metal-organic compounds

[Bis(2-pyridylmethyl)amine]dichlorido-zinc(II) chloroform solvate

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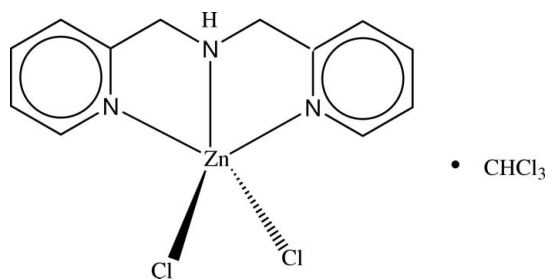Correspondence e-mail: skkang@cnu.ac.kr

The Zn atom in the title complex, $[ZnCl_2(C_{12}H_{13}N_3)]\cdot CHCl_3$, adopts a distorted square-pyramidal geometry, being coordinated by three N atoms of the tridentate dipicolylamine ligand and two Cl atoms. Intermolecular $N-H\cdots Cl$ hydrogen-bonding interactions link the molecules into centrosymmetric dimers.

Related literature

For general background see: Kirin *et al.* (2005); Storr *et al.* (2005); Tamamura *et al.* (2006); Lee *et al.* (2007) & Ojida *et al.* (2004). For related literature, see: Addison *et al.* (1984).

Experimental

Crystal data

$[ZnCl_2(C_{12}H_{13}N_3)]\cdot CHCl_3$	V = 1875.8 (3) Å³
M_r = 454.89	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 6.9650 (6) Å	μ = 2.02 mm⁻¹
b = 12.8654 (12) Å	T = 295 (2) K
c = 20.9341 (18) Å	$0.20 \times 0.18 \times 0.17$ mm
β = 90.335 (5)°	

Data collection

Bruker SMART CCD area-detector diffractometer	36984 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	4676 independent reflections
	3104 reflections with $I > 2\sigma(I)$
T_{min} = 0.661, T_{max} = 0.697	R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.132	
S = 1.03	
4676 reflections	$\Delta\rho_{max}$ = 0.85 e Å⁻³
203 parameters	$\Delta\rho_{min}$ = −0.76 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Zn—N1	2.159 (3)	Zn—Cl1	2.2919 (10)
Zn—N8	2.136 (3)	Zn—Cl2	2.2722 (9)
Zn—N15	2.170 (3)		
N1—Zn—N8	77.23 (12)	N8—Zn—Cl1	104.71 (9)
N1—Zn—N15	151.65 (12)	N8—Zn—Cl2	138.97 (9)
N1—Zn—Cl1	98.01 (9)	N15—Zn—Cl1	97.87 (9)
N1—Zn—Cl2	97.20 (9)	N15—Zn—Cl2	96.59 (8)
N8—Zn—N15	76.11 (12)	Cl1—Zn—Cl2	116.30 (4)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N8—H8···Cl2[i]	0.85 (4)	2.63 (4)	3.365 (3)	146 (3)

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supplementary materials

[Bis(2-pyridylmethyl)amine]dichloridozinc(II) chloroform solvate

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Comment

Transition metal complexes with di(2-picolyl)amine (dpa) or substituted-dpa ligands continue to be of interest in many fields in chemistry (Kirin *et al.*, 2005; Storr *et al.*, 2005; Tamamura *et al.*, 2006 & Lee *et al.*, 2007). Among them, Zn(II) complexes exhibit fluorescence and can be applied as fluorescent chemosensors (Ojida *et al.*, 2004). The Zn(II) center in the title [Zn(dpa)Cl$_2$] complex, characterized as a monochloroform solvate, (I), is five-coordinated by the three N atoms of the dpa ligand and two Cl atoms (Fig. 1 & Table 1). The coordination pattern of the three N atoms of the dpa ligand is meridional and forms a planar ZnN$_3$ arrangement and the overall coordination geometry is based on a square pyramid. The calculated trigonality index, τ, for Zn(dpa)Cl$_2$ in (I), of 0.21, is consistent with this conclusion ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid (Addison *et al.*, 1984)). Hydrogen bonding interactions of the type N—H···Cl link molecules into centrosymmetric dimeric aggregates (Table 2). Upon excitation at 400 nm, complex (I) exhibits an intense blue emission at 426 nm in DMF solution.

Experimental

All reagents and solvents were purchased from Aldrich and used without further purification. A mixture of ZnCl$_2$ (0.66 g, 5 mmol) and di(2-picolyl)amine (0.99 g, 5 mmol) in ethanol (20 ml) was stirred at room temperature under an nitrogen atmosphere. The precipitates were filtered off and recrystallized from chloroform to yield (I). ^{1}H NMR for dpa in (I) (d$_6$-DMSO, p.p.m.): δ: 8.76 (d, 2H), 8.00 (m, 2H), 7.55 (t, 4H), 4.90 (t, 1H), 4.13 (s, 4H).

Refinement

The N8—H atom was refined without constraint. The C-bound H atoms were included in the riding model approximation with C—H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C).
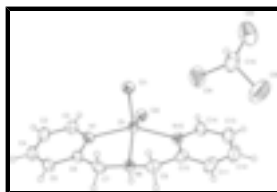
Figures

Fig. 1. Molecular structure of (I), showing the atom-numbering scheme and 30% probability ellipsoids.

(I)

Crystal data

$[ZnCl_2(C_{12}H_{13}N_3)]\cdot CHCl_3$	$F_{000} = 912$
$M_r = 454.89$	$D_x = 1.611$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
	$\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5802 reflections
$a = 6.9650$ (6) Å	$\theta = 2.5–23.5°$
$b = 12.8654$ (12) Å	$\mu = 2.02$ mm^{-1}
$c = 20.9341$ (18) Å	$T = 295$ (2) K
$\beta = 90.335$ (5)°	Block, colourless
$V = 1875.8$ (3) Å^3	$0.20 \times 0.18 \times 0.17$ mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{int} = 0.055$
φ and ω scans	$\theta_{max} = 28.4°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$\theta_{min} = 1.9°$
$T_{min} = 0.661$, $T_{max} = 0.697$	$h = -9 \rightarrow 9$
36984 measured reflections	$k = -17 \rightarrow 17$
4676 independent reflections	$l = -27 \rightarrow 27$
3104 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 1.569P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.132$	$\Delta\rho_{max} = 0.85$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.76$ e Å^{-3}
4676 reflections	Extinction correction: none
203 parameters	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Zn	0.58918 (5)	0.97733 (3)	0.110162 (18)	0.04221 (14)
Cl1	0.69504 (13)	0.90035 (8)	0.20260 (4)	0.0528 (2)
Cl2	0.80351 (14)	1.08035 (8)	0.05874 (4)	0.0566 (3)
N1	0.4222 (4)	1.1003 (3)	0.15276 (15)	0.0514 (7)
C2	0.4828 (7)	1.1957 (4)	0.1677 (2)	0.0665 (11)
H2	0.6083	1.2144	0.1581	0.08*
C3	0.3661 (8)	1.2674 (4)	0.1968 (2)	0.0819 (15)
H3	0.4118	1.3332	0.207	0.098*
C4	0.1807 (8)	1.2396 (5)	0.2105 (2)	0.0817 (15)
H4	0.0986	1.2869	0.2299	0.098*
C5	0.1169 (6)	1.1420 (4)	0.1956 (2)	0.0722 (13)
H5	−0.0084	1.1222	0.2047	0.087*
C6	0.2417 (5)	1.0731 (3)	0.16676 (16)	0.0521 (9)
C7	0.1865 (5)	0.9624 (3)	0.1518 (2)	0.0577 (10)
H7A	0.2079	0.9192	0.1892	0.069*
H7B	0.0512	0.9592	0.1408	0.069*
N8	0.3013 (4)	0.9232 (3)	0.09836 (15)	0.0462 (7)
H8	0.252 (5)	0.947 (3)	0.0644 (19)	0.045 (11)*
C9	0.3055 (6)	0.8096 (3)	0.0925 (2)	0.0553 (10)
H9A	0.185	0.7851	0.0745	0.066*
H9B	0.3218	0.7785	0.1344	0.066*
C10	0.4691 (6)	0.7776 (3)	0.04990 (17)	0.0517 (9)
C11	0.4684 (8)	0.6857 (3)	0.0160 (2)	0.0721 (13)
H11	0.3635	0.6411	0.0176	0.087*
C12	0.6275 (9)	0.6612 (4)	−0.0206 (2)	0.0844 (15)
H12	0.6321	0.599	−0.0431	0.101*
C13	0.7771 (8)	0.7294 (4)	−0.0231 (2)	0.0775 (14)
H13	0.884	0.7148	−0.048	0.093*
C14	0.7680 (6)	0.8190 (4)	0.01125 (19)	0.0597 (10)
H14	0.8708	0.865	0.0094	0.072*
N15	0.6173 (4)	0.8437 (2)	0.04767 (14)	0.0482 (7)
C16	0.9172 (9)	0.5298 (4)	0.1609 (2)	0.0859 (16)
H16	0.8947	0.4975	0.2026	0.103*
Cl3	1.1706 (3)	0.53673 (14)	0.14969 (12)	0.1342 (7)
Cl4	0.8241 (3)	0.65527 (13)	0.16368 (8)	0.1098 (5)
Cl5	0.8131 (5)	0.4523 (2)	0.10431 (13)	0.1840 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.0364 (2)	0.0507 (2)	0.0396 (2)	−0.00151 (17)	0.00611 (15)	−0.00004 (18)
Cl1	0.0524 (5)	0.0634 (6)	0.0426 (5)	0.0039 (4)	0.0040 (4)	0.0078 (4)
Cl2	0.0553 (5)	0.0690 (6)	0.0458 (5)	−0.0137 (5)	0.0094 (4)	0.0064 (4)
N1	0.0486 (17)	0.057 (2)	0.0483 (17)	0.0100 (14)	0.0022 (13)	0.0002 (15)

supplementary materials

C2	0.071 (3)	0.063 (3)	0.066 (3)	0.008 (2)	0.001 (2)	−0.010 (2)
C3	0.104 (4)	0.068 (3)	0.074 (3)	0.025 (3)	−0.009 (3)	−0.023 (3)
C4	0.086 (4)	0.098 (4)	0.062 (3)	0.043 (3)	−0.002 (2)	−0.022 (3)
C5	0.055 (2)	0.106 (4)	0.056 (3)	0.025 (3)	0.0048 (19)	−0.009 (3)
C6	0.045 (2)	0.074 (3)	0.0372 (18)	0.0155 (18)	0.0046 (15)	0.0008 (18)
C7	0.0410 (19)	0.074 (3)	0.058 (2)	0.0064 (18)	0.0086 (17)	0.008 (2)
N8	0.0393 (15)	0.058 (2)	0.0408 (16)	−0.0017 (14)	0.0009 (13)	0.0050 (15)
C9	0.053 (2)	0.055 (2)	0.059 (2)	−0.0118 (18)	0.0001 (18)	0.0050 (18)
C10	0.059 (2)	0.053 (2)	0.043 (2)	−0.0036 (18)	−0.0042 (16)	0.0019 (17)
C11	0.097 (4)	0.055 (3)	0.064 (3)	−0.005 (2)	−0.008 (3)	−0.009 (2)
C12	0.117 (5)	0.069 (3)	0.067 (3)	0.011 (3)	−0.001 (3)	−0.023 (3)
C13	0.089 (3)	0.082 (3)	0.061 (3)	0.016 (3)	0.013 (2)	−0.014 (3)
C14	0.059 (2)	0.070 (3)	0.050 (2)	0.010 (2)	0.0101 (18)	−0.003 (2)
N15	0.0487 (17)	0.0533 (18)	0.0426 (16)	−0.0011 (14)	0.0044 (13)	−0.0029 (14)
C16	0.128 (5)	0.071 (3)	0.059 (3)	0.006 (3)	0.009 (3)	−0.001 (2)
Cl3	0.1399 (17)	0.0955 (12)	0.168 (2)	0.0094 (11)	0.0342 (14)	0.0047 (12)
Cl4	0.1519 (15)	0.0851 (10)	0.0925 (10)	0.0336 (10)	0.0029 (10)	0.0020 (8)
Cl5	0.245 (3)	0.141 (2)	0.165 (2)	0.0070 (19)	−0.077 (2)	−0.0631 (17)

Geometric parameters (Å, °)

Zn—N1	2.159 (3)	C7—H7B	0.97
Zn—N8	2.136 (3)	N8—H8	0.85 (4)
Zn—N15	2.170 (3)	C9—C10	1.508 (5)
Zn—Cl1	2.2919 (10)	C9—H9A	0.97
Zn—Cl2	2.2722 (9)	C9—H9B	0.97
N1—C2	1.335 (5)	C10—N15	1.338 (5)
N1—C6	1.339 (5)	C10—C11	1.380 (6)
C2—C3	1.374 (6)	C11—C12	1.386 (7)
C2—H2	0.93	C11—H11	0.93
C3—C4	1.372 (8)	C12—C13	1.364 (7)
C3—H3	0.93	C12—H12	0.93
C4—C5	1.367 (7)	C13—C14	1.360 (6)
C4—H4	0.93	C13—H13	0.93
C5—C6	1.382 (6)	C14—N15	1.340 (5)
C5—H5	0.93	C14—H14	0.93
C6—C7	1.507 (6)	C16—Cl5	1.706 (6)
N8—C9	1.467 (5)	C16—Cl4	1.741 (5)
C7—N8	1.468 (5)	C16—Cl3	1.784 (7)
C7—H7A	0.97	C16—H16	0.98
N1—Zn—N8	77.23 (12)	C9—N8—Zn	108.4 (2)
N1—Zn—N15	151.65 (12)	C7—N8—Zn	108.3 (2)
N1—Zn—Cl1	98.01 (9)	C9—N8—H8	108 (3)
N1—Zn—Cl2	97.20 (9)	C7—N8—H8	107 (3)
N8—Zn—N15	76.11 (12)	Zn—N8—H8	111 (3)
N8—Zn—Cl1	104.71 (9)	N8—C9—C10	109.7 (3)
N8—Zn—Cl2	138.97 (9)	N8—C9—H9A	109.7
N15—Zn—Cl1	97.87 (9)	C10—C9—H9A	109.7
N15—Zn—Cl2	96.59 (8)	N8—C9—H9B	109.7

Cl1—Zn—Cl2	116.30 (4)	C10—C9—H9B	109.7
C2—N1—C6	119.0 (4)	H9A—C9—H9B	108.2
C2—N1—Zn	126.9 (3)	N15—C10—C11	121.8 (4)
C6—N1—Zn	114.1 (3)	N15—C10—C9	115.7 (3)
N1—C2—C3	122.3 (5)	C11—C10—C9	122.5 (4)
N1—C2—H2	118.9	C10—C11—C12	118.6 (5)
C3—C2—H2	118.9	C10—C11—H11	120.7
C4—C3—C2	118.6 (5)	C12—C11—H11	120.7
C4—C3—H3	120.7	C13—C12—C11	119.3 (5)
C2—C3—H3	120.7	C13—C12—H12	120.3
C5—C4—C3	119.8 (4)	C11—C12—H12	120.3
C5—C4—H4	120.1	C14—C13—C12	119.1 (5)
C3—C4—H4	120.1	C14—C13—H13	120.5
C4—C5—C6	119.0 (5)	C12—C13—H13	120.5
C4—C5—H5	120.5	N15—C14—C13	122.8 (4)
C6—C5—H5	120.5	N15—C14—H14	118.6
N1—C6—C5	121.4 (4)	C13—C14—H14	118.6
N1—C6—C7	116.1 (3)	C10—N15—C14	118.4 (3)
C5—C6—C7	122.4 (4)	C10—N15—Zn	114.2 (2)
N8—C7—C6	110.1 (3)	C14—N15—Zn	127.2 (3)
N8—C7—H7A	109.6	Cl5—C16—Cl4	114.1 (4)
C6—C7—H7A	109.6	Cl5—C16—Cl3	110.8 (3)
N8—C7—H7B	109.6	Cl4—C16—Cl3	109.1 (3)
C6—C7—H7B	109.6	Cl5—C16—H16	107.5
H7A—C7—H7B	108.2	Cl4—C16—H16	107.5
C9—N8—C7	114.7 (3)	Cl3—C16—H16	107.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8···Cl2[i]	0.85 (4)	2.63 (4)	3.365 (3)	146 (3)

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

Fig. 1