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## Dichlorobis(nicotinamide-*N*<sup>1</sup>-acetate-*O*)-zinc(II)

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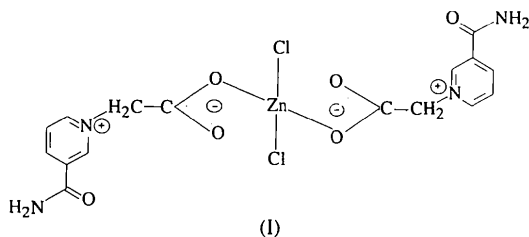
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### Abstract

The structure of [ZnCl<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>)<sub>2</sub>] containing the zwitterionic nicotinamide-*N*<sup>1</sup>-acetate ligand (3-carbamoylpyridinium-1-acetate) is described. The complex has slightly distorted tetrahedral geometry involving two Cl atoms [Zn—Cl 2.245 (1) Å] and two carboxy O atoms [Zn—O 2.014 (1) Å]. Molecules of the complex are connected by intermolecular hydrogen bonds of the type N—H...O, with N...O distances of 2.868 (3) and 3.030 (2) Å.

### Comment

In the course of our continuing investigation of zinc(II) formates and acetates containing additional organic ligands (Györyová, Balek & Zelenák, 1994; Györyová & Balek, 1993), with antifungal and antibacterial activity (Petrič, Györyová, Skoršepa & Melník, 1995), we isolated the compound dichlorobis(nicotinamide-*N*<sup>1</sup>-acetate)zinc(II), (I), containing the zwitterionic nicotinamide-*N*<sup>1</sup>-acetate ligand, as a product of the reaction of zinc(II) chloroacetate with nicotinamide.



The complex units of (I) have slightly distorted tetrahedral geometry, the coordination sphere consisting of two O atoms from zwitterionic nicotinamide-*N*<sup>1</sup>-acetate ligands and two chloro ligands, with the Zn centre lying on the crystallographic twofold rotation axis.

The distance from the carboxylate C atom to the O atom bonded to the metal [C—O1 1.268 (2) Å] is slightly longer than the distance to the unbonded carboxylate O atom [C—O2 1.224 (2) Å] owing to the

greater double-bond character in the latter case. The unbonded carboxylate O atom is involved in a weak Zn...O interaction [2.898 (2) Å]. This interaction may determine the orientation of the carboxy group. The pyridine ring is approximately orthogonal to the carboxy group [C1—C2—N1—C7 101.5 (2)°]. The N1—C2 bond is synperiplanar to the C1—O1 bond and antiperiplanar to the C1—O2 bond [N1—C2—C1—O1 and N1—C2—C1—O2 are 0.0 (3) and -178.0 (2)°, respectively].

The Zn—O bond lengths [2.014 (1) Å] are longer than those observed for the analogous complex [ZnBr<sub>2</sub>(CONH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>] [2.005 (2) Å; Zelenák, Györyová & Čisařová, 1995] or another complex with a zwitterionic carboxylate ligand, dichlorobis(pyridine betaine)zinc(II) [Zn—O 1.988 (3), 1.964 (2) Å; Chen & Mak, 1991].

Zn—Cl distances [2.245 (1) Å] are longer compared with those in dichlorobis(pyridine betaine)zinc(II) [2.238 (2), 2.262 (1) Å; Chen & Mak, 1991]. The Zn—X distance in the series of complexes of the type [ZnX<sub>2</sub>(CONH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>], where X = Cl, Br, increases with covalent radius of the coordinated halogen ligand.

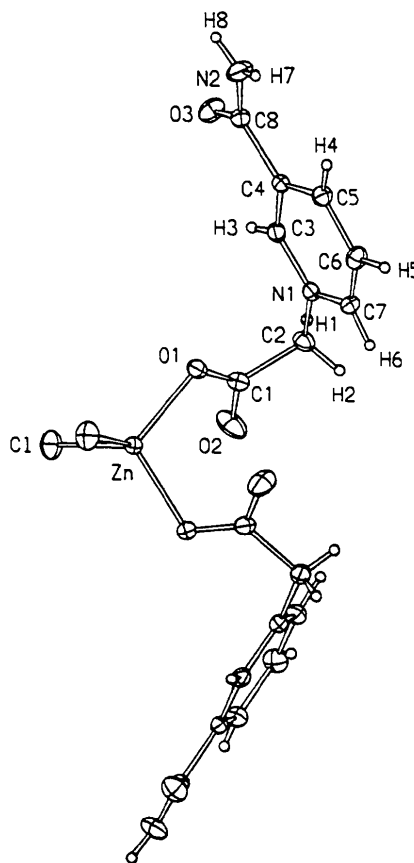


Fig. 1. View of [ZnCl<sub>2</sub>(CONH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>]. Displacement ellipsoids are plotted at the 50% probability level.

The molecules are stabilized by intermolecular hydrogen bonds between carboxylate and amino groups (Table 3).

## Experimental

Synthesis was carried out by reaction of zinc(II) chloroacetate and nicotinamide (molar ratio 1:2) in aqueous solution at 333 K. The reaction mixture was filtered then the solvent was allowed to evaporate slowly at room temperature. After several days colourless transparent crystals were isolated.

### Crystal data

[ZnCl<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 496.60  
 Monoclinic  
*C*2/*c*  
*a* = 13.7180 (10) Å  
*b* = 7.4307 (3) Å  
*c* = 18.4638 (9) Å  
 $\beta$  = 91.524 (5)°  
*V* = 1881.4 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.753 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 19.0–20.5°  
 $\mu$  = 1.634 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Hexagonal  
 0.43 × 0.43 × 0.32 mm  
 Colourless

### Data collection

CAD-4-MACHIII-PC diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 3539 measured reflections  
 1847 independent reflections  
 1689 observed reflections  
 [*I* > 3 $\sigma$ (*I*)]

*R*<sub>int</sub> = 0.0252  
 $\theta_{\max}$  = 25.97°  
*h* = -16 → 16  
*k* = -9 → 9  
*l* = 0 → 22  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 3.4%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0234  
*wR*(*F*<sup>2</sup>) = 0.0617  
*S* = 1.061  
 1847 reflections  
 165 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 2.3853P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001

$\Delta\rho_{\max} = 0.375 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.307 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.0176 (7)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Zn	0	0.28976 (4)	1/4	0.02388 (13)
Cl	0.09251 (4)	0.46841 (8)	0.18183 (3)	0.0413 (2)
O1	0.08051 (10)	0.1275 (2)	0.31528 (7)	0.0298 (3)
C1	0.11258 (13)	-0.0071 (3)	0.28108 (10)	0.0287 (4)
O2	0.11736 (13)	-0.0212 (2)	0.21520 (8)	0.0512 (5)
C3	0.20289 (13)	-0.0549 (2)	0.44047 (10)	0.0246 (4)

N1	0.13582 (11)	-0.1520 (2)	0.40322 (8)	0.0258 (3)
C4	0.19656 (12)	-0.0316 (2)	0.51406 (9)	0.0224 (4)
C7	0.06056 (14)	-0.2294 (3)	0.43696 (11)	0.0325 (4)
C8	0.27770 (13)	0.0764 (3)	0.54986 (10)	0.0269 (4)
C5	0.12015 (13)	-0.1120 (3)	0.54967 (10)	0.0283 (4)
C6	0.05212 (14)	-0.2117 (3)	0.51026 (12)	0.0344 (4)
C2	0.1457 (2)	-0.1714 (3)	0.32411 (10)	0.0337 (5)
O3	0.34648 (10)	0.1224 (2)	0.51331 (8)	0.0401 (4)
N2	0.2713 (2)	0.1124 (3)	0.61971 (10)	0.0400 (4)

Table 2. Selected geometric parameters (Å, °)

Zn—O1	2.014 (1)	N1—C2	1.478 (2)
Zn—Cl	2.245 (1)	C4—C5	1.387 (2)
O1—C1	1.268 (2)	C4—C8	1.510 (2)
C1—O2	1.224 (2)	C7—C6	1.368 (3)
C1—C2	1.519 (3)	C8—O3	1.223 (2)
C3—N1	1.344 (2)	C8—N2	1.322 (3)
C3—C4	1.375 (2)	C5—C6	1.383 (3)
N1—C7	1.349 (3)		
O1—Zn—O1 <sup>i</sup>	106.44 (8)	C7—N1—C2	120.4 (2)
O1—Zn—Cl	112.35 (4)	C3—C4—C5	118.9 (2)
O1—Zn—Cl <sup>i</sup>	109.12 (4)	C3—C4—C8	115.7 (2)
Cl—Zn—Cl <sup>i</sup>	107.52 (3)	C5—C4—C8	125.4 (2)
C1—O1—Zn	111.48 (11)	N1—C7—C6	120.1 (2)
O2—C1—O1	126.2 (2)	O3—C8—N2	123.6 (2)
O2—C1—C2	115.3 (2)	O3—C8—C4	118.5 (2)
O1—C1—C2	118.4 (2)	N2—C8—C4	117.8 (2)
N1—C3—C4	120.9 (2)	C6—C5—C4	119.3 (2)
C3—N1—C7	121.0 (2)	C7—C6—C5	119.9 (2)
C3—N1—C2	118.6 (2)	N1—C2—C1	113.9 (2)

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

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H7...O2 <sup>i</sup>	0.85 (3)	2.02 (3)	2.868 (3)	176 (3)
N2—H8...O1 <sup>ii</sup>	0.82 (3)	2.20 (3)	3.030 (2)	175 (3)

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

The Zn and Cl atoms were located from a Patterson synthesis and remaining non-H atoms from weighted Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference syntheses and allowed to refine freely with individual isotropic displacement parameters.

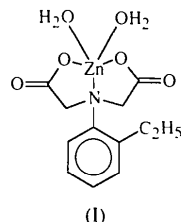
Data collection: CAD-4 diffractometer system. Cell refinement: CAD-4 diffractometer system. Data reduction: CAD-4 diffractometer system. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCR (Reference: NA1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Diaqua(2-ethylphenyliminodiacetato-*N,O,O'*)zinc(II)

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#### Abstract

The title complex, [Zn(C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>], has a coordination polyhedron around the Zn<sup>II</sup> atom that can be described as a square-based pyramid strongly distorted towards a trigonal bipyramid. The basal plane is defined by one N and two O atoms belonging to the tridentate ligand and one water O atom, while the axial position is occupied by another water O atom. The discrete molecules are grouped through hydrogen bonding into parallel double layers with the phenyl groups pointing outwards.

#### Comment

The crystal structure of the title zinc complex, (I), is made up of discrete neutral [Zn(L)(H<sub>2</sub>O)<sub>2</sub>] molecules, H<sub>2</sub>L being 2-ethylphenyliminodiacetic acid. These discrete molecules are assembled through hydrogen bonds into double chains along the *b* axis. The chains are then linked by means of further hydrogen bonds giving parallel double layers with phenyl groups pointing outwards. The layers, lying in *bc* planes, are stacked in an egg-carton fashion, by means of the phenyl groups, resulting in a close-packed arrangement.

In each molecule, the Zn atom constitutes the center of a five-coordinate ZnNO<sub>4</sub> polyhedron (Fig. 1). Two bonds are formed with the O atoms of two water molecules, while, as is usual in complexes formed by this type of ligand, there are three bonds to the doubly deprotonated L<sup>2-</sup> ligand involving atoms O(2), O(4) and N(1). This tridentate behaviour results in the formation of two five-membered rings having the Zn—N(1) bond in common. The dihedral angle between the least-squares planes of these rings is 166.9 (2)°.

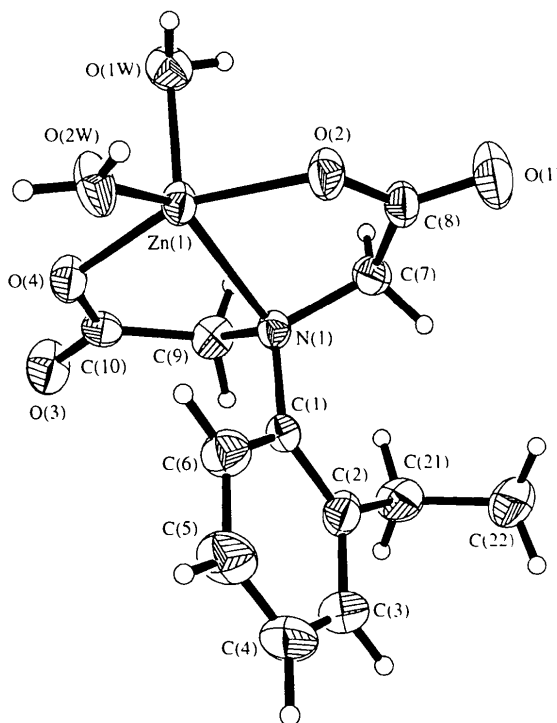


Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule. Ellipsoids are drawn at the 50% probability level.

The coordination environment around the Zn atom is, therefore, made up of four short bonds of around 2.0 Å involving the four O atoms and a longer bond of 2.258 (4) Å formed with the N atom of the ligand. This geometry may be described as an intermediate member of the continuous series between square-based pyramidal and trigonal-bipyramidal geometries. The dis-