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Dichlorido(4,7-dimethoxy-1,10-phenanthroline-κ^2N,N')zinc(II)

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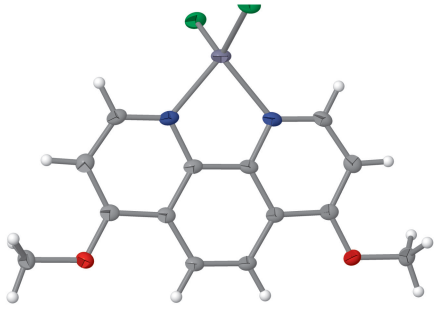
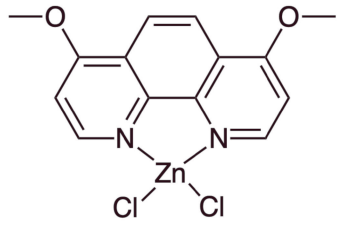
Structural data: full structural data are available from iucrdata.iucr.org

In the title complex, $[ZnCl_2(C_{14}H_{12}N_2O_2)]$, the Zn^{II} atom is located on a twofold rotation axis and is fourfold coordinated by two chlorido ligands and a bidentate 4,7-methoxy-1,10-phenanthroline ligand in a distorted tetrahedral environment. Weak π–π stacking interactions between adjacent 4,7-dimethoxy-1,10-phenanthroline rings [centroid-to-centroid distances = 3.5969 (11) and 3.7738 (11) Å] contribute to the alignment of the complexes in layers parallel to $(\bar{2}01)$.

3D view



Chemical scheme



Structure description

Over the last five years, metal complexes containing 4,7-dimethoxy-1,10-phenanthroline have garnered significant attention due to their catalytic activity (EL-Atawy *et al.*, 2018; Liu *et al.*, 2020) and potential as antitumor agents (Khoury *et al.*, 2022). Likewise, oxidovanadium(IV) complexes incorporating 4,7-dimethoxy-1,10-phenanthroline have been found to be effective against several cancer cell lines, including A2780 human ovarian adenocarcinoma and HCT116 human colorectal carcinoma (Choroba *et al.*, 2023). Currently, our research group focuses on creating metal complexes that have uses in biological systems. As part of this work, herein we present the synthesis and crystal structure of the title complex, which shows promise as a valuable precursor for the synthesis of novel zinc(II) complexes.

In the centrosymmetric crystal structure of the title complex, the zinc(II) atom is located on a twofold rotation axis (multiplicity 4, Wyckoff letter *e*) of space group *C*2/*c*. The coordination environment is that of a distorted tetrahedron defined by two pyridine nitrogen atoms from the 4,7-methoxy-1,10-phenanthroline ligand and two chlorido ligands (Fig. 1). The Zn—N bond lengths are in good agreement with comparable tetrahedral 1,10-phenanthroline complexes currently available in the Cambridge Structure Database (CSD, version 5.45, Nov 2023; Groom *et al.*, 2016): refcodes DUCBOT (Niu *et al.*, 2009); TOBGOH (Li *et al.*, 2008); GODCOU (Luo *et al.*, 2019); QEVLIQ

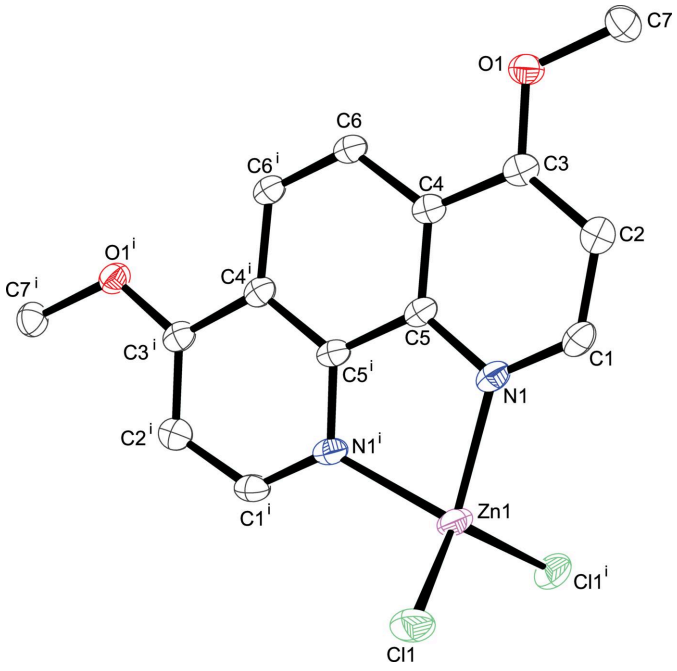


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level; H atoms are omitted for clarity. Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

(Cetin *et al.*, 2020); ZNPHAT (Reimann *et al.*, 1966). At this time no 4,7-dimethoxy-1,10-phenanthroline zinc metal complexes have been deposited in the database. Similar behavior is observed for the Zn—Cl bond lengths. The τ_4 descriptor value (Yang *et al.*, 2007) of 0.87 reflects the distortion from the perfect tetrahedral coordination ($\tau_4 = 1.0$). Numerical data of relevant bond lengths and angles are presented in Table 1.

The title complex packs into layers parallel to $(\bar{2}01)$ (Fig. 2). Contiguous pyridine rings show weak π–π stacking interactions, with centroid-to-centroid distances ($Cg\cdots Cg$) alternating between 3.5969 (11) and 3.7738 (11) Å, and offset distances of 1.370 and 1.822 Å, respectively. No other significant supramolecular interactions are present in the crystal packing of the title compound.

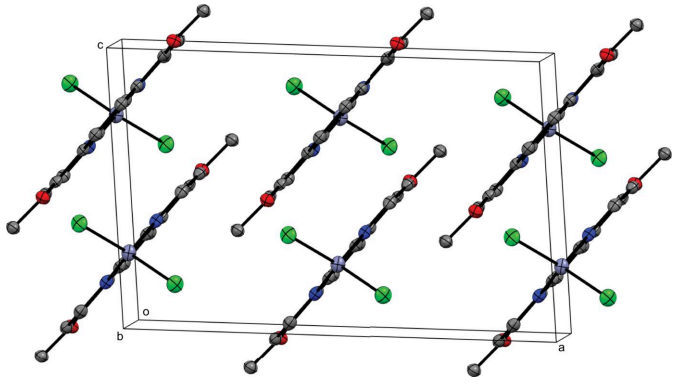


Figure 2
Perspective view of the crystal packing of the title complex approximately along the *b* axis; H atoms are omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.2186 (5)	Zn1—N1^{i}	2.0744 (18)
Zn1—Cl1^{i}	2.2186 (5)	Zn1—N1	2.0744 (18)
Cl1—Zn1—Cl1^{i}	120.75 (3)	N1^{i}—Zn1—Cl1	107.88 (4)
N1^{i}—Zn1—Cl1^{i}	116.53 (4)	N1—Zn1—Cl1^{i}	107.88 (4)
N1—Zn1—Cl1	116.53 (4)	N1^{i}—Zn1—N1	80.66 (9)

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[ZnCl_2(C_{14}H_{12}N_2O_2)]$
M_r	376.53
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	14.7877 (6), 9.9287 (4), 9.5230 (3)
β (°)	95.233 (4)
V (Å^3)	1392.36 (9)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	6.03
Crystal size (mm)	0.10 × 0.05 × 0.03
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.780, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6451, 1385, 1282
R_{int}	0.044
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.028, 0.078, 1.07
No. of reflections	1385
No. of parameters	97
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.54

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

The title complex was synthesized by the addition of 4,7-dimethoxy-1,10-phenanthroline (0.176 g, 0.733 mmol) to a 40.0 ml acetonitrile suspension of zinc(II) chloride (0.100 g, 0.733 mmol). After the ligand was added, the resulting solution was heated at 333 K and stirred for 2 h. The resulting solution was then filtrated using a PTFE syringe filter to obtain a clear solution. Crystal suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether over a saturated acetonitrile solution of the title complex.

Refinement

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

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full crystallographic data

IUCrData (2024). **9**, x240037 [https://doi.org/10.1107/S2414314624000373]

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Dichlorido(4,7-dimethoxy-1,10-phenanthroline-κ^2N,N')zinc(II)

Crystal data

$[ZnCl_2(C_{14}H_{12}N_2O_2)]$
M_r = 376.53
Monoclinic, $C2/c$
a = 14.7877 (6) Å
b = 9.9287 (4) Å
c = 9.5230 (3) Å
β = 95.233 (4)°
V = 1392.36 (9) Å^3
Z = 4
$F(000)$ = 760
D_x = 1.796 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 4164 reflections
θ = 4.6–76.0°
μ = 6.03 mm^{-1}
T = 100 K
Block, clear colourless
0.10 × 0.05 × 0.03 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2023)
T_{min} = 0.780, T_{max} = 1.000
6451 measured reflections
1385 independent reflections
1282 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 76.1°, θ_{min} = 5.4°
h = −18→17
k = −10→12
l = −7→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.078
S = 1.07
1385 reflections
97 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.5215P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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	0.13609 (4)	0.250000	0.02301 (15)
Cl1	0.39338 (4)	0.02563 (5)	0.35249 (5)	0.03050 (17)
O1	0.66212 (10)	0.65250 (14)	0.53657 (14)	0.0218 (3)
N1	0.56174 (11)	0.29536 (17)	0.36247 (16)	0.0199 (3)
C5	0.53355 (13)	0.4178 (2)	0.30988 (19)	0.0182 (4)
C4	0.56632 (13)	0.5410 (2)	0.36602 (19)	0.0183 (4)
C6	0.53195 (13)	0.6646 (2)	0.30625 (19)	0.0189 (4)
H6	0.553852	0.747773	0.345289	0.023*
C2	0.66450 (14)	0.4095 (2)	0.5321 (2)	0.0218 (4)
H2	0.711381	0.402937	0.606948	0.026*
C3	0.63399 (13)	0.5341 (2)	0.48287 (19)	0.0194 (4)
C1	0.62520 (13)	0.2938 (2)	0.4699 (2)	0.0214 (4)
H1	0.645131	0.208835	0.506840	0.026*
C7	0.73512 (14)	0.6509 (2)	0.6477 (2)	0.0239 (4)
H7A	0.789459	0.611872	0.612157	0.036*
H7B	0.717317	0.596632	0.726610	0.036*
H7C	0.748220	0.743207	0.679964	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0248 (2)	0.0126 (2)	0.0319 (2)	0.000	0.00398 (15)	0.000
Cl1	0.0338 (3)	0.0212 (3)	0.0364 (3)	−0.0083 (2)	0.0030 (2)	0.0048 (2)
O1	0.0250 (7)	0.0181 (7)	0.0219 (7)	−0.0025 (6)	−0.0002 (5)	−0.0008 (5)
N1	0.0218 (7)	0.0143 (8)	0.0243 (8)	0.0015 (7)	0.0068 (6)	0.0027 (6)
C5	0.0202 (9)	0.0141 (10)	0.0211 (8)	0.0012 (8)	0.0075 (7)	0.0012 (7)
C4	0.0196 (8)	0.0168 (10)	0.0192 (8)	−0.0011 (7)	0.0063 (7)	−0.0004 (7)
C6	0.0208 (9)	0.0147 (9)	0.0220 (9)	−0.0008 (8)	0.0058 (7)	−0.0009 (7)
C2	0.0221 (9)	0.0235 (11)	0.0206 (8)	0.0013 (8)	0.0050 (7)	0.0021 (8)
C3	0.0213 (9)	0.0185 (10)	0.0196 (9)	−0.0016 (8)	0.0076 (7)	0.0013 (7)
C1	0.0234 (9)	0.0174 (10)	0.0241 (9)	0.0032 (8)	0.0059 (7)	0.0052 (8)
C7	0.0239 (9)	0.0263 (11)	0.0210 (9)	−0.0028 (9)	−0.0005 (7)	0.0004 (8)

Geometric parameters (Å, º)

Zn1—Cl1	2.2186 (5)	C4—C3	1.429 (3)
Zn1—Cl1^{i}	2.2186 (5)	C6—C6^{i}	1.362 (4)
Zn1—N1^{i}	2.0744 (18)	C6—H6	0.9500
Zn1—N1	2.0744 (18)	C2—H2	0.9500
O1—C3	1.334 (2)	C2—C3	1.383 (3)
O1—C7	1.441 (2)	C2—C1	1.395 (3)
N1—C5	1.365 (3)	C1—H1	0.9500
N1—C1	1.324 (3)	C7—H7A	0.9800
C5—C5^{i}	1.442 (4)	C7—H7B	0.9800
C5—C4	1.404 (3)	C7—H7C	0.9800

C4—C6	1.427 (3)		
Cl1—Zn1—Cl1^{i}	120.75 (3)	C6^{i}—C6—C4	120.66 (11)
N1^{i}—Zn1—Cl1^{i}	116.53 (4)	C6^{i}—C6—H6	119.7
N1—Zn1—Cl1	116.53 (4)	C3—C2—H2	120.6
N1^{i}—Zn1—Cl1	107.88 (4)	C3—C2—C1	118.81 (19)
N1—Zn1—Cl1^{i}	107.88 (4)	C1—C2—H2	120.6
N1^{i}—Zn1—N1	80.66 (9)	O1—C3—C4	115.33 (18)
C3—O1—C7	117.29 (16)	O1—C3—C2	125.27 (18)
C5—N1—Zn1	112.59 (13)	C2—C3—C4	119.40 (19)
C1—N1—Zn1	129.60 (15)	N1—C1—C2	123.82 (19)
C1—N1—C5	117.74 (18)	N1—C1—H1	118.1
N1—C5—C5^{i}	117.08 (11)	C2—C1—H1	118.1
N1—C5—C4	123.58 (18)	O1—C7—H7A	109.5
C4—C5—C5^{i}	119.34 (11)	O1—C7—H7B	109.5
C5—C4—C6	119.99 (18)	O1—C7—H7C	109.5
C5—C4—C3	116.58 (18)	H7A—C7—H7B	109.5
C6—C4—C3	123.43 (18)	H7A—C7—H7C	109.5
C4—C6—H6	119.7	H7B—C7—H7C	109.5
Zn1—N1—C5—C5^{i}	1.0 (2)	C6—C4—C3—O1	1.8 (2)
Zn1—N1—C5—C4	−178.96 (14)	C6—C4—C3—C2	−178.77 (17)
Zn1—N1—C1—C2	176.64 (13)	C3—C4—C6—C6^{i}	179.3 (2)
N1—C5—C4—C6	−178.83 (16)	C3—C2—C1—N1	2.2 (3)
N1—C5—C4—C3	1.2 (3)	C1—N1—C5—C5^{i}	178.14 (19)
C5—N1—C1—C2	0.1 (3)	C1—N1—C5—C4	−1.8 (3)
C5^{i}—C5—C4—C6	1.2 (3)	C1—C2—C3—O1	176.58 (17)
C5^{i}—C5—C4—C3	−178.81 (19)	C1—C2—C3—C4	−2.8 (3)
C5—C4—C6—C6^{i}	−0.7 (3)	C7—O1—C3—C4	−175.50 (15)
C5—C4—C3—O1	−178.24 (15)	C7—O1—C3—C2	5.1 (3)
C5—C4—C3—C2	1.2 (2)		

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