Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(2,2′-Bipyridine-κ^2N,N')bis(4-chlorobenzoato-κO)zinc

Bi-Song Zhang,[a]* Hong-Line Zhu,[b] Jun Li,[a] Dong-Dong Dai[a] and Yi-Bao Peng[a]

[a]College of Materials Science and Chemical Engineering, Jinhua College of Profession and Technology, Jinhua, Zhejiang 321017, People's Republic of China, and [b]State Key Laboratory Base of Novel Functional Materials and Preparation, Science Center of Applied Solid State Chemistry Research, Ningbo University, Ningbo, Zhejiang 315211, People's Republic of China
Correspondence e-mail: zbs_jy@163.com

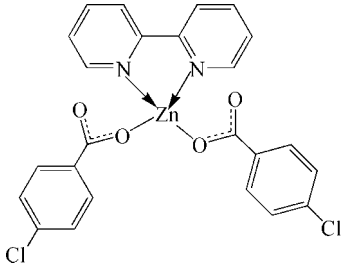
Received 10 February 2012; accepted 16 February 2012

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.007 Å; R factor = 0.041; wR factor = 0.121; data-to-parameter ratio = 13.4.

In the title compound, $[Zn(C_7H_4ClO_2)_2(C_{10}H_8N_2)]$, the Zn^{II} atom is coordinated by two O atoms from two 4-chlorobenzoate ligands and two N atoms from a chelating 2,2′-bipyridine (bpy) molecule in a distorted N_2O_2 tetrahedral geometry. The Zn^{II} atom is located on a twofold rotation axis, which also passes through the mid-point of the central C—C bond of the bpy ligand. In the crystal, weak C—H···O hydrogen bonds and π–π stacking interactions between the pyridine rings of the bpy ligands [centroid–centroid distance = 3.642 (3) Å] link the complex molecules into a two-dimensional supramolecular structure parallel to (100). An intramolecular C—H···O hydrogen bond is also observed.

Related literature

For zinc(II) complexes with substituted benzoate ligands, see: Aghabozorg *et al.* (2005); Chen *et al.* (2006); Hökelek *et al.* (2008); Lemoine *et al.* (2004); Liu *et al.* (1998); Wei *et al.* (2002, 2004); Xu *et al.* (2004); Ye & Zhang (2010); Zhang *et al.* (2009, 2010); Zhou *et al.* (2005).



Experimental

Crystal data

$[Zn(C_7H_4ClO_2)_2(C_{10}H_8N_2)]$
M_r = 532.68
Monoclinic, $P2/c$
a = 11.453 (2) Å
b = 8.4896 (17) Å
c = 12.337 (3) Å
β = 107.12 (3)°
V = 1146.4 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.34 mm^{-1}
T = 290 K
0.32 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.675, T_{max} = 0.787
8641 measured reflections
2012 independent reflections
1560 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.17
2012 reflections
150 parameters
48 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1^{i}	0.93	2.55	3.172 (6)	125
C3—H3···O2^{ii}	0.93	2.52	3.278 (5)	139
C11—H11···O1^{iii}	0.93	2.57	3.330 (5)	139

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge the financial support of the Education Office of Zhejiang Province (grant No. 20051316).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2516).

References

Aghabozorg, H., Nakhjavan, B., Zabihi, F., Ramezanipour, F. & Aghabozorg, H. R. (2005). *Acta Cryst.* E**61**, m2664–m2666.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Chen, H., Xu, X.-Y., Gao, J., Yang, X.-J., Lu, L.-D. & Wang, X. (2006). *Huaxue Shiji (Chem. React.)*, **28**, 478–480.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hökelek, T., Çaylak, N. & Necefoğlu, H. (2008). *Acta Cryst.* E**64**, m458–m459.
Lemoine, P., Bendada, K. & Viossat, B. (2004). *Acta Cryst.* C**60**, m489–m491.
Liu, C.-M., You, X.-Z. & Chen, W. (1998). *J. Coord. Chem.* **46**, 233–243.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wei, Y., Yuan, C. & Yang, P. (2004). *Acta Cryst.* E**60**, m1686–m1688.

Wei, D.-Y., Zheng, Y.-Q. & Lin, J.-L. (2002). *Z. Anorg. Allg. Chem.* **628**, 2005–2012.
Xu, H., Liang, Y., Su, Z., Zhao, Y., Shao, K., Zhang, H. & Yue, S. (2004). *Acta Cryst.* E**60**, m142–m144.
Ye, S.-F. & Zhang, B.-S. (2010). *Acta Cryst.* E**66**, m474.
Zhang, B.-Y., Nie, J.-J. & Xu, D.-J. (2009). *Acta Cryst.* E**65**, m880.
Zhang, B.-S., Ye, S.-F., Li, Y.-X. & Xu, W. (2010). *Acta Cryst.* E**66**, m1357–m1358.
Zhou, Y.-F., Lin, W.-J., Huang, Y.-G. & Hong, M.-C. (2005). *Acta Cryst.* E**61**, m177–m179.

supplementary materials

Acta Cryst. (2012). E**68**, m321–m322 [doi:10.1107/S160053681200699X]

(2,2′-Bipyridine-κ^2N,N')bis(4-chlorobenzoato-κO)zinc

Bi-Song Zhang, Hong-Line Zhu, Jun Li, Dong-Dong Dai and Yi-Bao Peng

Comment

Transition metal complexes with biochemical molecules show interesting physical and/or chemical properties, which may find applications in biological systems. The structure–function–coordination relationships of arylcarboxylates in Zn^{II} complexes of benzoic acid derivatives may alos be changed depending on the nature and positions of the substituted groups on the benzene ring. Zinc(II) complexes with substituted benzoic acid ligands have been reported (Aghabozorg *et al.*, 2005; Chen *et al.*, 2006; Hökelek *et al.*, 2008; Lemoine *et al.*, 2004; Liu *et al.*, 1998; Wei *et al.*, 2002, 2004; Xu *et al.*, 2004; Ye & Zhang, 2010; Zhang *et al.*, 2009, 2010). In this paper, we report the synthesis and structure of the title complex.

In the title compound, the Zn^{II} atom is coordinated by two O atoms and two N atoms from two 4-chlorobenzoate ligands and one 2,2′-bipyridine (bpy) molecule in a distorted ZnN_2O_2 tetrahedral geometry. The O1 atom of the 4-chlorobenzoate ligand has a weak interaction with the Zn^{II} atom [Zn1···O1 = 2.602 (3) Å]. A similar distance has been observed [Zn1···O2 = 2.653 (7)Å] (Zhou *et al.*, 2005). The Zn^{II} atom is located on a twofold rotation axis, which also passes through the mid-point of the C5—$C5^{i}$ bond [symmetry code: (i) -x, y, -z+1/2] of the bpy ligand. The bpy ligand exhibits nearly perfect coplanarity (r.m.s. deviation = 0.049 Å). In the crystal, weak C—H···O hydrogen bonds (Table 1) and π–π stacking interactions [centroid–centroid distance = 3.642 (3) Å] between adjacent bpy ligands link the complex molecules into a two-dimensional supramolecular structure parallel to (100).

Experimental

$ZnCl_2$ (0.0687 g, 0.504 mmol) was dissolved in appropriate amount of water and then 1M Na_2CO_3 solution was added. $ZnCO_3$ was obtained by filtration, which was then washed with distilled water for 5 times. The freshly prepared $ZnCO_3$, 2,2′-bipyridine (0.0388 g, 0.273 mmol) and 4-chlorobenzoic acid (0.0396 g, 0.255 mmol), CH_3OH/H_2O (v/v = 1:2, 15 ml) were mixed and stirred for 2 h. The resulting cream suspension was heated in a 23 ml Teflon-lined stainless steel autoclave at 433 K for 97 h. After the autoclave was cooled to room temperature within 43 h, the solid was filtered off. The resulting filtrate was allowed to stand at room temperature and slow evaporation for 6 weeks afforded colorless block single crystals.

Refinement

H atoms were placed in calculated positions and refined as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

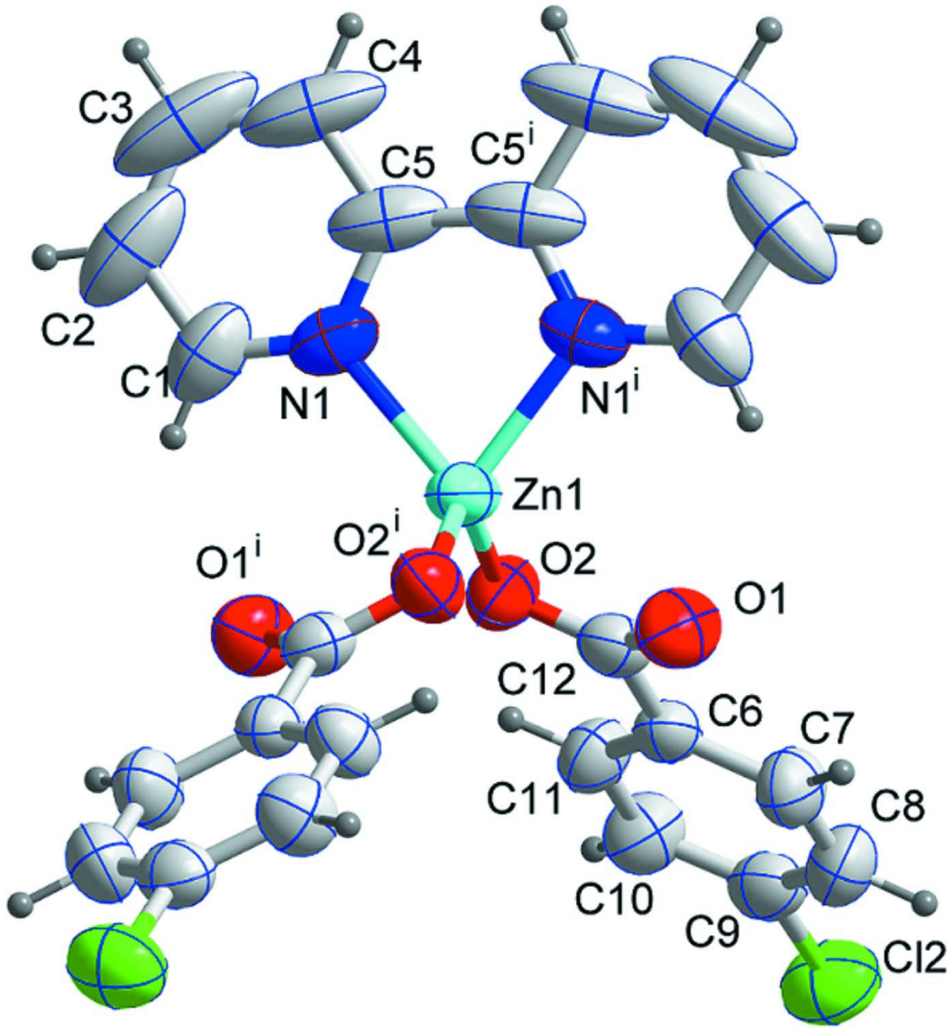


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) -x, y, -z+1/2.]

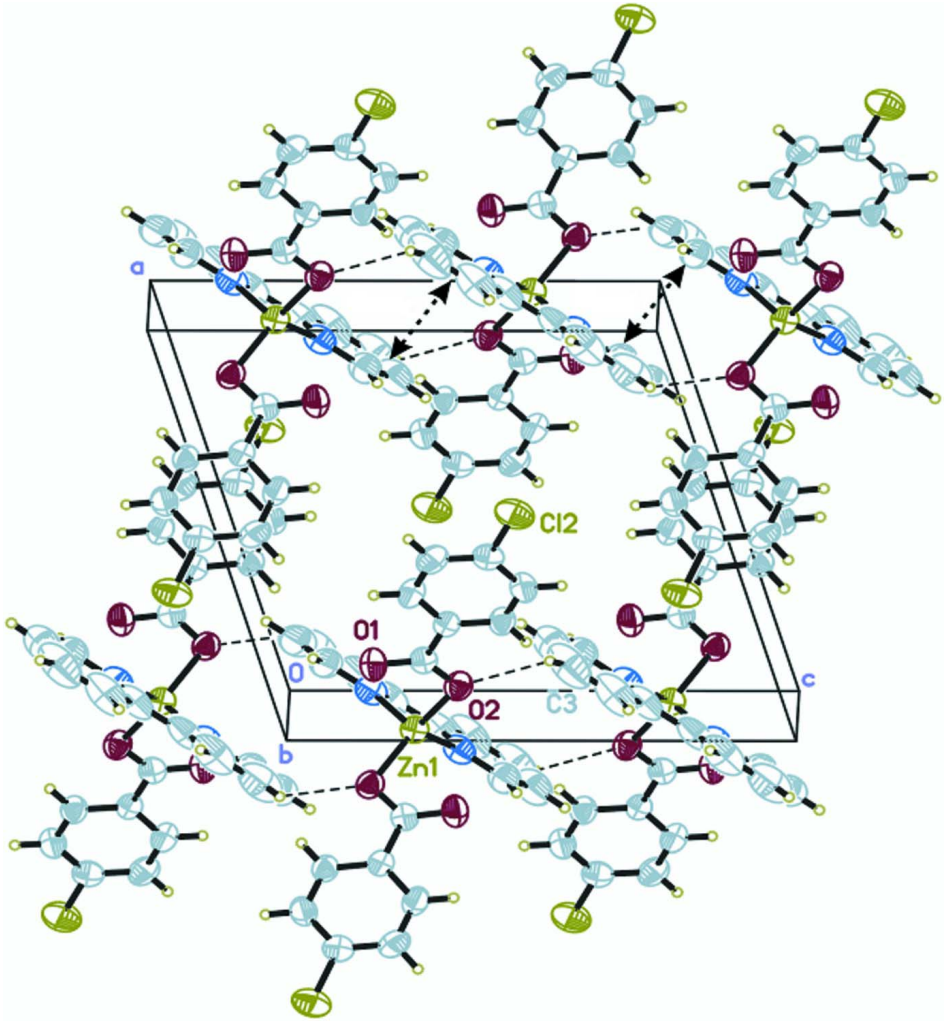


Figure 2

A view of the crystal packing, showing π–π interactions (dashed double arrows), with a centroid–centroid distance of 3.642 (3) Å, and C—H···O hydrogen bonds (dashed lines).

(2,2′-Bipyridine-κ^2N,N')bis(4-chlorobenzoato- κO)zinc(II)

Crystal data

$[Zn(C_7H_4ClO_2)_2(C_{10}H_8N_2)]$
M_r = 532.68
Monoclinic, $P2/c$
Hall symbol: -P 2yc
a = 11.453 (2) Å
b = 8.4896 (17) Å
c = 12.337 (3) Å
β = 107.12 (3)°
V = 1146.4 (5) Å^3
Z = 2
$F(000)$ = 540
D_x = 1.543 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6683 reflections
θ = 3.0–25.0°
μ = 1.34 mm^{-1}
T = 290 K
Block, colorless
0.32 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: rotation anode
Graphite monochromator
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.675, T_{max} = 0.787
8641 measured reflections
2012 independent reflections
1560 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −13→13
k = −9→10
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.17
2012 reflections
150 parameters
48 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
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.0000	0.78102 (6)	0.2500	0.0564 (2)
Cl2	0.59680 (10)	1.35611 (14)	0.61254 (11)	0.0912 (4)
O1	0.1788 (3)	0.9459 (3)	0.2186 (2)	0.0738 (7)
O2	0.1206 (2)	0.8948 (3)	0.3696 (2)	0.0650 (7)
C1	−0.1402 (4)	0.6021 (6)	0.3867 (4)	0.0889 (13)
H1	−0.1636	0.7013	0.4048	0.107*
C2	−0.1780 (5)	0.4710 (8)	0.4330 (5)	0.122 (2)
H2	−0.2269	0.4814	0.4808	0.146*
C3	−0.1427 (7)	0.3267 (9)	0.4076 (6)	0.144 (3)
H3	−0.1657	0.2369	0.4394	0.172*
C4	−0.0731 (6)	0.3138 (6)	0.3351 (5)	0.121 (2)
H4	−0.0493	0.2150	0.3168	0.145*
C5	−0.0377 (4)	0.4489 (4)	0.2888 (3)	0.0827 (13)
N1	−0.0713 (3)	0.5916 (3)	0.3171 (3)	0.0686 (8)
C6	0.2915 (3)	1.0622 (4)	0.3941 (3)	0.0512 (8)
C7	0.3756 (4)	1.1328 (5)	0.3489 (3)	0.0679 (10)
H7	0.3691	1.1184	0.2726	0.082*

C8	0.4688 (4)	1.2242 (5)	0.4152 (4)	0.0741 (11)
H8	0.5246	1.2720	0.3842	0.089*
C9	0.4779 (3)	1.2436 (4)	0.5275 (4)	0.0629 (10)
C10	0.3952 (4)	1.1763 (5)	0.5739 (3)	0.0690 (10)
H10	0.4017	1.1915	0.6501	0.083*
C11	0.3019 (3)	1.0853 (4)	0.5063 (3)	0.0614 (9)
H11	0.2455	1.0391	0.5375	0.074*
C12	0.1909 (3)	0.9613 (4)	0.3207 (3)	0.0553 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0659 (4)	0.0427 (3)	0.0618 (4)	0.000	0.0206 (3)	0.000
Cl2	0.0755 (7)	0.0805 (7)	0.1037 (9)	−0.0151 (6)	0.0048 (6)	−0.0030 (6)
O1	0.097 (2)	0.0728 (16)	0.0544 (16)	−0.0092 (15)	0.0258 (14)	−0.0083 (13)
O2	0.0722 (16)	0.0637 (15)	0.0639 (16)	−0.0123 (13)	0.0275 (13)	−0.0042 (12)
C1	0.080 (3)	0.105 (3)	0.081 (3)	−0.019 (2)	0.021 (2)	0.025 (2)
C2	0.104 (4)	0.151 (4)	0.097 (4)	−0.054 (4)	0.009 (3)	0.050 (4)
C3	0.165 (6)	0.116 (4)	0.110 (5)	−0.073 (4)	−0.021 (4)	0.058 (4)
C4	0.161 (5)	0.059 (3)	0.103 (4)	−0.040 (3)	−0.023 (3)	0.024 (3)
C5	0.104 (3)	0.0480 (18)	0.069 (3)	−0.013 (2)	−0.018 (2)	0.0074 (17)
N1	0.073 (2)	0.0545 (17)	0.070 (2)	−0.0075 (15)	0.0080 (16)	0.0108 (14)
C6	0.0590 (19)	0.0428 (16)	0.055 (2)	0.0036 (15)	0.0216 (15)	0.0031 (14)
C7	0.077 (3)	0.072 (2)	0.064 (2)	−0.006 (2)	0.035 (2)	−0.0049 (19)
C8	0.070 (3)	0.075 (3)	0.086 (3)	−0.012 (2)	0.038 (2)	0.002 (2)
C9	0.061 (2)	0.0511 (19)	0.074 (3)	0.0037 (17)	0.0154 (19)	0.0019 (17)
C10	0.079 (3)	0.072 (2)	0.054 (2)	−0.007 (2)	0.0172 (19)	−0.0008 (18)
C11	0.068 (2)	0.064 (2)	0.056 (2)	−0.0094 (18)	0.0234 (17)	0.0027 (17)
C12	0.065 (2)	0.0435 (17)	0.058 (2)	0.0065 (16)	0.0180 (17)	−0.0001 (15)

Geometric parameters (Å, º)

Zn1—O2	1.954 (2)	C4—H4	0.9300
Zn1—N1	2.082 (3)	C5—N1	1.347 (5)
Zn1—O1	2.602 (3)	C5—C5^{i}	1.466 (10)
Cl2—C9	1.740 (4)	C6—C11	1.368 (5)
O1—C12	1.233 (4)	C6—C7	1.384 (5)
O2—C12	1.272 (4)	C6—C12	1.506 (5)
C1—N1	1.329 (6)	C7—C8	1.377 (6)
C1—C2	1.377 (6)	C7—H7	0.9300
C1—H1	0.9300	C8—C9	1.368 (6)
C2—C3	1.356 (10)	C8—H8	0.9300
C2—H2	0.9300	C9—C10	1.368 (5)
C3—C4	1.366 (11)	C10—C11	1.382 (5)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.394 (6)	C11—H11	0.9300
O2—Zn1—O2^{i}	120.76 (15)	C2—C3—C4	119.6 (5)
O2—Zn1—N1	110.75 (11)	C2—C3—H3	120.2
O2^{i}—Zn1—N1	114.15 (11)	C4—C3—H3	120.2

O2—Zn1—N1^{i}	114.15 (11)	C3—C4—C5	119.9 (6)
O2^{i}—Zn1—N1^{i}	110.75 (11)	C3—C4—H4	120.1
N1—Zn1—N1^{i}	78.9 (2)	C5—C4—H4	120.1
O2—Zn1—C12	28.13 (10)	N1—C5—C4	119.6 (5)
O2^{i}—Zn1—C12	107.47 (11)	N1—C5—C5^{i}	115.9 (2)
N1—Zn1—C12	135.29 (12)	C4—C5—C5^{i}	124.5 (4)
N1^{i}—Zn1—C12	101.44 (12)	C1—N1—C5	119.8 (4)
O2—Zn1—C12^{i}	107.47 (11)	C1—N1—Zn1	125.5 (3)
O2^{i}—Zn1—C12^{i}	28.13 (10)	C5—N1—Zn1	114.6 (3)
N1—Zn1—C12^{i}	101.44 (12)	C11—C6—C7	118.8 (3)
N1^{i}—Zn1—C12^{i}	135.29 (12)	C11—C6—C12	120.9 (3)
C12—Zn1—C12^{i}	107.90 (14)	C7—C6—C12	120.3 (3)
O2—Zn1—O1	55.55 (9)	C8—C7—C6	120.9 (4)
O2^{i}—Zn1—O1	91.94 (10)	C8—C7—H7	119.6
N1—Zn1—O1	153.21 (11)	C6—C7—H7	119.6
N1^{i}—Zn1—O1	86.47 (11)	C9—C8—C7	119.0 (4)
C12—Zn1—O1	27.42 (9)	C9—C8—H8	120.5
C12^{i}—Zn1—O1	104.74 (10)	C7—C8—H8	120.5
O2—Zn1—O1^{i}	91.94 (10)	C10—C9—C8	121.2 (4)
O2^{i}—Zn1—O1^{i}	55.55 (9)	C10—C9—Cl2	119.5 (3)
N1—Zn1—O1^{i}	86.47 (11)	C8—C9—Cl2	119.3 (3)
N1^{i}—Zn1—O1^{i}	153.21 (11)	C9—C10—C11	119.3 (4)
C12—Zn1—O1^{i}	104.74 (10)	C9—C10—H10	120.4
C12^{i}—Zn1—O1^{i}	27.42 (9)	C11—C10—H10	120.4
O1—Zn1—O1^{i}	114.90 (12)	C6—C11—C10	120.8 (4)
C12—O1—Zn1	76.2 (2)	C6—C11—H11	119.6
C12—O2—Zn1	105.5 (2)	C10—C11—H11	119.6
N1—C1—C2	122.1 (5)	O1—C12—O2	122.8 (3)
N1—C1—H1	118.9	O1—C12—C6	120.7 (3)
C2—C1—H1	118.9	O2—C12—C6	116.5 (3)
C3—C2—C1	118.9 (6)	O1—C12—Zn1	76.4 (2)
C3—C2—H2	120.5	O2—C12—Zn1	46.41 (16)
C1—C2—H2	120.5	C6—C12—Zn1	162.9 (3)

Symmetry code: (i) $-x$, y, $-z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1^{i}	0.93	2.55	3.172 (6)	125
C3—H3···O2^{ii}	0.93	2.52	3.278 (5)	139
C11—H11···O1^{iii}	0.93	2.57	3.330 (5)	139

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