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Bis[3-(2-carboxyethenyl)pyridinium-1-acetato]dichloridozinc(II)

Xue-Hui Jing, Wei-Wei Sun and En-Qing Gao*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, People's Republic of China

Correspondence e-mail: eqgao@chem.ecnu.edu.cn

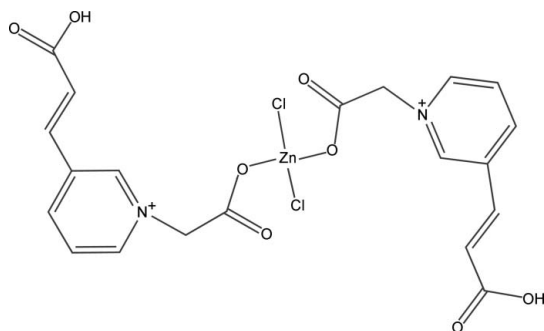
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.077; data-to-parameter ratio = 15.9.

In the title complex, $[\text{ZnCl}_2(\text{C}_{10}\text{H}_9\text{NO}_4)_2]$, the Zn^{II} ion lies on a twofold rotation axis and is four-coordinated by two carboxylate O atoms from two 3-(2-carboxyethenyl)pyridinium-1-acetate ligands in a monodentate mode and two Cl atoms in a distorted tetrahedral geometry. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into a double-chain structure extending parallel to $[101]$.

Related literature

For general background to hydrogen bonds, see: Beatty (2003); Liu *et al.* (2008); Steiner (2002). For related structures, see: Mao *et al.* (1999); Sun *et al.* (2009); Wu *et al.* (2006); Zhang *et al.* (2002).



Experimental

Crystal data

 $[\text{ZnCl}_2(\text{C}_{10}\text{H}_9\text{NO}_4)_2]$ $M_r = 550.63$ Monoclinic, $C2/c$ $a = 16.6247$ (6) Å $b = 7.1973$ (3) Å $c = 18.8873$ (7) Å $\beta = 108.685$ (1)° $V = 2140.81$ (14) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 1.45$ mm⁻¹ $T = 296$ K

0.12 × 0.12 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\text{min}} = 0.845$, $T_{\text{max}} = 0.893$

27422 measured reflections
2450 independent reflections
2309 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.077$
 $S = 1.06$
2450 reflections
154 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Selected bond lengths (Å).

Zn1—O1	1.9983 (13)	Zn1—Cl1	2.2566 (4)
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Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4B}\cdots\text{O2}^{\text{i}}$	0.97 (4)	1.60 (4)	2.560 (2)	169 (3)

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2249).

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supplementary materials

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Comment

As we know, hydrogen bond is the most important of all directional intermolecular interactions. It is operative in determining molecular conformation, molecular aggregation, and the function of a vast number of chemical systems ranging from inorganic to biological (Beatty, 2003; Liu *et al.*, 2008; Steiner, 2002). In this paper, we report the coordination and hydrogen-bond structure of the title complex derived from a zwitterionic dicarboxylic ligand, 1-carboxymethylpyridinium-3-acrylic acid. Zwitterionic dicarboxylic acids as ligands have received less attention in coordination chemistry than the common dicarboxylic acids, although an increasing number of coordination compounds with such ligands have been reported in recent years (Mao *et al.*, 1999; Wu *et al.*, 2006; Zhang *et al.*, 2002).

The molecular structure is shown in Fig. 1. The Zn^{II} ion, lying on a twofold rotation axis, is coordinated by two Cl atoms and the two zwitterionic ligands through carboxylate O atoms, with a distorted tetrahedral coordination geometry. The Zn—Cl and Zn—O distances lie in the usual range for a tetrahedral Zn^{II} center (Table 1). The zwitterionic ligand is neutral with an anionic *N*-acetate group in a monodentate coordination mode and a cationic pyridinium ring. The acrylic group remains protonated and uncoordinated. This is in contrast with the only previous coordination compound with this ligand, [Ni₃(C₁₀H₈NO₄)₂(N₃)₄(H₂O)₂].5H₂O (Sun *et al.*, 2009), in which both carboxylate groups are deprotonated and coordinated in a bidentate bridging mode, giving an extended coordination network. As shown in Fig. 2, the mononuclear complex molecules in the title compound are associated into a one-dimensional chain along the [101] direction through intermolecular O—H...O hydrogen bonds (Table 2). The hydrogen bond involves the acrylic hydroxyl group (O4—H4B) from one molecule and the uncoordinated acetate O atom (O2) from another molecule.

Experimental

The zwitterionic ligand was synthesized from ethyl pyridine-3-acrylate and ethyl bromoacetate according to the procedure for similar compounds (Mao *et al.*, 1999). A mixture of the ligand (0.021 g, 0.10 mmol), ZnCl₂ (0.014 g, 0.10 mmol), NaN₃ (0.026 g, 0.40 mmol), ethanol (1.0 ml) and H₂O (2.0 ml) was sealed in a Teflon-lined autoclave and heated at 343 K for 3 d, then cooled to room temperature at a rate of 5 K h⁻¹, giving a pale yellow solution. Slow evaporation of the solution at room temperature for several days afforded colorless block crystals of the title compound (yield 46%). Analysis, calculated for C₂₀H₁₈Cl₂N₂O₈Zn: C 27.22, H 3.43, N 22.22%; found: C 27.11, H 3.82, N 22.50%. FT—IR (KBr, cm⁻¹): 3530*m*, 3348*br*, 2084*vs*, 2059*vs*, 1630*vs*, 1582 *s*, 1505*m*, 1461*w*, 1388*vs*, 1307*m*, 985*m*.

Refinement

H atoms attached to C atoms were placed at calculated positions and refined as riding atoms, with C—H = 0.93 (CH) and 0.97 (CH₂) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The carboxylic H atom (H4B) was located from a difference Fourier map and refined isotropically.

Figures

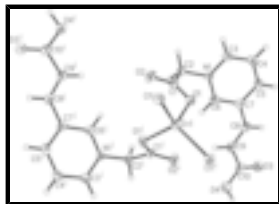


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, y, -z + 1/2$.]

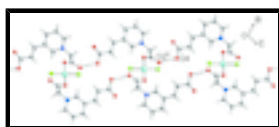


Fig. 2. One-dimensional chain structure connected through intermolecular O—H...O hydrogen bonds (dashed lines). [Symmetry code: (ii) $x - 1/2, -y + 3/2, z - 1/2$.]

Bis[3-(2-carboxyethenyl)pyridinium-1-acetato]dichloridozinc(II)

Crystal data

[ZnCl₂(C₁₀H₉NO₄)₂]

$M_r = 550.63$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 16.6247\ (6)\ \text{\AA}$

$b = 7.1973\ (3)\ \text{\AA}$

$c = 18.8873\ (7)\ \text{\AA}$

$\beta = 108.685\ (1)^\circ$

$V = 2140.81\ (14)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1120$

$D_x = 1.708\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 9202 reflections

$\theta = 2.3\text{--}26.0^\circ$

$\mu = 1.45\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colorless

$0.12 \times 0.12 \times 0.08\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2001)

$T_{\min} = 0.845, T_{\max} = 0.893$

27422 measured reflections

2450 independent reflections

2309 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.3^\circ$

$h = -21 \rightarrow 20$

$k = -9 \rightarrow 8$

$l = -24 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.077$

$S = 1.06$

2450 reflections

154 parameters

Primary atom site location: structure-invariant direct methods

$$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 2.553P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.21438 (4)	0.2500	0.02879 (10)
C1	0.10900 (11)	0.5110 (3)	0.25776 (10)	0.0324 (4)
C2	0.14353 (12)	0.6811 (3)	0.22916 (10)	0.0360 (4)
H2A	0.1139	0.7904	0.2379	0.043*
H2B	0.2032	0.6953	0.2576	0.043*
C3	0.20158 (11)	0.6192 (3)	0.12864 (11)	0.0370 (4)
H3A	0.2525	0.5883	0.1649	0.044*
C4	0.19519 (13)	0.6114 (3)	0.05458 (12)	0.0432 (4)
H4A	0.2413	0.5734	0.0405	0.052*
C5	0.12009 (13)	0.6600 (3)	0.00115 (11)	0.0395 (4)
H5A	0.1155	0.6563	-0.0492	0.047*
C6	0.06027 (11)	0.7173 (2)	0.09822 (10)	0.0318 (4)
H6A	0.0146	0.7511	0.1137	0.038*
C7	0.05107 (12)	0.7146 (2)	0.02242 (10)	0.0323 (4)
C8	-0.02829 (13)	0.7712 (3)	-0.03508 (10)	0.0371 (4)
H8A	-0.0273	0.7784	-0.0840	0.044*
C9	-0.10021 (13)	0.8126 (3)	-0.02414 (11)	0.0401 (4)
H9A	-0.1045	0.8061	0.0237	0.048*
C10	-0.17521 (12)	0.8700 (3)	-0.08844 (10)	0.0380 (4)
N1	0.13464 (9)	0.6713 (2)	0.14914 (8)	0.0290 (3)
O1	0.06462 (9)	0.39902 (19)	0.21043 (7)	0.0371 (3)
O2	0.12548 (10)	0.5002 (2)	0.32652 (7)	0.0509 (4)
O3	-0.17174 (10)	0.9091 (3)	-0.14938 (9)	0.0574 (4)
O4	-0.24415 (10)	0.8769 (3)	-0.07066 (9)	0.0592 (5)
H4B	-0.290 (2)	0.919 (5)	-0.1137 (19)	0.091 (11)*
Cl1	0.07978 (3)	0.02552 (6)	0.34083 (2)	0.03619 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03138 (16)	0.03059 (16)	0.02483 (15)	0.000	0.00960 (11)	0.000
C1	0.0285 (8)	0.0387 (9)	0.0288 (8)	-0.0027 (7)	0.0075 (6)	0.0018 (7)
C2	0.0417 (9)	0.0378 (9)	0.0263 (8)	-0.0084 (8)	0.0076 (7)	-0.0012 (7)
C3	0.0288 (8)	0.0389 (9)	0.0422 (9)	0.0025 (7)	0.0099 (7)	0.0063 (8)
C4	0.0391 (10)	0.0484 (11)	0.0485 (11)	0.0031 (8)	0.0231 (8)	0.0044 (9)
C5	0.0492 (11)	0.0384 (9)	0.0343 (9)	-0.0016 (8)	0.0183 (8)	0.0024 (8)
C6	0.0289 (8)	0.0313 (8)	0.0345 (9)	0.0009 (6)	0.0090 (7)	0.0001 (7)

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C7	0.0356 (9)	0.0271 (8)	0.0308 (8)	-0.0020 (6)	0.0059 (7)	0.0030 (6)
C8	0.0411 (10)	0.0382 (9)	0.0283 (8)	-0.0014 (8)	0.0060 (7)	0.0027 (7)
C9	0.0447 (10)	0.0434 (10)	0.0292 (9)	0.0027 (8)	0.0077 (8)	-0.0009 (8)
C10	0.0422 (10)	0.0332 (9)	0.0329 (9)	0.0023 (7)	0.0040 (7)	-0.0018 (7)
N1	0.0304 (7)	0.0282 (6)	0.0268 (7)	-0.0021 (5)	0.0069 (5)	0.0026 (5)
O1	0.0436 (7)	0.0394 (7)	0.0300 (6)	-0.0126 (6)	0.0142 (5)	-0.0051 (5)
O2	0.0545 (9)	0.0663 (10)	0.0266 (6)	-0.0263 (8)	0.0056 (6)	0.0030 (6)
O3	0.0447 (8)	0.0801 (12)	0.0441 (8)	0.0034 (8)	0.0094 (7)	0.0092 (8)
O4	0.0445 (8)	0.0929 (14)	0.0360 (8)	0.0210 (9)	0.0070 (6)	0.0123 (8)
Cl1	0.0369 (2)	0.0387 (2)	0.0321 (2)	0.00658 (17)	0.00991 (17)	0.00704 (16)

Geometric parameters (Å, °)

Zn1—O1	1.9983 (13)	C5—C7	1.388 (3)
Zn1—Cl1	2.2566 (4)	C5—H5A	0.9300
C1—O2	1.241 (2)	C6—N1	1.342 (2)
C1—O1	1.253 (2)	C6—C7	1.390 (3)
C1—C2	1.522 (3)	C6—H6A	0.9300
C2—N1	1.472 (2)	C7—C8	1.473 (2)
C2—H2A	0.9700	C8—C9	1.311 (3)
C2—H2B	0.9700	C8—H8A	0.9300
C3—N1	1.343 (2)	C9—C10	1.493 (3)
C3—C4	1.370 (3)	C9—H9A	0.9300
C3—H3A	0.9300	C10—O3	1.204 (3)
C4—C5	1.376 (3)	C10—O4	1.294 (3)
C4—H4A	0.9300	O4—H4B	0.97 (4)
O1 ⁱ —Zn1—O1	96.63 (8)	C4—C5—H5A	120.0
O1 ⁱ —Zn1—Cl1 ⁱ	115.43 (4)	C7—C5—H5A	120.0
O1—Zn1—Cl1 ⁱ	111.82 (4)	N1—C6—C7	120.43 (17)
O1 ⁱ —Zn1—Cl1	111.82 (4)	N1—C6—H6A	119.8
O1—Zn1—Cl1	115.43 (4)	C7—C6—H6A	119.8
Cl1 ⁱ —Zn1—Cl1	105.92 (3)	C5—C7—C6	118.26 (17)
O2—C1—O1	126.04 (17)	C5—C7—C8	119.55 (17)
O2—C1—C2	116.10 (16)	C6—C7—C8	122.18 (17)
O1—C1—C2	117.82 (15)	C9—C8—C7	126.40 (18)
N1—C2—C1	113.62 (15)	C9—C8—H8A	116.8
N1—C2—H2A	108.8	C7—C8—H8A	116.8
C1—C2—H2A	108.8	C8—C9—C10	120.04 (18)
N1—C2—H2B	108.8	C8—C9—H9A	120.0
C1—C2—H2B	108.8	C10—C9—H9A	120.0
H2A—C2—H2B	107.7	O3—C10—O4	123.81 (18)
N1—C3—C4	120.36 (17)	O3—C10—C9	123.98 (19)
N1—C3—H3A	119.8	O4—C10—C9	112.19 (17)
C4—C3—H3A	119.8	C6—N1—C3	121.35 (16)
C3—C4—C5	119.60 (18)	C6—N1—C2	119.36 (15)
C3—C4—H4A	120.2	C3—N1—C2	119.28 (15)
C5—C4—H4A	120.2	C1—O1—Zn1	115.16 (11)
C4—C5—C7	119.98 (18)	C10—O4—H4B	109 (2)

O2—C1—C2—N1	170.27 (17)	C8—C9—C10—O4	169.7 (2)
O1—C1—C2—N1	-12.1 (2)	C7—C6—N1—C3	-1.0 (3)
N1—C3—C4—C5	1.0 (3)	C7—C6—N1—C2	178.06 (16)
C3—C4—C5—C7	-0.7 (3)	C4—C3—N1—C6	-0.2 (3)
C4—C5—C7—C6	-0.4 (3)	C4—C3—N1—C2	-179.18 (18)
C4—C5—C7—C8	178.33 (19)	C1—C2—N1—C6	82.1 (2)
N1—C6—C7—C5	1.2 (3)	C1—C2—N1—C3	-98.9 (2)
N1—C6—C7—C8	-177.45 (16)	O2—C1—O1—Zn1	11.0 (3)
C5—C7—C8—C9	174.5 (2)	C2—C1—O1—Zn1	-166.35 (13)
C6—C7—C8—C9	-6.8 (3)	O1 ⁱ —Zn1—O1—C1	57.77 (12)
C7—C8—C9—C10	179.31 (18)	Cl1 ⁱ —Zn1—O1—C1	178.59 (12)
C8—C9—C10—O3	-11.8 (3)	Cl1—Zn1—O1—C1	-60.24 (14)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4B \cdots O2 ⁱⁱ	0.97 (4)	1.60 (4)	2.560 (2)	169 (3)

Symmetry codes: (ii) $x-1/2, -y+3/2, z-1/2$.

Fig. 1

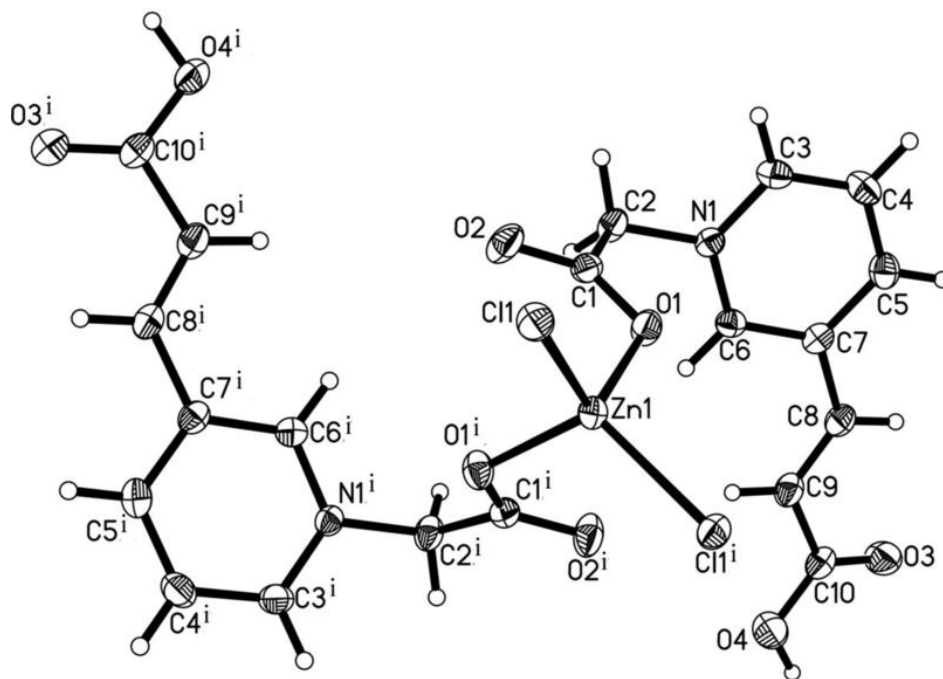


Fig. 2

