (19)
Cl1—Zn1—O2	97.40 (5)	C15—C10—C11	119.6 (2)
C2—O1—Zn1	111.33 (13)	O2—C11—C12	125.2 (2)
C11—O2—Zn1	109.79 (12)	O2—C11—C10	115.16 (19)
C11—O2—H2	109 (2)	C12—C11—C10	119.6 (2)
Zn1—O2—H2	136 (2)	C11—C12—C13	120.4 (2)
C19—O3—H3	109 (2)	C11—C12—H12	119.8
C9—N1—C1	118.9 (2)	C13—C12—H12	119.8
C9—N1—Zn1	129.73 (17)	C14—C13—C12	121.6 (2)
C1—N1—Zn1	110.92 (14)	C14—C13—H13	119.2
C18—N2—C10	118.31 (19)	C12—C13—H13	119.2
C18—N2—Zn1	122.72 (15)	C13—C14—C15	119.2 (2)
C10—N2—Zn1	117.44 (14)	C13—C14—H14	120.4
N1—C1—C6	122.56 (19)	C15—C14—H14	120.4
N1—C1—C2	116.5 (2)	C10—C15—C14	119.6 (2)
C6—C1—C2	121.0 (2)	C10—C15—C16	117.0 (2)
O1—C2—C3	124.4 (2)	C14—C15—C16	123.4 (2)
O1—C2—C1	118.4 (2)	C17—C16—C15	119.6 (2)
C3—C2—C1	117.3 (2)	C17—C16—H16	120.2
C2—C3—C4	121.4 (2)	C15—C16—H16	120.2
C2—C3—H3A	119.3	C16—C17—C18	119.5 (2)
C4—C3—H3A	119.3	C16—C17—H17	120.2
C5—C4—C3	121.8 (2)	C18—C17—H17	120.2
C5—C4—H4	119.1	N2—C18—C17	122.8 (2)
C3—C4—H4	119.1	N2—C18—H18	118.6

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C4—C5—C6	119.0 (2)	C17—C18—H18	118.6
C4—C5—H5	120.5	O3—C19—H19A	109.5
C6—C5—H5	120.5	O3—C19—H19B	109.5
C1—C6—C5	119.5 (2)	H19A—C19—H19B	109.5
C1—C6—C7	116.9 (2)	O3—C19—H19C	109.5
C5—C6—C7	123.6 (2)	H19A—C19—H19C	109.5
C8—C7—C6	119.7 (2)	H19B—C19—H19C	109.5
C8—C7—H7	120.2		
N1—Zn1—O1—C2	-7.37 (15)	N1—C1—C6—C5	-178.8 (2)
N2—Zn1—O1—C2	-151.09 (15)	C2—C1—C6—C5	-0.1 (3)
Cl1—Zn1—O1—C2	99.82 (15)	N1—C1—C6—C7	0.9 (3)
O2—Zn1—O1—C2	-84.30 (18)	C2—C1—C6—C7	179.6 (2)
O1—Zn1—O2—C11	-92.97 (18)	C4—C5—C6—C1	-1.3 (3)
N1—Zn1—O2—C11	-167.77 (16)	C4—C5—C6—C7	179.1 (2)
N2—Zn1—O2—C11	-20.70 (15)	C1—C6—C7—C8	-0.8 (3)
Cl1—Zn1—O2—C11	83.19 (15)	C5—C6—C7—C8	178.9 (2)
O1—Zn1—N1—C9	179.1 (2)	C6—C7—C8—C9	0.1 (3)
N2—Zn1—N1—C9	-92.0 (2)	C1—N1—C9—C8	-0.5 (3)
Cl1—Zn1—N1—C9	68.3 (2)	Zn1—N1—C9—C8	-171.85 (17)
O2—Zn1—N1—C9	-29.6 (2)	C7—C8—C9—N1	0.6 (4)
O1—Zn1—N1—C1	7.27 (15)	C18—N2—C10—C15	-3.6 (3)
N2—Zn1—N1—C1	96.13 (18)	Zn1—N2—C10—C15	162.71 (18)
Cl1—Zn1—N1—C1	-103.50 (15)	C18—N2—C10—C11	175.6 (2)
O2—Zn1—N1—C1	158.53 (15)	Zn1—N2—C10—C11	-18.1 (3)
O1—Zn1—N2—C18	-22.1 (2)	Zn1—O2—C11—C12	-163.1 (2)
N1—Zn1—N2—C18	-106.6 (2)	Zn1—O2—C11—C10	18.3 (2)
Cl1—Zn1—N2—C18	92.65 (19)	N2—C10—C11—O2	-2.4 (3)
O2—Zn1—N2—C18	-173.9 (2)	C15—C10—C11—O2	176.8 (2)
O1—Zn1—N2—C10	172.22 (17)	N2—C10—C11—C12	178.9 (2)
N1—Zn1—N2—C10	87.8 (2)	C15—C10—C11—C12	-1.9 (4)
Cl1—Zn1—N2—C10	-73.00 (17)	O2—C11—C12—C13	-177.4 (2)
O2—Zn1—N2—C10	20.40 (16)	C10—C11—C12—C13	1.2 (4)
C9—N1—C1—C6	-0.3 (3)	C11—C12—C13—C14	-0.5 (4)
Zn1—N1—C1—C6	172.59 (18)	C12—C13—C14—C15	0.5 (4)
C9—N1—C1—C2	-179.0 (2)	N2—C10—C15—C14	-178.9 (2)
Zn1—N1—C1—C2	-6.1 (2)	C11—C10—C15—C14	2.0 (3)
Zn1—O1—C2—C3	-173.89 (19)	N2—C10—C15—C16	2.6 (3)
Zn1—O1—C2—C1	6.3 (3)	C11—C10—C15—C16	-176.6 (2)
N1—C1—C2—O1	-0.1 (3)	C13—C14—C15—C10	-1.3 (4)
C6—C1—C2—O1	-178.8 (2)	C13—C14—C15—C16	177.2 (2)
N1—C1—C2—C3	-179.9 (2)	C10—C15—C16—C17	0.9 (3)
C6—C1—C2—C3	1.3 (3)	C14—C15—C16—C17	-177.5 (2)
O1—C2—C3—C4	179.0 (2)	C15—C16—C17—C18	-3.2 (4)
C1—C2—C3—C4	-1.2 (3)	C10—N2—C18—C17	1.1 (4)
C2—C3—C4—C5	-0.2 (4)	Zn1—N2—C18—C17	-164.42 (19)
C3—C4—C5—C6	1.4 (4)	C16—C17—C18—N2	2.3 (4)

Hydrogen-bond geometry (Å, °)

$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
O2—H2···O3	0.84 (1)	1.71 (1)	2.547 (2)	170 (3)
O3—H3···O1 ⁱ	0.84 (1)	1.76 (1)	2.592 (2)	176 (3)

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

supplementary materials

Fig. 1

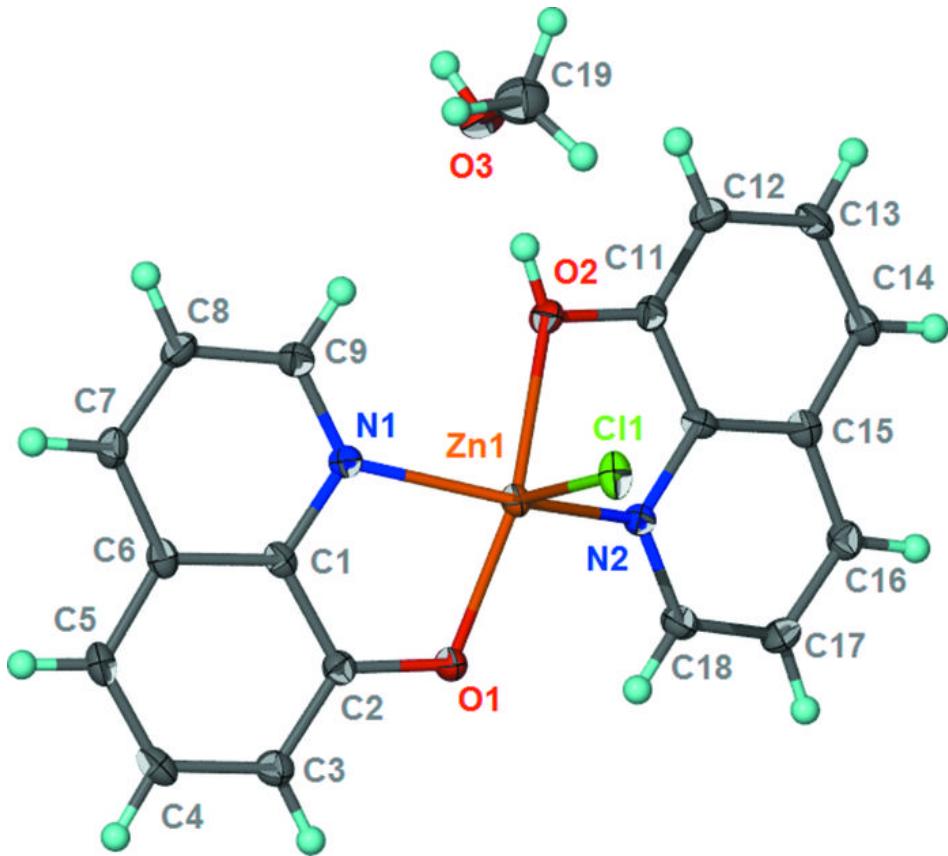


Fig. 2

