

Bis[μ -2-[(1,5-diaza-1-cyclooctyl)-methyl]phenolato- $N,N',O:O$]bis-[chlorozinc(II)] diacetone solvate: design of a square-pyramidal ZnN_2O_2Cl complex

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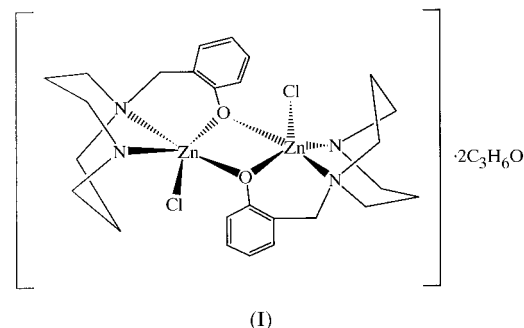
The title complex, $[Zn_2(C_{13}H_{19}N_2O)_2Cl_2] \cdot 2C_3H_6O$, resides on a crystallographic inversion center. The two Zn^{II} centers bridged by the phenoxo groups are in pentacoordinated distorted square-pyramidal coordination environments with an intramolecular $Zn \cdots Zn$ distance of 3.175 (3) Å. The mesocyclic ligand takes a boat–chair conformation and an H atom from the 1,5-diazacyclooctane ring effectively blocks the axial coordination site opposite the Cl ligand to form the ZnN_2O_2Cl geometry. The crystal structure is stabilized by a $N-H \cdots O$ hydrogen bond between the amino group and an acetone molecule.

Comment

Zinc, the second most abundant transition metal in biology, functions as the active site of hydrolytic enzymes such as carboxypeptidase and carbonic anhydrase, where it is in a hard-donor coordination environment of nitrogen and oxygen (Lipscomb & Strater, 1996). There are numerous structural studies on zinc-containing complexes in which the Zn atom is generally found to assume a tetrahedral geometry. Corresponding studies on the less common pentacoordinated zinc complexes are relatively rare (Yam *et al.*, 2000). Geometries other than four-coordinate are interesting in view of the possibility of the zinc adopting a penta-, tri- or perhaps even hexacoordinated structure in the functional states of the biological system (Brand *et al.*, 1996). As most of the zinc complexes with unusual coordination numbers were discovered more by accident than by design or with special ligand systems, the factors governing pentacoordination are still largely unknown (Zhang *et al.*, 1991).

1,5-Diazacyclooctane (DACO) is a typical example of a diazamesocycle, which usually shows an interesting 'boat–chair' conformation when binding to metal ions, and such a conformation blocks the sixth coordination from the apical

site resulting in a pentacoordinate complex (Musker, 1992; Grapperhaus & Darensbourg, 1998). In our ongoing studies of 1,5-diazacyclooctane ligands, we have obtained a series of pentacoordinate complexes with a variety of metals: Cu^{II} (Bu *et al.*, 2000), Co^{II} (Du, Shang *et al.*, 2000), Ni^{II} (Bu *et al.*, 2001) and Cd^{II} (Du, Weng *et al.*, 2000). However, the crystal structures of zinc(II) complexes of DACO ligands have not yet been reported. In this paper, we report the crystal structure of a novel phenoxo-bridged binuclear zinc(II) complex, (I), with a distorted square-pyramidal ZnN_2O_2Cl geometry of 1-(2-hydroxybenzyl)-1,5-diazacyclooctane.



The structure of (I) comprises a neutral binuclear entity and an uncoordinated acetone molecule (Fig. 1). Each molecule results from the pairing of two mononuclear units related by a crystallographic center of symmetry. Each Zn^{II} center in this complex is bound by five donor atoms occupying the vertices of a distorted square-pyramidal coordination environment, with $\tau = 0.27$ (Addison *et al.*, 1984), which is used to describe the degree of distortion for pentacoordinated complexes ($\tau = 0$ for an ideal square pyramid and $\tau = 1$ for an ideal trigonal bipyramid). Two bridging O atoms of the deprotonated pendant phenol groups and two nitrogen donors of the DACO

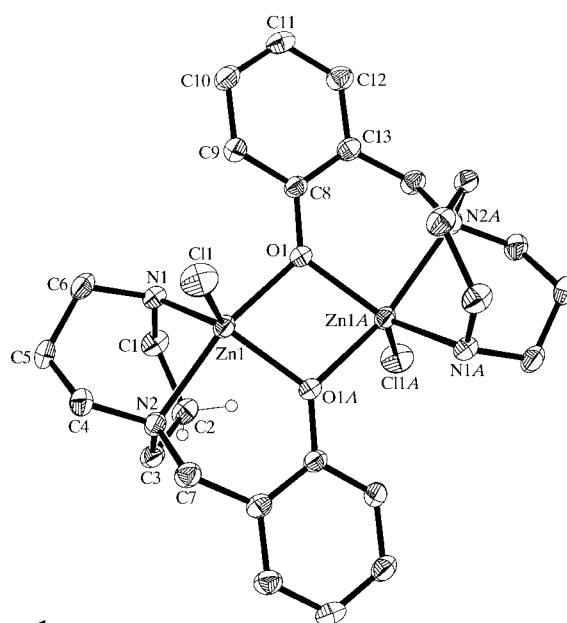


Figure 1

An ORTEP (Johnson, 1976) view of the title complex with 30% probability ellipsoids. The acetone molecules and H atoms have been omitted for clarity.

ring of the ligand comprise the basal plane, and each axial coordination site is occupied by a chloride anion. The Zn^{II} ion deviates from the basal mean equatorial plane of the square pyramid towards the apical Cl1 atom by *ca* 0.61 Å.

The two Zn^{II} centers are equivalently bridged by two phenoxo oxygen anions of the parallel phenol rings, which are bound asymmetrically to Zn^{II} at slightly different distances of 2.0056 (15) *versus* 2.1109 (16) Å (Table 1). The Zn–O–Zn bridging angle is 100.92 (7)° and the two Zn^{II} centers are separated by 3.175 (3) Å.

The ligand adopts a 'boat-chair' conformation and gives rise with each Zn^{II} center to two five-membered chelate rings, which enhance the coordination ability to Zn^{II}. The central methylene C–H group of the boat form in DACO shields the Zn^{II} center [H2B–Zn1 distance of 2.749 (3) Å], which effectively blocks the sixth coordination position to give this novel pentacoordinated Zn^{II} complex.

In this structure, each amino group of the ligand forms an N–H···O hydrogen bond with an acetone molecule. The N···O separation is 3.038 (3) Å, the H···O separation 2.278 Å and the bond angle 141°, which are within the normal range for weak interactions (Sasada, 1984).

Experimental

The title complex was synthesized by mixing ZnCl₂ (27 mg, 0.2 mmol) and 1-(2-hydroxybenzyl)-1,5-diazacyclooctane (44 mg, 0.2 mmol) in acetone–water. The reaction mixture was filtered and colorless single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent [yield 49 mg (65%)]. FT-IR data (KBr pellet, cm⁻¹): 3439 (*b*), 3290 (*m*), 2923 (*w*), 2843 (*w*), 1705 (*s*), 1593 (*s*), 1568 (*m*), 1484 (*vs*), 1453 (*s*), 1280 (*vs*), 1271 (*vs*), 1127 (*m*), 1016 (*s*), 881 (*s*), 755 (*s*). Analysis calculated for the title complex: C 50.81, H 6.66, N 7.41%; found: C 50.68, H 6.81, N 7.22%.

Crystal data

[Zn ₂ (C ₁₃ H ₁₉ N ₂ O) ₂ Cl ₂] ₂ ·2C ₃ H ₆ O	Z = 1
<i>M_r</i> = 756.40	<i>D_x</i> = 1.414 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
<i>a</i> = 8.8173 (14) Å	Cell parameters from 3683 reflections
<i>b</i> = 10.8916 (17) Å	θ = 2.1–25.0°
<i>c</i> = 11.2986 (17) Å	μ = 1.54 mm ⁻¹
α = 115.254 (3)°	<i>T</i> = 293 (2) K
β = 99.964 (3)°	Prism, colorless
γ = 106.135 (3)°	0.30 × 0.15 × 0.10 mm
<i>V</i> = 888.0 (2) Å ³	

Data collection

Bruker SMART 1000 diffractometer	3129 independent reflections
ω scans	2718 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan [SAINT (Bruker, 1998) and SADABS (Sheldrick, 1996)]	<i>R</i> _{int} = 0.017
<i>T</i> _{min} = 0.655, <i>T</i> _{max} = 0.861	θ _{max} = 25.0°
3735 measured reflections	<i>h</i> = -10 → 10
	<i>k</i> = -12 → 12
	<i>l</i> = -11 → 13

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.0111P]$
<i>R</i> (<i>F</i>) = 0.030	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> (<i>F</i> ²) = 0.075	(Δ / σ) _{max} = 0.005
<i>S</i> = 1.02	$\Delta\rho$ _{max} = 0.27 e Å ⁻³
3129 reflections	$\Delta\rho$ _{min} = -0.29 e Å ⁻³
199 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Zn1–O1 ⁱ	2.0056 (15)	Zn1–N2	2.2298 (19)
Zn1–N1	2.0998 (19)	Zn1–Cl1	2.2781 (7)
Zn1–O1	2.1109 (16)		
O1 ⁱ –Zn1–N1	133.30 (7)	O1 ⁱ –Zn1–Cl1	111.63 (5)
O1 ⁱ –Zn1–O1	79.08 (7)	N1–Zn1–Cl1	115.04 (6)
N1–Zn1–O1	92.62 (7)	O1–Zn1–Cl1	102.18 (5)
O1 ⁱ –Zn1–N2	89.13 (7)	N2–Zn1–Cl1	99.84 (5)
N1–Zn1–N2	81.63 (7)	Zn1 ⁱ –O1–Zn1	100.92 (7)
O1–Zn1–N2	157.62 (7)		

Symmetry code: (i) $-x, 1 - y, -z$.

Table 2

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>
N1–H1C···O2 ⁱ	0.91	2.28	3.038 (3)	141

Symmetry code: (i) $x, 1 + y, z$.

H atoms were placed in idealized positions and were allowed to ride on their parent atom (C–H = 0.93–0.97 Å). The *U*_{iso} values for the H atoms were set to be 1.2*U*_{eq} of the parent atom values.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1029). Services for accessing these data are described at the back of the journal.

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