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Dichlorido(2,2′-methylenedipyridine)zinc(II)

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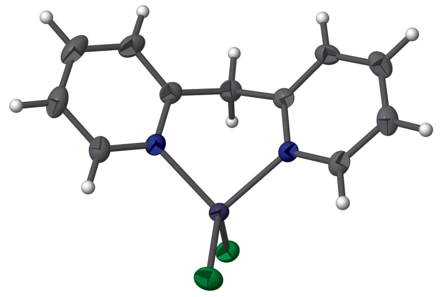
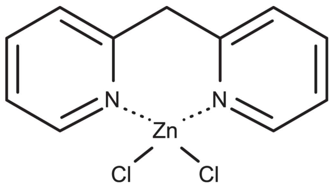
The title complex, [ZnCl$_2$(C$_{11}$H$_{10}$N$_2$)], crystallizes in the $P2_1/c$ space group with di-2-pyridylmethane acting as a bidentate ligand coordinating the zinc atom in a distorted tetrahedral geometry. The asymmetric unit consists of a single molecule of the title complex. The title complex folds with an angle of 53.82 (5)° between the planes of the two pyridine rings. The crystal packing is stabilized by hydrogen bonds and π–π interactions involving both pyridine rings.

3D view



Chemical scheme



Structure description

Polynuclear d^{10} metal complexes are known to possess luminescence properties and have been studied extensively (Yam & Lo, 1999). Mononuclear d^{10} metal complexes such as the title compound were first synthesized by Friedrich *et al.* (1962) in a search for new methods of producing known dyes. A few years later, Black *et al.* (1967) produced a series of bidentate chelate complexes including the title complex. Di-2-pyridylmethane can be coupled to form tetra-2-pyridylethane, which in turn can be oxidized further to form tetra-2-pyridylethylene. Both tetra-2-pyridylethane and the ethylene derivative have been used as a ligands in metal coordination chemistry (D'Alessandro *et al.*, 2003). Herein we report the crystal structure of the title compound, Fig. 1, which we produced serendipitously in an attempt to prepare a tetra-2-pyridyl derivative, Fig. 2.

The asymmetric unit of the title compound consists of one molecule on a general position. The two pyridine rings are planar to within 0.0076 (13)Å and 0.0071 (11) Å and are inclined to one another at a dihedral angle of 53.82 (5)°, Fig. 3. The Zn^{II} atom coordinates in a distorted tetrahedral geometry with the 2,2′-methylenedipyridine unit acting as a bidentate chelating ligand through the N atoms of the two pyridine rings.

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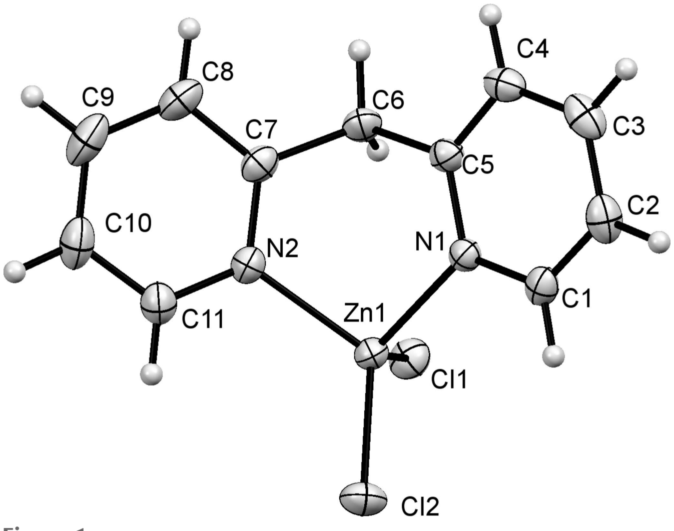

Figure 1
The structure of the title complex with displacement ellipsoids drawn at the 50% probability level.

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

*Cg*1 is the centroid of the N1/C1–C5 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$Cl1$^{\rm i}$	0.95	2.89	3.7719 (19)	154
C11—H11$\cdots$Cl2$^{\rm ii}$	0.95	2.86	3.591 (2)	134
C10—H10$\cdots$$Cg1^{\rm iii}$	0.95	2.99	3.718 (2)	135

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

C—H$\cdots\pi$ and π–π interactions are observed between molecules of the title compound. Two π–π interactions involve both pyridine rings, Fig. 4, with distances of 3.8843 (5) and 3.5828 (11) Å, respectively, between the centroids of the N2/C7–C11 pyridine rings running along the *b*-axis direction and between the centroids of the N1/C1–C5 pyridine rings running along the $[\overline{13}, 7, 0]$ direction. The H10$\cdots\pi$ (N1/C1–C5) interaction distance is 2.99 Å, which is just outside the H$\cdots$Cp distance of 2.9 Å suggested for such contacts (Takahashi *et al.*, 2001). C—H$\cdots$Cl interactions are also observed (Table 1).

A search of the CSD (Groom *et al.*, 2016) found five complexes that utilize bis(2-pyridyl)methane as a ligand and nine complexes with related di-2-pyridylketone ligands. Metals reported in these structures are Zn$^{\rm II}$, Pt$^{\rm II}$, and Pt$^{\rm IV}$ for the di-2-pyridylketone structures [refcodes ERAPUI (Crowder *et al.*, 2004), LUCBOA (Katsoulakou *et al.*, 2002), SIQZEX (Lo *et al.*, 2015), XARDOK, XARDUQ, XARFAY, XARFAC, XARFIG, XAVRIW (Zhang *et al.*, 2005)] with the majority being Pt complexes. Bis(2-pyridyl)methane complexes are found for Pt$^{\rm II}$, Cu$^{\rm I}$, Re$^{\rm I}$, Hg$^{\rm I}$, and Li cations. [refcodes CASXUQ (Elie *et al.*, 2017), HEWPIL (Gornitzka & Stalke, 1994), MPYHGA (Marti *et al.*, 2005), SAXVOD (Zhang *et al.*, 2005), YIFJEC (Canty *et al.*, 1980)]. Of the previously mentioned organometallic complexes, only the Zn$^{\rm II}$ chloride complexed with di-2-pyridylketone structure (LUCBOA; Katsoulakou *et al.*, 2002) has a tetrahedral coor-

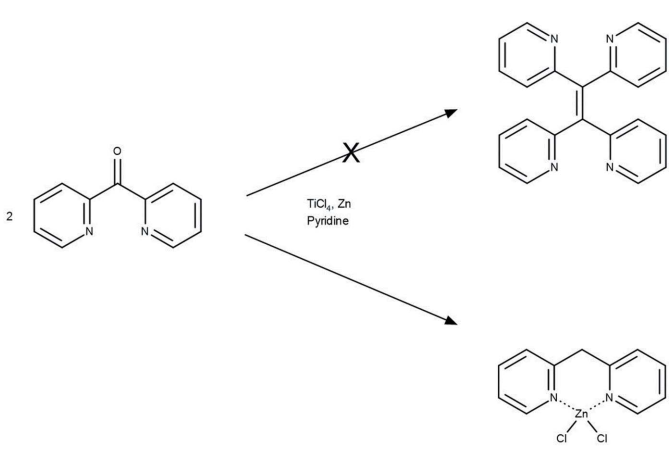

Figure 2
Expected and actual reaction schemes leading to the synthesis of the title complex.

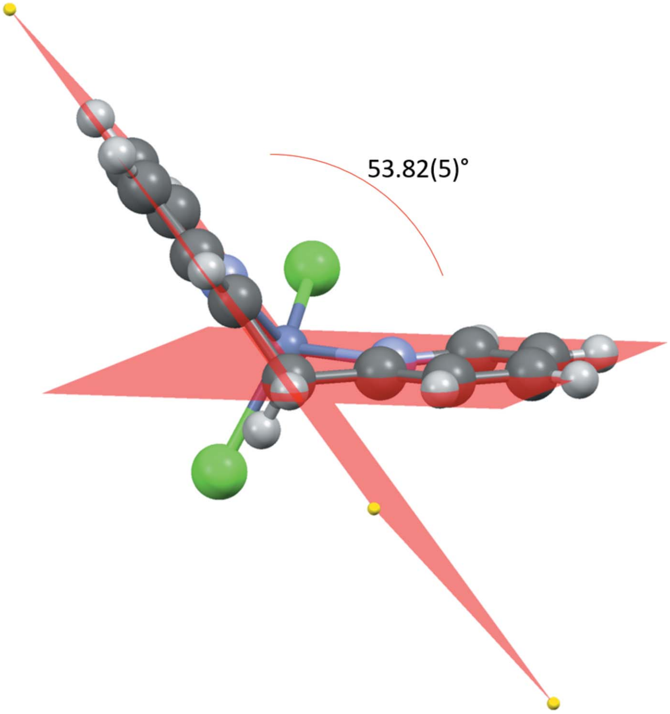

Figure 3
A plot showing the dihedral angle between the two pyridine rings in the title complex.

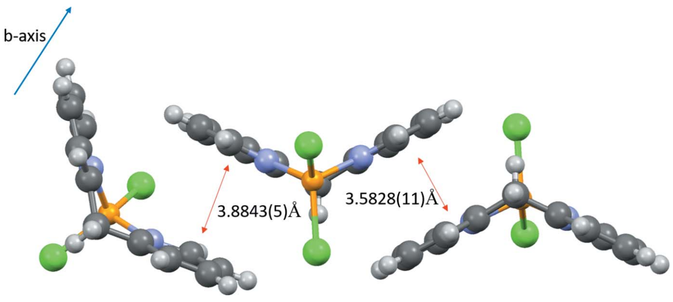

Figure 4
π–π interactions between adjacent molecules of the title complex.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[ZnCl_2(C_{11}H_{10}N_2)]$
M_r	306.48
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	12.1865 (8), 7.6666 (5), 14.1087 (9)
β (°)	111.467 (2)
V (Å^3)	1226.72 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.41
Crystal size (mm)	0.30 × 0.28 × 0.18
Data collection	
Diffractometer	Bruker D8 Venture Photon 100
Absorption correction	Multi-scan (*SADABS*; Bruker *et al.*, 2015)
$T_{\min}$, $T_{\max}$	0.935, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36532, 2535, 2403
$R_{\rm int}$	0.037
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.058, 1.06
No. of reflections	2535
No. of parameters	145
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.61, −0.39

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick 2015*a*), *SHELXL2016/6* (Sheldrick 2015*b*), *Mercury* (Macrae *et al.*, 2006) and *SHELXTL* (Sheldrick 2008).

dination about the metal. The tetrahedron has close to ideal bond angles due to the conformation of the di-2-pyridylketone ligand.

Synthesis and crystallization

The synthesis of the title compound was performed using previously reported methods for McMurry coupling (McMurry *et al.*, 1974; McMurry, 1989) but the reaction resulted in the formation of the title compound rather than a coupled product similar to that previously published·(Qi *et al.*, 2016), Fig. 2. The synthesis of the title complex was carried out under a nitrogen atmosphere with a 250 mL three-necked round-bottomed flask charged with Zn metal (0.17g, 1.74mmol) and cooled to −78°C. Then $TiCl_4$ (0.11mL, 1.74mmol) and pyridine (0.14mL, 1.7mmol) were added slowly, resulting in a green solution. The catalyst mixture was allowed to warm to room temperature then refluxed for an hour then cooled to −78°C, at which point di-2-pyridylketone (0.32g, 1.74mmol) in 50mL of THF was added, producing a dark-blue solution. The reaction mixture was allowed to return to room temperature then refluxed for four h. The reaction mixture was then allowed to return to room temperature and the THF was removed under vacuum. The mixture left in the reaction flask was extracted three times with dichloromethane (DCM). The solvent was removed under vacuum to produce the title compound as an off-white powder. The title compound was recrystallized from DCM.

Refinement

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

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full crystallographic data

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Crystal data

$[ZnCl_2(C_{11}H_{10}N_2)]$
M_r = 306.48
Monoclinic, $P2_1/c$
a = 12.1865 (8) Å
b = 7.6666 (5) Å
c = 14.1087 (9) Å
β = 111.467 (2)°
V = 1226.72 (14) Å^3
Z = 4
$F(000)$ = 616
D_x = 1.659 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9749 reflections
θ = 3.1–30.5°
μ = 2.41 mm^{-1}
T = 100 K
Block, colourless
0.30 × 0.28 × 0.18 mm

Data collection

Bruker D8 Venture Photon 100 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker *et al.*, 2015)
T_{min} = 0.935, T_{max} = 1.000
36532 measured reflections
2535 independent reflections
2403 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.5°, θ_{min} = 3.0°
$h = -15 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.058
S = 1.06
2535 reflections
145 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.6222P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.25054 (2)	0.61335 (2)	0.78613 (2)	0.02155 (8)
Cl1	0.15845 (4)	0.86959 (5)	0.76835 (3)	0.02930 (11)
Cl2	0.28554 (4)	0.47187 (6)	0.93074 (3)	0.03149 (11)
N1	0.16497 (11)	0.45954 (17)	0.66353 (10)	0.0204 (3)
N2	0.39694 (12)	0.62986 (17)	0.74807 (11)	0.0232 (3)
C1	0.09591 (14)	0.3254 (2)	0.66831 (13)	0.0244 (3)
H1	0.085816	0.302370	0.730777	0.029*
C2	0.03931 (15)	0.2204 (2)	0.58533 (14)	0.0296 (4)
H2	−0.010838	0.128510	0.589795	0.036*
C3	0.05713 (16)	0.2519 (2)	0.49547 (14)	0.0315 (4)
H3	0.019904	0.180510	0.437488	0.038*
C4	0.12949 (16)	0.3878 (2)	0.49059 (13)	0.0274 (4)
H4	0.143354	0.409786	0.429657	0.033*
C5	0.18135 (14)	0.4911 (2)	0.57555 (12)	0.0221 (3)
C6	0.25566 (16)	0.6490 (2)	0.57328 (13)	0.0274 (4)
H6A	0.256931	0.661095	0.503825	0.033*
H6B	0.217720	0.754678	0.587617	0.033*
C7	0.38120 (15)	0.6402 (2)	0.64853 (14)	0.0254 (4)
C8	0.47631 (18)	0.6456 (3)	0.61739 (16)	0.0339 (4)
H8	0.464084	0.654296	0.547079	0.041*
C9	0.58986 (18)	0.6380 (3)	0.68982 (18)	0.0390 (5)
H9	0.656123	0.643384	0.669675	0.047*
C10	0.60542 (17)	0.6227 (2)	0.79139 (17)	0.0359 (4)
H10	0.682304	0.614734	0.842075	0.043*
C11	0.50713 (16)	0.6192 (2)	0.81785 (15)	0.0295 (4)
H11	0.517557	0.609015	0.887723	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02095 (11)	0.02503 (12)	0.02011 (11)	−0.00055 (7)	0.00920 (8)	−0.00067 (7)
Cl1	0.0301 (2)	0.0269 (2)	0.0332 (2)	0.00416 (16)	0.01431 (18)	0.00072 (16)
Cl2	0.0407 (2)	0.0332 (2)	0.0219 (2)	0.00119 (18)	0.01292 (18)	0.00326 (16)
N1	0.0189 (6)	0.0213 (7)	0.0206 (6)	0.0017 (5)	0.0068 (5)	0.0028 (5)
N2	0.0215 (7)	0.0233 (7)	0.0261 (7)	−0.0007 (5)	0.0101 (6)	0.0005 (5)
C1	0.0201 (8)	0.0236 (8)	0.0283 (9)	0.0024 (6)	0.0076 (6)	0.0067 (7)
C2	0.0250 (8)	0.0191 (8)	0.0387 (10)	−0.0006 (6)	0.0046 (7)	0.0028 (7)
C3	0.0309 (9)	0.0245 (9)	0.0313 (9)	0.0050 (7)	0.0021 (7)	−0.0064 (7)
C4	0.0305 (9)	0.0299 (9)	0.0209 (8)	0.0076 (7)	0.0083 (7)	0.0008 (7)
C5	0.0214 (7)	0.0238 (8)	0.0207 (8)	0.0037 (6)	0.0072 (6)	0.0037 (6)
C6	0.0299 (9)	0.0299 (9)	0.0231 (8)	−0.0026 (7)	0.0106 (7)	0.0061 (7)
C7	0.0280 (9)	0.0216 (8)	0.0299 (9)	−0.0013 (6)	0.0143 (7)	0.0029 (7)
C8	0.0369 (10)	0.0336 (10)	0.0402 (11)	−0.0010 (8)	0.0249 (9)	0.0048 (8)
C9	0.0311 (10)	0.0353 (10)	0.0608 (14)	0.0021 (8)	0.0287 (10)	0.0098 (9)
C10	0.0211 (9)	0.0334 (10)	0.0509 (12)	−0.0002 (7)	0.0105 (8)	0.0069 (8)

C11	0.0238 (9)	0.0300 (9)	0.0324 (9)	−0.0018 (7)	0.0075 (7)	0.0012 (7)

Geometric parameters (Å, º)

Zn1—N1	2.0372 (14)	C4—C5	1.382 (2)
Zn1—N2	2.0466 (14)	C4—H4	0.9500
Zn1—Cl2	2.2101 (5)	C5—C6	1.519 (2)
Zn1—Cl1	2.2306 (5)	C6—C7	1.511 (2)
N1—C1	1.346 (2)	C6—H6A	0.9900
N1—C5	1.349 (2)	C6—H6B	0.9900
N2—C11	1.346 (2)	C7—C8	1.382 (2)
N2—C7	1.348 (2)	C8—C9	1.388 (3)
C1—C2	1.380 (3)	C8—H8	0.9500
C1—H1	0.9500	C9—C10	1.380 (3)
C2—C3	1.383 (3)	C9—H9	0.9500
C2—H2	0.9500	C10—C11	1.379 (3)
C3—C4	1.383 (3)	C10—H10	0.9500
C3—H3	0.9500	C11—H11	0.9500

N1—Zn1—N2	92.15 (6)	N1—C5—C4	121.35 (16)
N1—Zn1—Cl2	111.45 (4)	N1—C5—C6	116.91 (14)
N2—Zn1—Cl2	112.35 (4)	C4—C5—C6	121.70 (15)
N1—Zn1—Cl1	109.52 (4)	C7—C6—C5	114.08 (14)
N2—Zn1—Cl1	111.53 (4)	C7—C6—H6A	108.7
Cl2—Zn1—Cl1	117.084 (18)	C5—C6—H6A	108.7
C1—N1—C5	119.28 (14)	C7—C6—H6B	108.7
C1—N1—Zn1	122.33 (11)	C5—C6—H6B	108.7
C5—N1—Zn1	118.37 (11)	H6A—C6—H6B	107.6
C11—N2—C7	119.28 (15)	N2—C7—C8	121.10 (17)
C11—N2—Zn1	122.44 (12)	N2—C7—C6	117.13 (15)
C7—N2—Zn1	118.13 (11)	C8—C7—C6	121.76 (17)
N1—C1—C2	122.05 (16)	C7—C8—C9	119.38 (19)
N1—C1—H1	119.0	C7—C8—H8	120.3
C2—C1—H1	119.0	C9—C8—H8	120.3
C1—C2—C3	118.60 (16)	C10—C9—C8	119.28 (18)
C1—C2—H2	120.7	C10—C9—H9	120.4
C3—C2—H2	120.7	C8—C9—H9	120.4
C4—C3—C2	119.57 (16)	C11—C10—C9	118.67 (18)
C4—C3—H3	120.2	C11—C10—H10	120.7
C2—C3—H3	120.2	C9—C10—H10	120.7
C5—C4—C3	119.11 (17)	N2—C11—C10	122.26 (19)
C5—C4—H4	120.4	N2—C11—H11	118.9
C3—C4—H4	120.4	C10—C11—H11	118.9

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···Cl1^{i}	0.95	2.89	3.7719 (19)	154
C11—H11···Cl2^{ii}	0.95	2.86	3.591 (2)	134
C10—H10···*Cg*1^{iii}	0.95	2.99	3.718 (2)	135

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) −*x*+1, −*y*+1, −*z*+2; (iii) −*x*+1, *y*+1/2, −*z*+3/2.