

# Chloro(diethylamino)tris( $\mu$ -diethylcarbamato)dizinc(II): an example of the generality of the threefold paddlewheel structure in carbamatozinc chemistry

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## Key indicators

Single-crystal X-ray study  
T = 173 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
Disorder in main residue  
R factor = 0.023  
wR factor = 0.056  
Data-to-parameter ratio = 12.6

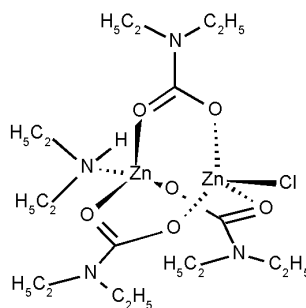
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex,  $[\text{Zn}_2(\text{C}_5\text{H}_{10}\text{NO}_2)_3\text{Cl}(\text{C}_4\text{H}_{11}\text{N})]$  or  $[\text{Zn}_2\{\text{O}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_3\text{Cl}\{\text{HN}(\text{C}_2\text{H}_5)_2\}]$ , consists of a dinuclear  $\text{Zn}_2(\text{O}_2\text{CNEt}_2)_3^+$  core bridged by three diethylcarbamate ligands in a  $\mu_{1,3}$  manner and capped by chloride and diethylamine ligands. This threefold paddlewheel structure is common in carbamatozinc coordination chemistry.

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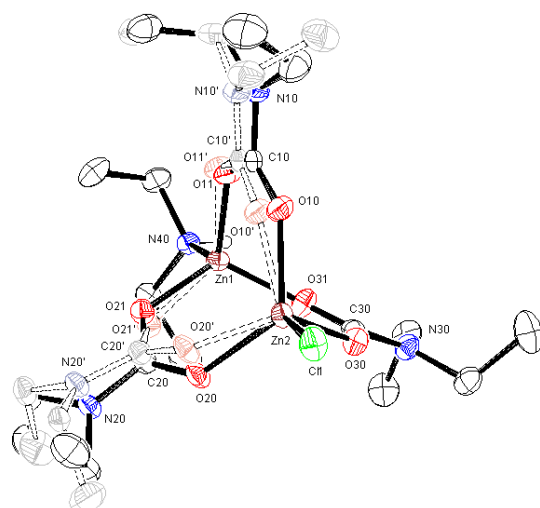
## Comment

The title compound, (I), was synthesized by direct reaction of zinc chloride, diethylamine, and carbon dioxide in tetrahydrofuran. It contains a dinuclear  $\text{Zn}_2\{\text{O}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_3^+$  core bridged by three diethylcarbamate ligands in a  $\mu_{1,3}$  mode (Fig. 1). The terminal coordination site on Zn1 is occupied by an unmodified diethylamine ligand. A chloride anion completes the pseudo-tetrahedral coordination shell on Zn2. The complex is best regarded as having a pseudo-threefold symmetric paddlewheel structure. In the crystal structure, the Zn1–N40 and Zn2–Cl1 bonds are not collinear. This forces the C30–O31–Zn1 angle to be almost  $12^\circ$  larger than the C30–O30–Zn2 angle and the Zn2 $\cdots$ O31 distance to be 0.24 Å shorter than the Zn1 $\cdots$ O30 distance, in a manner reminiscent of the carboxylate shift distortion in carboxylate-bridged complexes (Rardin *et al.*, 1991). The complex exhibits a solution NMR spectrum showing only a single type of carbamate ligand, indicative of average threefold symmetry.



(I)

The threefold paddlewheel motif has been previously observed in  $\text{Zn}_2\{\text{O}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_3(\text{NC}_6\text{H}_5)\text{CH}_3$  (Malik *et al.*, 1995) and in  $[\text{Zn}_2\{\text{O}_2\text{CN}(\text{CH}_3)_2\}_3][\text{Me}_2\text{NH}_2]$  (Klunker *et al.*, 1998). Anhydrous zinc benzoate (Guseinov *et al.*, 1984) and crotonate (Clegg *et al.*, 1986) have a similar  $\text{Zn}_2\text{L}_3^+$  core as the basic structural unit. The formation of the  $\text{Zn}_2\text{L}_3^+$  core with bifunctional  $\mu_{1,3}$  ligands is driven by the propensity for the  $d^{10}$   $\text{Zn}^{2+}$  ion to form a four-coordinate pseudo-tetrahedral coordination shell. This does not favor formation of the fourfold paddlewheel structure that is observed in carbamates



**Figure 1**  
ORTEP drawing of (I), with 35% probability displacement ellipsoids. H atoms have been omitted for clarity. Minor disorder components are indicated by dashed bonds.

of divalent chromium (Chisholm *et al.*, 1978) and copper (Agostinelli *et al.*, 1988). As a result, exposure of (I) to excess CO<sub>2</sub> does not result in conversion of the fourth diethylamine to diethyl carbamate, consistent with the structural stability of the Zn<sub>2</sub>{O<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>3</sub><sup>+</sup> core. Increasing the carbamate–metal ratio instead results in formation of mononuclear pseudo-octahedral complexes, such as [(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>Zn{O<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}] (Malik *et al.*, 1995), which is structurally related to the dihydrate of zinc acetate, [Zn(CH<sub>3</sub>OO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Ishioka *et al.*, 1997).

## Experimental

All manipulations were performed under an atmosphere of anhydrous N<sub>2</sub>. 14.7 mmol ZnCl<sub>2</sub> and 59.0 mmol NHET<sub>2</sub> were combined in tetrahydrofuran and stirred under 1 atm CO<sub>2</sub> for 22 h. A white solid consisting of the diethylammonium chloride salt was removed by filtration. The filtrate was reduced under vacuum to give 3.75 g crude (I) (86.6% yield). The powder was recrystallized by slow evaporation of a solution in tetrahydrofuran to give (I) as clear X-ray-quality crystals.

### Crystal data

[Zn <sub>2</sub> (C <sub>5</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>3</sub> Cl(C <sub>4</sub> H <sub>11</sub> N)]	Mo K $\alpha$ radiation
$M_r = 587.75$	Cell parameters from 5348 reflections
Orthorhombic, <i>Pbca</i>	
$a = 16.3204$ (12) Å	$\theta = 2.2$ – $24.9^\circ$
$b = 17.8489$ (13) Å	$\mu = 1.90$ mm <sup>-1</sup>
$c = 18.6636$ (14) Å	$T = 173$ (2) K
$V = 5436.7$ (7) Å <sup>3</sup>	Irregular block, colorless
$Z = 8$	$0.35 \times 0.35 \times 0.20$ mm
$D_x = 1.436$ Mg m <sup>-3</sup>	

### Data collection

Bruker SMART CCD area-detector diffractometer	4807 independent reflections
$\omega$ and $\varphi$ scans	3841 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{int} = 0.035$
$T_{min} = 0.539$ , $T_{max} = 0.681$	$\theta_{max} = 25.0^\circ$
27 209 measured reflections	$h = -19 \rightarrow 19$
	$k = -21 \rightarrow 14$
	$l = -20 \rightarrow 22$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.056$   
 $S = 1.02$   
 4807 reflections  
 381 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.4305P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.002$   
 $\Delta\rho_{max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.38$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Zn1–Zn2	3.2975 (4)	O11–C10	1.265 (4)
Zn1–O11	1.922 (8)	C10–N10	1.352 (3)
Zn1–O21	1.923 (6)	O10'–C10'	1.268 (7)
Zn1–O31	1.9265 (14)	O11'–C10'	1.270 (7)
Zn1–O21'	1.942 (16)	C10'–N10'	1.352 (7)
Zn1–O11'	1.98 (2)	O20–C20	1.273 (4)
Zn1–N40	2.0302 (16)	O21–C20	1.275 (5)
Zn2–O20'	1.881 (9)	C20–N20	1.349 (4)
Zn2–O10'	1.953 (14)	O20'–C20'	1.269 (6)
Zn2–O30	1.9527 (13)	O21'–C20'	1.272 (7)
Zn2–O10	1.955 (5)	C20'–N20'	1.347 (7)
Zn2–O20	1.988 (4)	O30–C30	1.275 (2)
Zn2–Cl1	2.2262 (6)	O31–C30	1.271 (2)
O10–C10	1.268 (3)	C30–N30	1.349 (2)
O11–Zn1–N40	108.7 (2)	O20–Zn2–Cl1	107.94 (13)
O21–Zn1–N40	103.48 (19)	O11–C10–O10	124.4 (4)
O31–Zn1–N40	102.42 (6)	O10'–C10'–O11'	124.6 (11)
O21'–Zn1–N40	102.4 (5)	O20–C20–O21	125.2 (4)
O11'–Zn1–N40	104.1 (6)	O20'–C20'–O21'	123.4 (10)
O20'–Zn2–Cl1	103.6 (3)	C30–O30–Zn2	127.14 (13)
O10'–Zn2–Cl1	108.0 (5)	C30–O31–Zn1	139.11 (13)
O30–Zn2–Cl1	112.89 (4)	O31–C30–O30	124.80 (18)
O10–Zn2–Cl1	104.83 (17)		

Two of the three bridging *N,N*-diethylcarbamate ligands are disordered. The first (O10 through C14) is disordered in a 0.727 (5):0.273 (5) ratio. The second (O20 through C24) is disordered in a 0.718 (5):0.282 (5) ratio. In both instances, one ethyl group is oriented on each side of the ligand plane, thus causing all atoms within each ligand to be disordered. For each pair of atoms within *ca* 0.5 Å, the anisotropic displacement parameters (ADP values) were constrained to be the same. Some atoms greater than 0.5 Å apart were restrained to have similar ADP values. Similarity restraints were applied to 1,2 (directly bonded) and 1,3 distances within each disordered ligand. No molecular plane restraints were imposed, since these were deemed unnecessary; 192 restraints were used in total. The *X*–H H atoms were positioned geometrically with respect to their environment, with *X*–H placement distances as follows: H–C(methyl) = 0.98 Å, H–C(methylene) = 0.99 Å and H–N = 0.93 Å.  $U_{iso}(H)$  values were allowed to ride on the  $U_{eq}$  values of their host atoms, 1.2 times for C(methylene) and 1.5 times for C(methyl).

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 1999); program(s) used to solve structure: SHELXTL (Sheldrick, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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