Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dichlorido(2,9-dimethoxy-1,10-phenanthroline-κ^2N,N')zinc(II)

Cao-Yuan Niu,* Hui Su, Lei Meng and Chun-Hong Kou

College of Sciences, Henan Agricultural University, Zhengzhou 450002, People's Republic of China
Correspondence e-mail: niu_cy2000@yahoo.com.cn

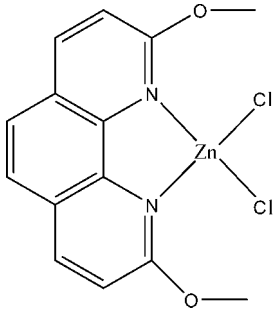
Received 13 June 2009; accepted 28 June 2009

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.065; data-to-parameter ratio = 18.0.

In the crystal structure of the title compound, $[ZnCl_2(C_{14}H_{12}N_2O_2)]$, the Zn^{II} center is four-coordinated by two N atoms from one 2,9-dimethoxy-1,10-phenanthroline ligand and two Cl atoms. The coordination geometry is distorted tetrahedral, as the Zn—N bond distances are shorter than the Zn—Cl distances, and the Cl—Zn—N and Cl—Zn—Cl bond angles are much larger than the N—Zn—N angle. For the ligand, the O and C atoms of the methoxy groups are almost in the plane defined by the phenanthroline ring. The two O atoms deviate from the phenanthroline mean plane by 0.076 (2) and 0.084 (2) Å, and the two methyl C atoms deviate from the phenanthroline mean plane by 0.035 (3) and 0.361 (3) Å. There are medium π–π stacking interactions between two parallel phenanthroline rings with a centroid–centroid distance of 3.7860 (2) Å and a dihedral angle between the plane defined by the two parallel phenanthroline rings of 1.13 (5)°.

Related literature

For background information, see: Majumder *et al.* (2006); Bie *et al.* (2006). For the synthesis, see: Pijper *et al.* (1984).



Experimental

Crystal data

$[ZnCl_2(C_{14}H_{12}N_2O_2)]$
M_r = 376.53
Monoclinic, $P2_1/c$
a = 9.0494 (8) Å
b = 10.3783 (9) Å
c = 16.3517 (14) Å
β = 99.022 (1)°
V = 1516.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.98 mm^{-1}
T = 291 K
0.27 × 0.14 × 0.10 mm

Data collection

Bruker APEXII CCD detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.616, T_{max} = 0.835
9326 measured reflections
3465 independent reflections
2917 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.065
S = 1.03
3465 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.0659 (14)	Zn1—Cl1	2.2007 (6)
Zn1—N2	2.0911 (14)	Zn1—Cl2	2.2219 (6)
N1—Zn1—N2	80.58 (6)	N1—Zn1—Cl2	110.66 (4)
N1—Zn1—Cl1	113.27 (4)	N2—Zn1—Cl2	108.06 (4)
N2—Zn1—Cl1	120.54 (4)	Cl1—Zn1—Cl2	117.82 (2)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

We are grateful to Mrs Li for her assistance with the X-ray crystallographic analysis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2228).

References

Bie, H. Y., Wei, J., Yu, J. H., Wang, T. G., Lu, J. & Xu, J. Q. (2006). *Mater. Lett.* **60**, 2475–2479.
Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR. Bonn, Germany.
Majumder, A., Westerhausen, M., Kneifel, A. N., Sutter, J.-P., Daro, N. & Mitra, S. (2006). *Inorg. Chim. Acta*, **359**, 3841–3846.
Pijper, P. L., Van der Goot, H., Timmerman, H. & Nauta, W. T. (1984). *Eur. J. Med. Chem.* **19**, 399-404.
Sheldrick, G. M. (1996). *SADABS* . Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1994). *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Acta Cryst. (2009). E**65**, m869 [**doi:10.1107/S160053680902491X**]

Dichlorido(2,9-dimethoxy-1,10-phenanthroline-κ^2N,N')zinc(II)

C.-Y. Niu, H. Su, L. Meng and C.-H. Kou

Comment

The compound 1,10-phenanthroline was reported to be used to synthesize some potential strong luminescent materials with d^{10} metals. It can be predicted that the title compound that composed of a derivative of 1,10-phenanthroline and a d^{10} metal zinc would possess strong ligand to ligand or metal perturbed ligand to ligand emissions (Majumder *et al.*, 2006; Bie, *et al.*, 2006). 2,9-Dimethoxy-1,10-phenanthroline and 2,9-Diethoxy-1,10-phenanthroline as derivatives of 1,10-phenanthroline were synthesized at early time and they possess antimycoplasmal activity in the presence of copper (Pijper, *et al.*, 1984).

The title compound (I) is a mononuclear zinc(II) complex of 2,9-dimethoxy-1,10-phenanthroline (shown as Fig.1). The zinc metal centre is four coordinated to two nitrogen atoms (N1, N2) from the 1,10-phenanthroline ring and two independent chlorine atoms (Cl1, Cl2), defining a deformed tetrahedron coordination geometry around the metal center. The Zn—Cl bond distances are 2.2007 (6) and 2.2219 (6) Å, which are longer than the Zn—N bond distances from 2.0659 (14) to 2.0911 (14) Å. The Cl—Zn—N and Cl—Zn—Cl bond angles are at the range of 108.06 (4) to 120.54 (4) °, which are larger than that of N—Zn—N [80.58 (6)°]. Furthermore, there are medium π-π stackings between two parallel phenanthroline rings from two symmetry-related monomers with the centroid-to-centroid distances of about 3.7860 (2) Å and dihedral angle of 1.13 (5) ° (Fig. 2). For the ligand, two methoxy groups are basically coplanar to the phenanthroline ring. Two oxygen atoms deviate from the phenanthroline plane by 0.076 (2) and 0.084 (2) Å, and two methyl carbon atoms deviate from the phenanthroline plane by 0.035 (3) and 0.361 (3) Å.

Three-dimensional supramolecular structure of the title compound is formed *via* the above-mentioned π-π stackings and weak van der waals interactions. Some interesting packings along three crystallographic directions can be seen from Fig. 3.

Experimental

The organic ligand 2,9-dimethoxy-1,10-phenanthroline was prepared according to the procedure of literature (Pijper, *et al.*, 1984). The slow evaporation of mixture of the ligand (0.022 g, 0.1 mmol) and zinc dichloride (0.014 g, 0.1 mmol) in 30 ml me thanol afforded suitable colourless block crystals in about 7 days (yield 45%).

Refinement

Carbon-bound H atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C) for aromatic H atoms; C—H = 0.96 Å and U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms;]. The final difference Fourier map had a highest peak at 0.85 Å from atom Cl2 and a deepest hole at 0.59 Å from atom Cl2, but were otherwise featureless.

Figures

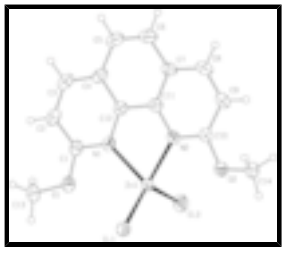


Fig. 1. A view of the Zn^{II} coordination environment in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

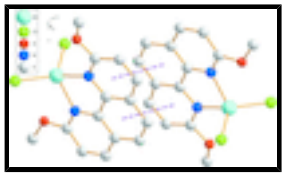


Fig. 2. Packing diagram showing the π-π interaction (purple dotted line). All H atoms have been omitted for clarity.

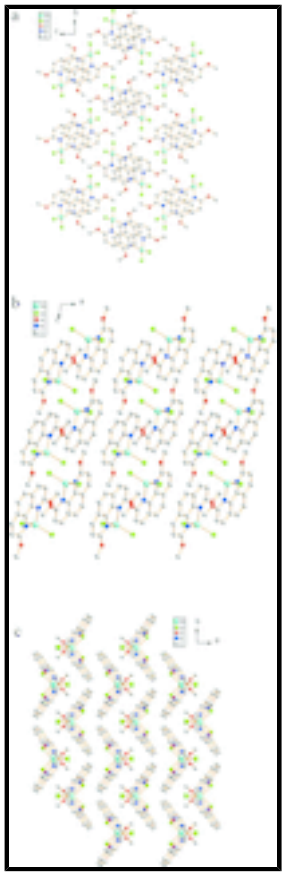


Fig. 3. Diagrams showing the three-dimensional packing forms along three crystallographic directions.

Dichlorido(2,9-dimethoxy-1,10-phenanthroline-κ^2*N*,*N*')zinc(II)

Crystal data

$[ZnCl_2(C_{14}H_{12}N_2O_2)]$	F_{000} = 760
M_r = 376.53	D_x = 1.649 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å

Hall symbol: -P 2ybc	Cell parameters from 4023 reflections
a = 9.0494 (8) Å	θ = 2.3–27.9º
b = 10.3783 (9) Å	μ = 1.98 mm^{-1}
c = 16.3517 (14) Å	T = 291 K
β = 99.0220 (10)º	Block, colorless
V = 1516.7 (2) Å^3	0.27 × 0.14 × 0.10 mm
Z = 4	

Data collection

Bruker APEXII CCD detector diffractometer	3465 independent reflections
Radiation source: fine-focus sealed tube	2917 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.017
T = 291 K	θ_{max} = 27.5º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −7→11
T_{min} = 0.616, T_{max} = 0.835	k = −13→13
9326 measured reflections	l = −21→21

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.025	H-atom parameters constrained
$wR(F^2)$ = 0.065	$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.4767P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ = 0.001
3465 reflections	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
192 parameters	$\Delta\rho_{min}$ = −0.25 e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.85210 (2)	0.73107 (2)	0.142693 (13)	0.03691 (8)
Cl1	1.07679 (6)	0.76186 (5)	0.21365 (3)	0.05122 (14)
Cl2	0.68839 (6)	0.89157 (5)	0.13748 (4)	0.05898 (15)
O1	0.99184 (17)	0.81556 (14)	−0.01403 (8)	0.0502 (3)
O2	0.71476 (16)	0.58258 (13)	0.28668 (8)	0.0481 (3)
N1	0.85558 (16)	0.65629 (14)	0.02592 (9)	0.0366 (3)
N2	0.73776 (16)	0.55838 (14)	0.15361 (9)	0.0360 (3)
C1	0.9193 (2)	0.70500 (19)	−0.03500 (11)	0.0405 (4)
C2	0.9063 (3)	0.6460 (2)	−0.11341 (12)	0.0502 (5)
H2	0.9523	0.6820	−0.1550	0.060*
C3	0.8256 (3)	0.5361 (2)	−0.12718 (12)	0.0519 (5)
H3	0.8160	0.4967	−0.1788	0.062*
C4	0.7557 (2)	0.48020 (19)	−0.06404 (12)	0.0447 (4)
C5	0.6660 (2)	0.3663 (2)	−0.07373 (14)	0.0548 (5)
H5	0.6523	0.3232	−0.1242	0.066*
C6	0.6011 (2)	0.3201 (2)	−0.01103 (14)	0.0540 (5)
H6	0.5415	0.2468	−0.0192	0.065*
C7	0.6228 (2)	0.38262 (18)	0.06829 (13)	0.0434 (4)
C8	0.5595 (2)	0.3401 (2)	0.13704 (14)	0.0500 (5)
H8	0.4985	0.2675	0.1319	0.060*
C9	0.5859 (2)	0.40325 (19)	0.21063 (13)	0.0464 (5)
H9	0.5437	0.3748	0.2557	0.056*
C10	0.6789 (2)	0.51305 (18)	0.21712 (12)	0.0391 (4)
C11	0.71040 (19)	0.49372 (17)	0.07990 (11)	0.0369 (4)
C12	0.7758 (2)	0.54491 (17)	0.01209 (11)	0.0367 (4)
C13	1.0711 (3)	0.8779 (2)	−0.07353 (13)	0.0554 (5)
H13A	1.1445	0.8199	−0.0891	0.083*
H13B	1.1199	0.9540	−0.0492	0.083*
H13C	1.0014	0.9013	−0.1217	0.083*
C14	0.6826 (3)	0.5280 (2)	0.36304 (12)	0.0536 (5)
H14A	0.5763	0.5196	0.3604	0.080*
H14B	0.7216	0.5834	0.4083	0.080*
H14C	0.7285	0.4447	0.3712	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03791 (13)	0.03966 (13)	0.03454 (12)	−0.00516 (9)	0.01002 (9)	−0.00396 (8)
Cl1	0.0399 (3)	0.0714 (4)	0.0431 (3)	−0.0099 (2)	0.0087 (2)	−0.0143 (2)
Cl2	0.0501 (3)	0.0513 (3)	0.0795 (4)	0.0074 (2)	0.0226 (3)	−0.0024 (3)
O1	0.0623 (9)	0.0531 (8)	0.0391 (7)	−0.0104 (7)	0.0201 (6)	0.0019 (6)
O2	0.0561 (9)	0.0513 (8)	0.0389 (7)	−0.0155 (7)	0.0138 (6)	0.0014 (6)
N1	0.0378 (8)	0.0402 (9)	0.0323 (7)	0.0027 (6)	0.0071 (6)	−0.0009 (6)
N2	0.0342 (8)	0.0367 (8)	0.0370 (8)	−0.0032 (6)	0.0057 (6)	0.0017 (6)

C1	0.0419 (10)	0.0461 (11)	0.0342 (9)	0.0081 (8)	0.0083 (8)	0.0043 (8)
C2	0.0608 (13)	0.0582 (13)	0.0339 (10)	0.0133 (10)	0.0148 (9)	0.0022 (9)
C3	0.0647 (14)	0.0557 (13)	0.0348 (10)	0.0144 (11)	0.0057 (9)	−0.0088 (9)
C4	0.0468 (11)	0.0458 (11)	0.0392 (10)	0.0126 (9)	−0.0006 (8)	−0.0068 (8)
C5	0.0601 (13)	0.0487 (12)	0.0520 (12)	0.0071 (10)	−0.0030 (10)	−0.0183 (10)
C6	0.0510 (12)	0.0410 (11)	0.0661 (14)	−0.0020 (9)	−0.0028 (10)	−0.0123 (10)
C7	0.0364 (10)	0.0381 (10)	0.0530 (11)	0.0008 (8)	−0.0007 (8)	−0.0035 (8)
C8	0.0405 (11)	0.0411 (11)	0.0660 (14)	−0.0081 (9)	0.0011 (10)	0.0013 (10)
C9	0.0405 (11)	0.0448 (11)	0.0544 (12)	−0.0067 (8)	0.0087 (9)	0.0086 (9)
C10	0.0353 (9)	0.0400 (10)	0.0422 (10)	−0.0016 (7)	0.0065 (8)	0.0039 (8)
C11	0.0322 (9)	0.0356 (9)	0.0411 (9)	0.0038 (7)	0.0006 (7)	−0.0018 (7)
C12	0.0345 (9)	0.0377 (10)	0.0365 (9)	0.0072 (7)	0.0009 (7)	−0.0021 (7)
C13	0.0574 (13)	0.0644 (14)	0.0490 (12)	−0.0040 (11)	0.0226 (10)	0.0113 (10)
C14	0.0590 (13)	0.0624 (14)	0.0427 (11)	−0.0119 (11)	0.0179 (10)	0.0042 (9)

Geometric parameters (Å, °)

Zn1—N1	2.0659 (14)	C4—C5	1.429 (3)
Zn1—N2	2.0911 (14)	C5—C6	1.347 (3)
Zn1—Cl1	2.2007 (6)	C5—H5	0.9300
Zn1—Cl2	2.2219 (6)	C6—C7	1.436 (3)
O1—C1	1.340 (2)	C6—H6	0.9300
O1—C13	1.449 (2)	C7—C11	1.395 (3)
O2—C10	1.343 (2)	C7—C8	1.410 (3)
O2—C14	1.442 (2)	C8—C9	1.358 (3)
N1—C1	1.327 (2)	C8—H8	0.9300
N1—C12	1.363 (2)	C9—C10	1.411 (3)
N2—C10	1.325 (2)	C9—H9	0.9300
N2—C11	1.368 (2)	C11—C12	1.438 (3)
C1—C2	1.409 (3)	C13—H13A	0.9600
C2—C3	1.354 (3)	C13—H13B	0.9600
C2—H2	0.9300	C13—H13C	0.9600
C3—C4	1.417 (3)	C14—H14A	0.9600
C3—H3	0.9300	C14—H14B	0.9600
C4—C12	1.401 (3)	C14—H14C	0.9600
N1—Zn1—N2	80.58 (6)	C7—C6—H6	119.6
N1—Zn1—Cl1	113.27 (4)	C11—C7—C8	116.32 (18)
N2—Zn1—Cl1	120.54 (4)	C11—C7—C6	119.39 (19)
N1—Zn1—Cl2	110.66 (4)	C8—C7—C6	124.29 (19)
N2—Zn1—Cl2	108.06 (4)	C9—C8—C7	121.19 (18)
Cl1—Zn1—Cl2	117.82 (2)	C9—C8—H8	119.4
C1—O1—C13	119.03 (15)	C7—C8—H8	119.4
C10—O2—C14	117.89 (15)	C8—C9—C10	118.47 (19)
C1—N1—C12	118.68 (16)	C8—C9—H9	120.8
C1—N1—Zn1	128.47 (13)	C10—C9—H9	120.8
C12—N1—Zn1	112.80 (11)	N2—C10—O2	113.56 (16)
C10—N2—C11	118.48 (16)	N2—C10—C9	122.41 (18)
C10—N2—Zn1	129.50 (13)	O2—C10—C9	124.03 (17)
C11—N2—Zn1	111.65 (11)	N2—C11—C7	123.09 (17)

N1—C1—O1	112.80 (16)	N2—C11—C12	117.31 (16)
N1—C1—C2	122.24 (19)	C7—C11—C12	119.60 (17)
O1—C1—C2	124.95 (17)	N1—C12—C4	123.06 (17)
C3—C2—C1	118.91 (19)	N1—C12—C11	117.18 (15)
C3—C2—H2	120.5	C4—C12—C11	119.76 (17)
C1—C2—H2	120.5	O1—C13—H13A	109.5
C2—C3—C4	120.96 (18)	O1—C13—H13B	109.5
C2—C3—H3	119.5	H13A—C13—H13B	109.5
C4—C3—H3	119.5	O1—C13—H13C	109.5
C12—C4—C3	116.14 (19)	H13A—C13—H13C	109.5
C12—C4—C5	119.19 (19)	H13B—C13—H13C	109.5
C3—C4—C5	124.66 (18)	O2—C14—H14A	109.5
C6—C5—C4	121.18 (19)	O2—C14—H14B	109.5
C6—C5—H5	119.4	H14A—C14—H14B	109.5
C4—C5—H5	119.4	O2—C14—H14C	109.5
C5—C6—C7	120.8 (2)	H14A—C14—H14C	109.5
C5—C6—H6	119.6	H14B—C14—H14C	109.5
N2—Zn1—N1—C1	−177.42 (16)	C7—C8—C9—C10	−0.1 (3)
Cl1—Zn1—N1—C1	−58.12 (16)	C11—N2—C10—O2	178.99 (16)
Cl2—Zn1—N1—C1	76.72 (16)	Zn1—N2—C10—O2	−8.7 (2)
N2—Zn1—N1—C12	5.17 (12)	C11—N2—C10—C9	−1.9 (3)
Cl1—Zn1—N1—C12	124.47 (11)	Zn1—N2—C10—C9	170.42 (14)
Cl2—Zn1—N1—C12	−100.69 (12)	C14—O2—C10—N2	−167.68 (17)
N1—Zn1—N2—C10	−179.01 (17)	C14—O2—C10—C9	13.3 (3)
Cl1—Zn1—N2—C10	69.45 (17)	C8—C9—C10—N2	1.8 (3)
Cl2—Zn1—N2—C10	−70.22 (16)	C8—C9—C10—O2	−179.18 (18)
N1—Zn1—N2—C11	−6.24 (12)	C10—N2—C11—C7	0.3 (3)
Cl1—Zn1—N2—C11	−117.78 (11)	Zn1—N2—C11—C7	−173.33 (14)
Cl2—Zn1—N2—C11	102.56 (11)	C10—N2—C11—C12	−179.91 (16)
C12—N1—C1—O1	178.81 (15)	Zn1—N2—C11—C12	6.43 (19)
Zn1—N1—C1—O1	1.5 (2)	C8—C7—C11—N2	1.3 (3)
C12—N1—C1—C2	0.5 (3)	C6—C7—C11—N2	−179.37 (17)
Zn1—N1—C1—C2	−176.81 (14)	C8—C7—C11—C12	−178.48 (17)
C13—O1—C1—N1	178.04 (17)	C6—C7—C11—C12	0.9 (3)
C13—O1—C1—C2	−3.7 (3)	C1—N1—C12—C4	−1.1 (3)
N1—C1—C2—C3	0.2 (3)	Zn1—N1—C12—C4	176.62 (14)
O1—C1—C2—C3	−177.93 (19)	C1—N1—C12—C11	178.97 (16)
C1—C2—C3—C4	−0.3 (3)	Zn1—N1—C12—C11	−3.35 (19)
C2—C3—C4—C12	−0.2 (3)	C3—C4—C12—N1	0.9 (3)
C2—C3—C4—C5	178.6 (2)	C5—C4—C12—N1	−177.93 (17)
C12—C4—C5—C6	−0.2 (3)	C3—C4—C12—C11	−179.10 (17)
C3—C4—C5—C6	−178.9 (2)	C5—C4—C12—C11	2.0 (3)
C4—C5—C6—C7	−1.4 (3)	N2—C11—C12—N1	−2.2 (2)
C5—C6—C7—C11	1.0 (3)	C7—C11—C12—N1	177.58 (16)
C5—C6—C7—C8	−179.7 (2)	N2—C11—C12—C4	177.84 (16)
C11—C7—C8—C9	−1.4 (3)	C7—C11—C12—C4	−2.4 (3)
C6—C7—C8—C9	179.3 (2)		

Fig. 1

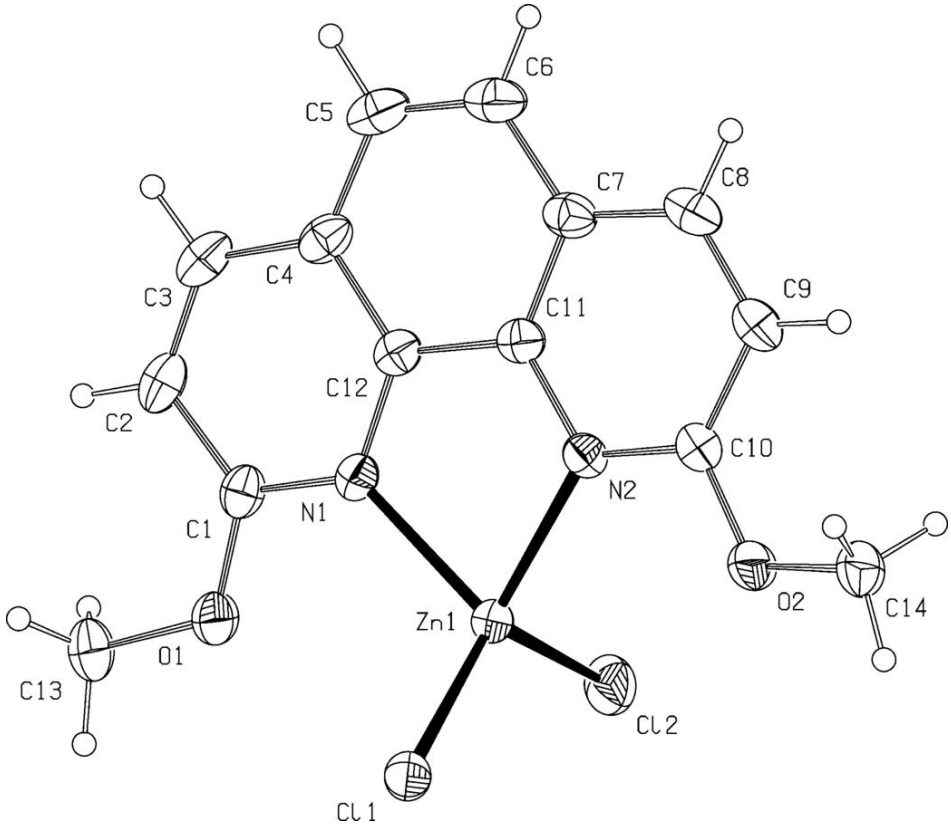

C6
C5
C7
C8
C4
C3
C11
C9
C12
C2
C10
N2
N1
C1
O2
C14
Zn1
O1
C13
Cl2
Cl1

Fig. 2

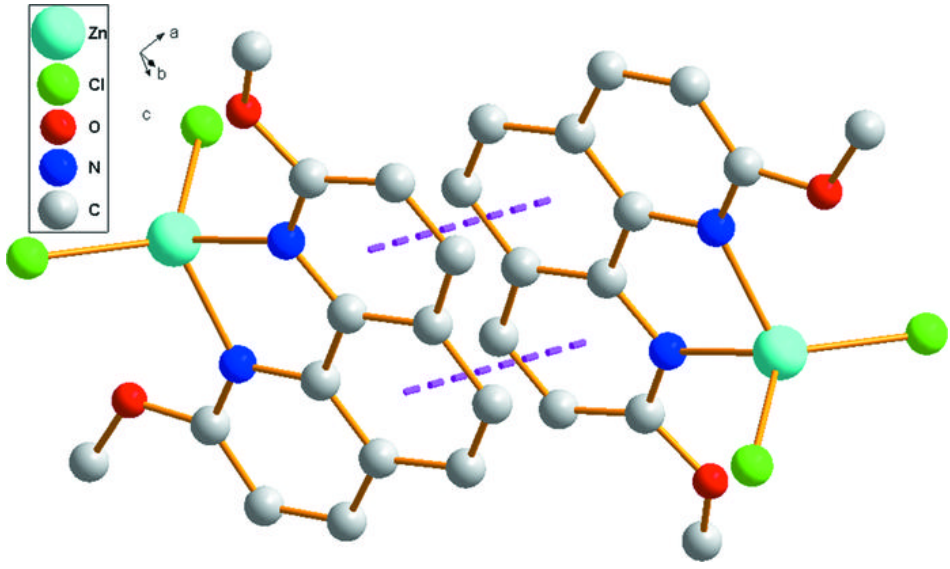


Fig. 3