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Ring contraction in a dinuclear zinc(II) complex of a Robson macrocycle

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.056
wR factor = 0.154
Data-to-parameter ratio = 19.6

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

The [2+2] cyclocondensation reaction between sodium 2,6-diformyl-4-chlorophenolate and benzyldiethylenetriamine, using the sodium template method, followed by transmetallation with $Zn(CH_3COO)_2 \cdot 2H_2O$, gave an unexpected 18-membered macrocyclic product in which ring contractions have occurred to produce two imidazolidine rings. In the macrocyclic complex, [μ-3,17-dibenzyl-13,27-dichloro-3,6,9,-17,20,23-hexaazapentacyclo[23.3.1.1^{11,15}.0^{2,6}.0^{16,20}]triaconta-1(29),9,11(30),12,14,23,25,27-octaene-29,30-diolato]bis[(acetato-κO)zinc(II)] ethanol 1.75-solvate 0.25-hydrate, [Zn_2-($C_{38}H_{38}Cl_2N_6O_2$)(CH_3COO)$_2$]·1.75C_2H_6O·0.25H_2O, each of the two Zn^{II} ions has a distorted trigonal bipyramidal environment.

Comment

Ring contractions have been reported to occur for Schiff base macrocycles as a consequence of nucleophilic addition of secondary amines across an adjacent imine bond (Drew *et al.*, 1981; Adams *et al.*, 1987; Menif *et al.*, 1990). The reaction between sodium 2,6-diformyl-4-chlorophenolate and benzyl-diethylenetriamine, followed by transmetallation with $Zn(CH_3COO)_2 \cdot 2H_2O$, was investigated with the aim of producing a corresponding 24-membered Schiff base macrocycle complex. However, we instead obtained an 18-membered macrocyclic product resulting from an unexpected ring-contraction reaction (Chantrapromma *et al.*, 2002). Herein we report the structure of the Zn^{II} complex, (I), of this 18-membered macrocyclic product.

·1.75(C_2H_5OH)·0.25(H_2O)

(I)
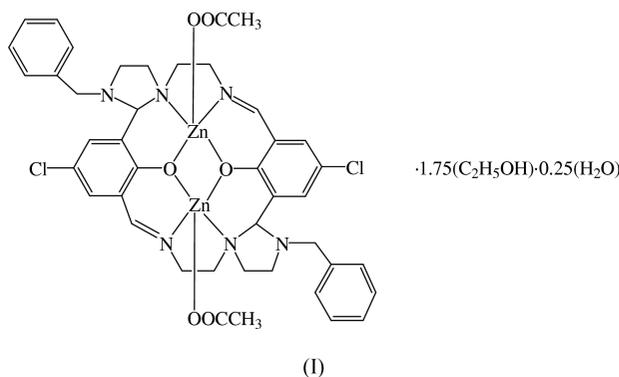
The asymmetric unit of (I) consists of a molecule of the Zn complex, one ethanol solvent molecule, a disordered ethanol molecule with an occupancy of 0.75 and a disordered water molecule with an occupancy of 0.25, *viz.* [Zn_2($C_{38}H_{38}$-$Cl_2N_6O_2$)(CH_3COO)$_2$]·1.75C_2H_6O·0.25H_2O. A displacement ellipsoid plot of (I) is shown in Fig. 1. The coordination geometry around each Zn^{II} is distorted trigonal bipyramidal, with the basal planes composed of atoms O1, O5, and N3 for
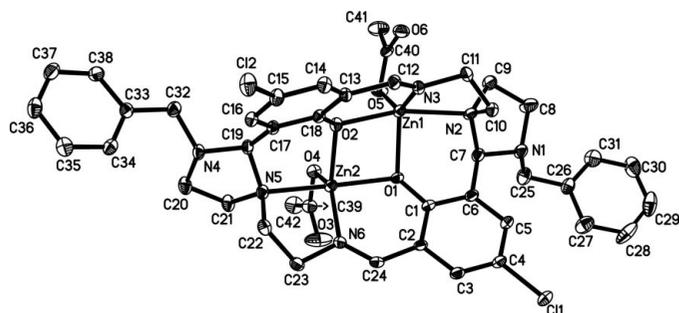
Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms, water and the ethanol solvate molecules have been omitted for clarity.

Zn1, and O2, O4, and N6 for Zn2. The bond lengths and angles are comparable to those reported for the dinuclear Zn^{II} complexes of Robson macrocycles (Adams *et al.*, 1995; Fang *et al.*, 2000; Huang *et al.*, 2001).

The conformation of the macrocycle is 'crown-like', with the carbon skeleton bent back so as to present the two O atoms to the Zn^{II} ions. This is evident from the dihedral angle of 76.8 (2)° between the two chlorophenyl rings. Of the two imidazolidine rings, one adopts an envelope conformation, whereas the other adopts a half-chair conformation. The N3—C12 [1.286 (4) Å] and N6—C24 [1.288 (4) Å] bond distances confirm the double-bond character of these bonds. The N atoms of the imidazolidine rings are involved in weak intramolecular interactions: H5···N1 = 2.52 Å, H16···N4 = 2.55 Å and H34···N4 = 2.49 Å. The crystal structure is stabilized by weak intermolecular C—H···O interactions and O—H···O hydrogen bonds (Table 2).

The formation of the 18-membered ring may be a result of further reaction of the initial 24-membered ring, by the nucleophilic additions of the two tertiary amine groups across the C7—N2 and C19—N5 bonds to form two imidazolidine rings, concomitant with the benzyl migration from N2 to N1 and also from N5 to N4.

Experimental

The title compound was derived from the [2+2] cyclocondensation between sodium 2,6-diformyl-4-chlorophenolate (1 mmol) and benzyldiethylenetriamine (1 mmol) in ethanol (30 ml), using a sodium template method (Gou & Fenton, 1994) and transmetallation with $Zn(CH_3COO)_2·2H_2O$ (1 mmol) in ethanol (25 ml). The solution was refluxed for 1 h under inert nitrogen. After the reaction was complete, the resulting hot clear solution was filtered and left to cool. After several days, yellow single crystals [m.p. (decomposition) 488–497 K] were deposited.

Crystal data

[Zn₂(C₃₈H₃₈Cl₂N₆O₂)(C₂H₃O₂)₂]·
1.75C₂H₆O·0.25H₂O
$M_r = 1015.60$
Monoclinic, $P2_1/c$
$a = 26.0725 (4)$ Å
$b = 9.5836 (1)$ Å
$c = 19.7483 (1)$ Å
$\beta = 103.658 (1)°$
$V = 4794.94 (9)$ Å³
$Z = 4$

$D_x = 1.407$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 8192
reflections
$\theta = 2.4–28.3°$
$\mu = 1.17$ mm⁻¹
$T = 293 (2)$ K
Slab, pale yellow
$0.54 \times 0.44 \times 0.26$ mm

Data collection

Siemens SMART CCD area-
detector diffractometer
ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
$T_{min} = 0.571$, $T_{max} = 0.751$
28105 measured reflections

11428 independent reflections
7553 reflections with $I > 2\sigma(I)$
$R_{int} = 0.093$
$\theta_{max} = 28.2°$
$h = -30 \rightarrow 34$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.154$
$S = 0.97$
11428 reflections
584 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å⁻³
$\Delta\rho_{min} = -1.04$ e Å⁻³
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0035 (4)

Table 1
Selected geometric parameters (Å, °).

Zn1—O5	1.979 (3)	Zn2—N6	2.034 (3)
Zn1—N3	2.032 (3)	Zn2—O1	2.070 (2)
Zn1—O1	2.071 (2)	Zn2—O2	2.083 (2)
Zn1—O2	2.123 (2)	Zn2—O4	1.979 (2)
Zn1—N2	2.219 (3)	Zn2—N5	2.226 (3)
O5—Zn1—N3	141.26 (11)	O1—Zn1—O2	79.43 (9)
O5—Zn1—O1	102.72 (10)	O5—Zn1—N2	101.75 (11)
N3—Zn1—O1	115.93 (10)	N3—Zn1—N2	82.36 (12)
O5—Zn1—O2	96.87 (10)	O1—Zn1—N2	88.87 (9)
N3—Zn1—O2	88.01 (10)	O2—Zn1—N2	159.82 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O4	0.82	2.07	2.835 (4)	158
C3—H3···O6ⁱ	0.93	2.49	3.332 (4)	151
C12—H12···O7ⁱⁱ	0.93	2.43	3.295 (5)	154
C14—H14···O7ⁱⁱ	0.93	2.51	3.338 (5)	149
C24—H24···O6ⁱ	0.93	2.43	3.285 (4)	154
C29—H29···O5ⁱⁱⁱ	0.93	2.43	3.226 (6)	143

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

All H atoms were fixed geometrically and allowed to ride on the atoms to which they were attached using *SHELXTL* (Sheldrick, 1997) defaults. The O atom of the water molecule was refined isotropically.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

metal-organic papers

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