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Dichlorido(4,4′-dimethyl-2,2′-bipyridine-κ^2N,N')-zinc(II) acetonitrile monosolvate

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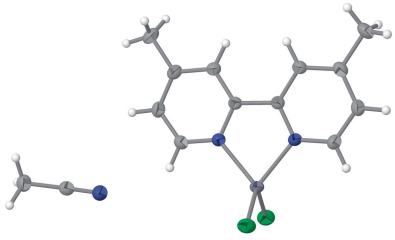
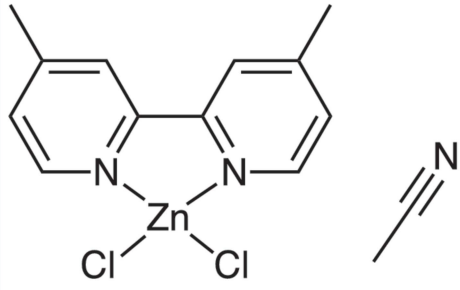
Structural data: full structural data are available from iucrdata.iucr.org

In the title complex, $[ZnCl_2(C_{12}H_{12}N_2)]\cdot CH_3CN$, the zinc(II) atom is fourfold coordinated by two chloride ligands and a bidentate 4,4′-dimethyl-2,2′-bipyridine ligand in a distorted tetrahedral shape with a molecule of acetonitrile sitting in the outer coordination sphere of the complex. π–π stacking interactions between the pyridyl rings in adjacent molecules contribute to the alignment of the complexes in columns parallel to the *a* axis.

3D view



Chemical scheme



Structure description

Over the last decade, metal complexes of 4,4′-dimethyl-2,2′-bipyridine have garnered significant attention due to their photophysical properties (Tamer *et al.*, 2020; Queiroz *et al.*, 2022), electrocatalytic activity (Ogihara *et al.*, 2018; Taylor *et al.*, 2018), and potential as antitumor agents (Amani *et al.*, 2014). Recently, platinum complexes incorporating 4,4′-dimethyl-2,2′-bipyridine were found to be effective against several cancer cell lines, including L1210 murine leukemia, HT29 human colon carcinoma, and U87 human glioblastoma (Pages *et al.*, 2015). Our research group interest currently lies in synthesizing metal complexes with applications in biological systems; as part of our research in this area, herein, we describe the synthesis and structure of the title complex, which promises to be a useful starting material in the synthesis of novel zinc(II) complexes.

The asymmetric unit contains one molecule of the title compound and one solvent molecule of acetonitrile. The zinc(II) atom exhibits a distorted tetrahedral cooordination environment defined by two pyridine nitrogen atoms from the 4,4′-dimethyl-2,2′-bipyridine ligand and two chlorido ligands (Fig. 1). The Zn—N bond lengths are in good agreement with the comparable bromide analog complex currently available in the CSD (version 5.43 with update June 2022; Alizadeh *et al.*, 2010, refcode DURYAR) and with other 2,2′-bipyridine-based zinc(II) complexes (Khan & Tuck, 1984, refcode CEFFOI;

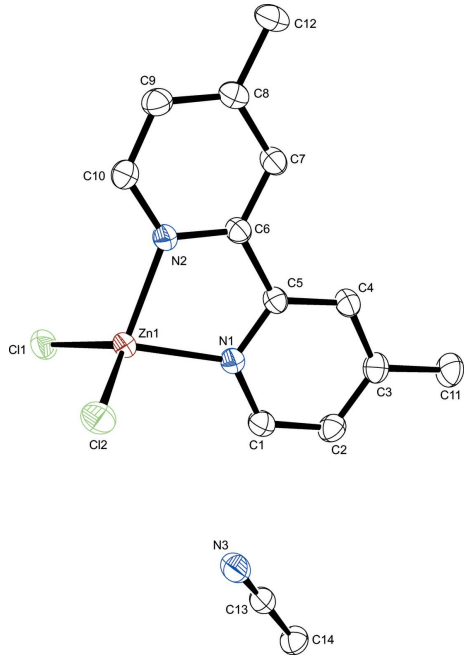


Figure 1
The structures of the molecular entities of the title compound with displacement ellipsoids drawn at the 50% probability level; H atoms are omitted for clarity.

Hossienifard *et al.*, 2011, refcode DAKMUZ; Nauha *et al.*, 2016, refcode EMERAR; Khalighi *et al.*, 2008, refcode POFKOL). Similar behavior is observed for the Zn—Cl bond lengths. The small bite angle N2—Zn1—N1 of 80.19 (7)° reflects the distortion from the ideal tetrahedral coordination. Numerical data of relevant bonds and angles are presented in Table 1.

The title complex packs into layers extending parallel to the *bc* plane that are packed along the *a*-axis direction (Fig. 2). Contiguous pyridine rings show π–π stacking interactions, with centroid-to-centroid distances ($Cg\cdots Cg$) alternating between 3.718 (1) Å and 3.725 (1) Å, and offset distances of 1.166 and 1.191 Å, respectively (Fig. 3). No other significant supramolecular interaction is present in the crystal packing of the title compound.

Synthesis and crystallization

Zinc(II) chloride (0.370 g, 2.71 mmol) was added to a methanol solution (40 ml) of 4,4′-dimethyl-2,2′-bipyridine (0.500 g, 2.71 mmol). After stirring for 30 min, the resulting suspension was filtrated to obtain a white precipitate of the title compound (0.470 g, 54%). Crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether over a saturated acetonitrile solution of the title compound at 277 K.

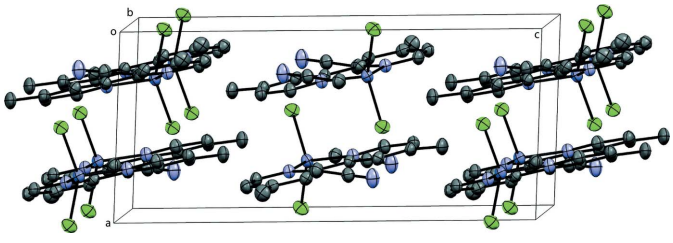


Figure 2
Perspective view of the crystal packing of the title complex approximately along the *b* axis; H atoms are omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.2065 (6)	Zn1—N1	2.0570 (17)
Zn1—Cl2	2.2005 (6)	Zn1—N2	2.0562 (17)
Cl2—Zn1—Cl1	116.82 (2)	N2—Zn1—Cl1	110.49 (5)
N1—Zn1—Cl1	117.12 (5)	N2—Zn1—Cl2	117.59 (5)
N1—Zn1—Cl2	109.48 (5)	N2—Zn1—N1	80.19 (7)

Table 2
Experimental details.

Crystal data	
Chemical formula	$[ZnCl_2(C_{12}H_{12}N_2)]\cdot C_2H_3N$
M_r	361.56
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	7.2893 (1), 13.3443 (2), 16.1667 (3)
β (°)	92.486 (2)
V (Å^3)	1571.06 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	5.23
Crystal size (mm)	0.26 × 0.10 × 0.05
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.467, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15078, 3137, 2851
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.089, 1.07
No. of reflections	3137
No. of parameters	184
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.75

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

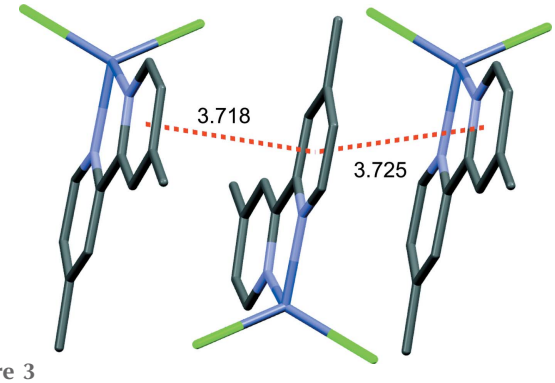


Figure 3
Capped sticks representation of the title molecule showing π–π stacking interactions (red). H atoms and acetonitrile molecule are omitted for clarity.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2022). **7**, x221149 [https://doi.org/10.1107/S241431462201149X]

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Crystal data

$[ZnCl_2(C_{12}H_{12}N_2)]\cdot C_2H_3N$
M_r = 361.56
Monoclinic, $P2_1/c$
a = 7.2893 (1) Å
b = 13.3443 (2) Å
c = 16.1667 (3) Å
β = 92.486 (2)°
V = 1571.06 (4) Å^3
Z = 4
$F(000)$ = 736
D_x = 1.529 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 7600 reflections
θ = 4.3–75.6°
μ = 5.23 mm^{-1}
T = 100 K
Plank, clear colourless
0.26 × 0.10 × 0.05 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, 2020)
T_{min} = 0.467, T_{max} = 1.000
15078 measured reflections
3137 independent reflections
2851 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 76.3°, θ_{min} = 4.3°
h = −9→8
k = −16→11
l = −20→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
S = 1.07
3137 reflections
184 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.740P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 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	0.26341 (4)	0.28826 (2)	0.57710 (2)	0.02312 (11)
Cl1	0.52433 (7)	0.21775 (4)	0.61998 (3)	0.03091 (14)
Cl2	0.01137 (8)	0.20050 (4)	0.59191 (4)	0.03469 (15)
N1	0.2201 (2)	0.43399 (12)	0.61281 (10)	0.0234 (3)
N2	0.2934 (2)	0.35984 (12)	0.46587 (10)	0.0238 (3)
C6	0.2711 (3)	0.46056 (15)	0.46862 (12)	0.0229 (4)
C5	0.2270 (3)	0.50205 (15)	0.55085 (12)	0.0224 (4)
N3	0.2294 (3)	0.42938 (15)	0.88678 (12)	0.0386 (5)
C4	0.1954 (3)	0.60303 (15)	0.56446 (13)	0.0257 (4)
H4	0.199479	0.649436	0.520011	0.031*
C7	0.2912 (3)	0.51951 (15)	0.39878 (13)	0.0258 (4)
H7	0.275570	0.590064	0.401893	0.031*
C1	0.1812 (3)	0.46558 (16)	0.68887 (13)	0.0271 (4)
H1	0.174326	0.417554	0.731999	0.032*
C8	0.3344 (3)	0.47496 (16)	0.32421 (13)	0.0271 (4)
C2	0.1508 (3)	0.56532 (16)	0.70690 (13)	0.0287 (4)
H2	0.125591	0.585262	0.761657	0.034*
C10	0.3363 (3)	0.31691 (16)	0.39416 (13)	0.0277 (4)
H10	0.352298	0.246295	0.392476	0.033*
C3	0.1576 (3)	0.63621 (15)	0.64396 (13)	0.0279 (4)
C9	0.3580 (3)	0.37158 (16)	0.32278 (13)	0.0287 (4)
H9	0.388748	0.338853	0.273078	0.034*
C13	0.2438 (3)	0.47359 (16)	0.94688 (14)	0.0296 (4)
C12	0.3516 (3)	0.53683 (18)	0.24735 (14)	0.0350 (5)
H12A	0.232760	0.539310	0.216670	0.053*
H12B	0.443377	0.506603	0.212485	0.053*
H12C	0.389982	0.604955	0.262723	0.053*
C14	0.2648 (3)	0.52852 (18)	1.02426 (14)	0.0334 (5)
H14A	0.321179	0.593786	1.014092	0.050*
H14B	0.343360	0.490338	1.063596	0.050*
H14C	0.143993	0.538499	1.047313	0.050*
C11	0.1310 (3)	0.74589 (17)	0.66062 (16)	0.0360 (5)
H11A	0.248128	0.781058	0.656074	0.054*
H11B	0.086842	0.754766	0.716555	0.054*
H11C	0.040579	0.773390	0.620108	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02849 (17)	0.01792 (16)	0.02321 (17)	0.00069 (9)	0.00410 (11)	0.00276 (9)
Cl1	0.0305 (3)	0.0271 (3)	0.0353 (3)	0.00510 (18)	0.0030 (2)	0.00574 (19)
Cl2	0.0334 (3)	0.0319 (3)	0.0392 (3)	−0.0078 (2)	0.0068 (2)	0.0031 (2)
N1	0.0274 (8)	0.0205 (8)	0.0223 (8)	0.0008 (6)	0.0021 (6)	0.0005 (6)
N2	0.0300 (8)	0.0187 (8)	0.0227 (8)	0.0000 (6)	0.0028 (6)	0.0006 (6)
C6	0.0253 (9)	0.0213 (9)	0.0221 (9)	−0.0014 (7)	0.0002 (7)	0.0011 (7)

C5	0.0235 (9)	0.0209 (9)	0.0225 (9)	0.0001 (7)	−0.0017 (7)	0.0013 (8)
N3	0.0588 (13)	0.0285 (10)	0.0286 (10)	−0.0025 (9)	0.0040 (9)	−0.0004 (8)
C4	0.0292 (10)	0.0215 (10)	0.0260 (10)	0.0001 (8)	−0.0014 (8)	0.0013 (8)
C7	0.0300 (10)	0.0226 (9)	0.0245 (10)	−0.0007 (8)	−0.0015 (8)	0.0028 (8)
C1	0.0322 (10)	0.0261 (10)	0.0229 (10)	0.0009 (8)	0.0013 (8)	0.0023 (8)
C8	0.0286 (10)	0.0297 (10)	0.0229 (10)	−0.0003 (8)	−0.0004 (8)	0.0038 (8)
C2	0.0318 (10)	0.0292 (11)	0.0253 (10)	0.0011 (8)	0.0021 (8)	−0.0046 (8)
C10	0.0336 (10)	0.0235 (10)	0.0262 (10)	−0.0001 (8)	0.0027 (8)	−0.0028 (8)
C3	0.0285 (10)	0.0233 (10)	0.0317 (11)	0.0003 (8)	−0.0012 (8)	−0.0033 (8)
C9	0.0329 (10)	0.0309 (11)	0.0224 (9)	−0.0009 (8)	0.0018 (8)	−0.0025 (8)
C13	0.0344 (11)	0.0267 (10)	0.0280 (11)	0.0008 (8)	0.0023 (8)	0.0025 (9)
C12	0.0434 (13)	0.0386 (12)	0.0229 (10)	0.0005 (10)	0.0010 (9)	0.0083 (9)
C14	0.0374 (12)	0.0341 (12)	0.0288 (11)	0.0012 (9)	0.0009 (9)	−0.0042 (9)
C11	0.0435 (13)	0.0233 (11)	0.0414 (13)	−0.0009 (9)	0.0024 (10)	−0.0075 (9)

Geometric parameters (Å, º)

Zn1—Cl1	2.2065 (6)	C8—C9	1.390 (3)
Zn1—Cl2	2.2005 (6)	C8—C12	1.502 (3)
Zn1—N1	2.0570 (17)	C2—H2	0.9500
Zn1—N2	2.0562 (17)	C2—C3	1.392 (3)
N1—C5	1.355 (3)	C10—H10	0.9500
N1—C1	1.342 (3)	C10—C9	1.380 (3)
N2—C6	1.355 (3)	C3—C11	1.502 (3)
N2—C10	1.342 (3)	C9—H9	0.9500
C6—C5	1.488 (3)	C13—C14	1.452 (3)
C6—C7	1.389 (3)	C12—H12A	0.9800
C5—C4	1.386 (3)	C12—H12B	0.9800
N3—C13	1.138 (3)	C12—H12C	0.9800
C4—H4	0.9500	C14—H14A	0.9800
C4—C3	1.398 (3)	C14—H14B	0.9800
C7—H7	0.9500	C14—H14C	0.9800
C7—C8	1.392 (3)	C11—H11A	0.9800
C1—H1	0.9500	C11—H11B	0.9800
C1—C2	1.382 (3)	C11—H11C	0.9800
Cl2—Zn1—Cl1	116.82 (2)	C1—C2—C3	119.29 (19)
N1—Zn1—Cl1	117.12 (5)	C3—C2—H2	120.4
N1—Zn1—Cl2	109.48 (5)	N2—C10—H10	118.8
N2—Zn1—Cl1	110.49 (5)	N2—C10—C9	122.41 (19)
N2—Zn1—Cl2	117.59 (5)	C9—C10—H10	118.8
N2—Zn1—N1	80.19 (7)	C4—C3—C11	120.37 (19)
C5—N1—Zn1	114.53 (13)	C2—C3—C4	118.13 (19)
C1—N1—Zn1	126.54 (14)	C2—C3—C11	121.5 (2)
C1—N1—C5	118.89 (17)	C8—C9—H9	120.3
C6—N2—Zn1	114.51 (13)	C10—C9—C8	119.47 (19)
C10—N2—Zn1	126.48 (14)	C10—C9—H9	120.3
C10—N2—C6	118.99 (17)	N3—C13—C14	178.8 (3)

N2—C6—C5	115.42 (17)	C8—C12—H12A	109.5
N2—C6—C7	121.21 (18)	C8—C12—H12B	109.5
C7—C6—C5	123.36 (18)	C8—C12—H12C	109.5
N1—C5—C6	115.31 (17)	H12A—C12—H12B	109.5
N1—C5—C4	121.51 (18)	H12A—C12—H12C	109.5
C4—C5—C6	123.18 (18)	H12B—C12—H12C	109.5
C5—C4—H4	120.2	C13—C14—H14A	109.5
C5—C4—C3	119.63 (19)	C13—C14—H14B	109.5
C3—C4—H4	120.2	C13—C14—H14C	109.5
C6—C7—H7	120.1	H14A—C14—H14B	109.5
C6—C7—C8	119.85 (19)	H14A—C14—H14C	109.5
C8—C7—H7	120.1	H14B—C14—H14C	109.5
N1—C1—H1	118.7	C3—C11—H11A	109.5
N1—C1—C2	122.54 (19)	C3—C11—H11B	109.5
C2—C1—H1	118.7	C3—C11—H11C	109.5
C7—C8—C12	120.8 (2)	H11A—C11—H11B	109.5
C9—C8—C7	118.07 (19)	H11A—C11—H11C	109.5
C9—C8—C12	121.12 (19)	H11B—C11—H11C	109.5
C1—C2—H2	120.4		

Zn1—N1—C5—C6	−2.1 (2)	C6—C7—C8—C12	178.3 (2)
Zn1—N1—C5—C4	178.15 (15)	C5—N1—C1—C2	−1.1 (3)
Zn1—N1—C1—C2	−178.79 (15)	C5—C6—C7—C8	179.38 (19)
Zn1—N2—C6—C5	−0.7 (2)	C5—C4—C3—C2	−0.8 (3)
Zn1—N2—C6—C7	178.55 (15)	C5—C4—C3—C11	177.39 (19)
Zn1—N2—C10—C9	−178.35 (16)	C7—C6—C5—N1	−177.36 (19)
N1—C5—C4—C3	0.8 (3)	C7—C6—C5—C4	2.4 (3)
N1—C1—C2—C3	1.0 (3)	C7—C8—C9—C10	0.7 (3)
N2—C6—C5—N1	1.8 (3)	C1—N1—C5—C6	179.95 (18)
N2—C6—C5—C4	−178.40 (18)	C1—N1—C5—C4	0.2 (3)
N2—C6—C7—C8	0.2 (3)	C1—C2—C3—C4	−0.1 (3)
N2—C10—C9—C8	−0.2 (3)	C1—C2—C3—C11	−178.2 (2)
C6—N2—C10—C9	−0.3 (3)	C10—N2—C6—C5	−178.96 (18)
C6—C5—C4—C3	−179.00 (18)	C10—N2—C6—C7	0.2 (3)
C6—C7—C8—C9	−0.7 (3)	C12—C8—C9—C10	−178.3 (2)