

Bis{ μ -N-[(1-methylimidazol-2-yl)methyl]- β -alanine}bis[dichlorozinc(II)] dihydrate

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.012$ Å

R factor = 0.083

wR factor = 0.233

Data-to-parameter ratio = 15.2

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

In the title complex, $[\text{Zn}_2\text{Cl}_4(\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, the Zn^{II} atoms have slightly distorted tetrahedral coordination geometry. The ligands bridge the two Zn^{II} atoms *via* an imidazole N atom and an O atom of the carboxylate group. The molecule is centrosymmetric.

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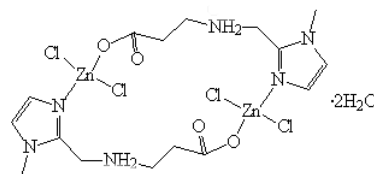
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Comment

Metal complexes of imidazole and its derivatives are of current interest in the investigation of model complexes relevant to metalloenzymes, since imidazole, a residue of histidine, is frequently found to ligate metal ions in the active centres of metalloenzymes (Wilcox, 1997; Strater *et al.*, 1995; Vanhooke *et al.*, 1996). Although some zinc(II) complexes containing imidazole have been reported (Abufarag & Vahrenkamp, 1995; Breslow *et al.*, 1983; Tang *et al.*, 1978), only a limited number of known zinc(II) complexes contain both imidazole and a carboxylate (Long *et al.*, 2000).

Recently, we have synthesized a series of imidazole-containing compounds, which are used as structural models of some metalloenzymes and in crystal engineering (Long *et al.*, 1999; Yang *et al.*, 2000, 2001). In the course of our systematic study of metal complexes of imidazole-like ligands, we have isolated the title compound, (I), and report here its preparation and crystal structure.



(I)

The crystal structure of (I) consists of discrete binuclear $[\text{Zn}_2\text{Cl}_4(\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4)_2]$ molecules and uncoordinated water molecules (Fig. 1). The dinuclear molecule is centrosymmetric. Each Zn atom in the complex is coordinated tetrahedrally by two Cl atoms, a carboxylate O atom and an N atom of the imidazole group in the ligand. The tetrahedron is slightly distorted, with angles ranging from $104.7(3)$ to $116.4(2)^\circ$ (Table 1). The Cl—Zn—Cl angle is $113.37(10)^\circ$, probably to minimize the Cl \cdots Cl interaction (Edixhoven *et al.*, 1973).

The bond lengths and angles in the imidazole rings are similar to those in related compounds, including the corresponding Cu^{II} , Fe^{II} and Mn^{II} complexes (Yang *et al.*, 1999, 2001). The bond lengths to Zn are comparable with those in other tetrahedrally coordinated Zn^{II} complexes (Yang *et al.*, 1999; Burth *et al.*, 1998; Long *et al.*, 2000; Randy & Michael,

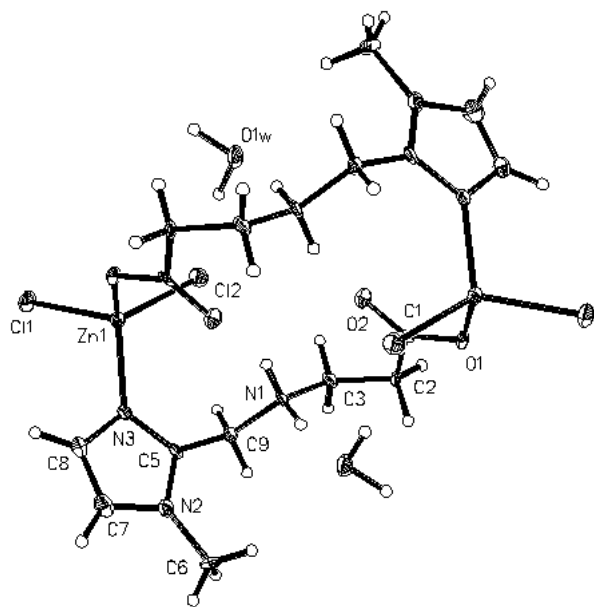


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

1981). The N1–C9 bond length is 1.524 (10) Å, indicative of N–C single-bond character, implying the successful reduction of the imine groups of the Schiff base intermediate compound.

In the title complex, two potentially tetradentate ligands (with imidazole N, secondary amino N and two carboxylate O atoms) are bidentate, bridging a pair of Zn^{II} atoms *via* an imidazole N atom and one carboxylate O atom. The N atom of the secondary amino group is not coordinated to Zn, but is protonated and forms hydrogen bonds with water molecules (Table 2), in contrast with Zn^{II} and Cu^{II} complexes with similar ligands (Long *et al.*, 1999, 2000).

The structure of (I) is consolidated by extensive inter- and intramolecular hydrogen bonds, which produce a three-dimensional network (Fig. 2).

Experimental

1-Methyl-imidazole-2-carbaldehyde (1.0 mmol, 0.11 g) in dry methanol (5.0 ml) was added to a solution of β-alanine (1.0 mmol, 0.089 g) in dry methanol (10 ml) containing NaOH (1.0 mmol, 0.040 g). The mixture was refluxed for 2 h, then the yellowish solution was cooled in an ice bath and reduced with an excess of NaBH₄ (2.0 mmol, 0.0740 g) in methanol. The colour slowly discharged, and after 3 h the solution was acidified with 3 M HCl. The resulting solid was filtered off, a solution of Zn(CH₃COO)₂·2H₂O (1.0 mmol, 0.218 g) and a solution of NaClO₄ (1.0 mmol, 1.20 g) in aqueous methanol (20 ml, 1:1 v/v) were added to the filtrate, and the pH was adjusted to about 5.5. After filtration, the solution was allowed to stand in air at room temperature for 10 d. Single crystals of (I) suitable for X-ray diffraction were collected.

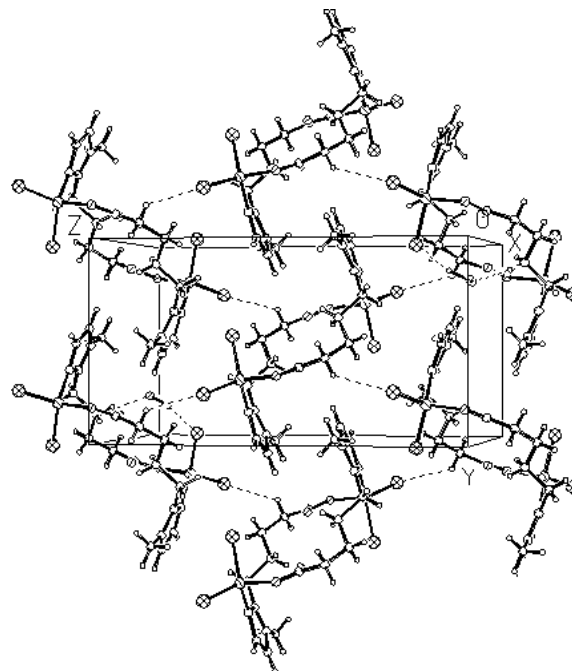


Figure 2
The molecular packing of (I), viewed approximately down the *a* axis, with the hydrogen bonding shown as dashed lines.

Crystal data

[Zn₂Cl₄(C₈H₁₃N₃O₄)₂]·2H₂O
M_r = 675.00
 Monoclinic, *P*2₁/*c*
a = 8.729 (1) Å
b = 9.267 (1) Å
c = 16.942 (1) Å
 β = 99.52 (2)°
V = 1351.6 (2) Å³
Z = 2

D_x = 1.659 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 25 reflections
 θ = 4.0–54.0°
 μ = 2.21 mm⁻¹
T = 293 (2) K
 Column, colourless
 0.30 × 0.15 × 0.10 mm

Data collection

Siemens R3m diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.679, *T_{max}* = 0.801
 2498 measured reflections
 2348 independent reflections
 1484 reflections with *I* > 2σ(*I*)

R_{int} = 0.091
 θ_{max} = 25.0°
h = 0 → 10
k = 0 → 11
l = -20 → 19
 2 standard reflections every 118 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.084
wR (*F*²) = 0.233
S = 1.03
 2348 reflections
 154 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.1143*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.003
 Δρ_{max} = 0.81 e Å⁻³
 Δρ_{min} = -1.18 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1–O1 ⁱ	1.960 (6)	Zn1–Cl1	2.225 (2)
Zn1–N3	1.995 (6)	Zn1–Cl2	2.256 (2)
O1 ⁱ –Zn1–N3	104.7 (3)	O1 ⁱ –Zn1–Cl2	105.82 (18)
O1 ⁱ –Zn1–Cl1	106.37 (17)	N3–Zn1–Cl2	116.4 (2)
N3–Zn1–Cl1	109.3 (2)	Cl1–Zn1–Cl2	113.37 (10)

Symmetry code: (i) 1 – *x*, –*y*, 2 – *z*.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1WA \cdots Cl2$	1.17	2.19	3.338 (6)	165
$O1W-H1WB \cdots O1^{ii}$	1.02	1.80	2.824 (8)	177
$N1-H1B \cdots O1W^d$	0.90	1.95	2.838 (9)	169
$N1-H1A \cdots O2^f$	0.90	2.23	3.036 (9)	149

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

The H atoms of the water molecule were found in a difference synthesis and refined as riding. Other H atoms were positioned geometrically, with $C-H = 0.96$ and $N-H = 0.90$ Å, and were refined as riding. For all H atoms, $U_{iso}(H) = 0.08$ Å². The highest peak and deepest hole in the difference Fourier map are located 1.56 and 1.18 Å, respectively, from atoms Cl2 and Zn1.

Data collection: *R3m Software* (Siemens, 1990); cell refinement: *R3m Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

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