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Dichloro{2-[*N*-(2-hydroxyethylammonio-ethyl)iminomethyl]phenolate}zinc(II)

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Key indicators

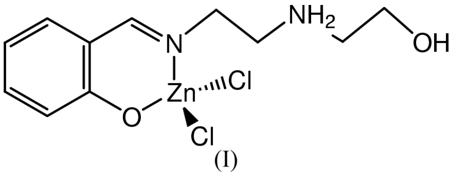
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.022
wR factor = 0.058
Data-to-parameter ratio = 16.7

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

In the title compound, [$ZnCl_2(C_{11}H_{16}N_2O_2)$], the Zn atom is four-coordinated by one N atom and one O atom from the bidentate 2-[*N*-(2-hydroxyethylammonioethyl)iminomethyl]-phenolate ligand and two Cl atoms in a distorted tetrahedral geometry. In the crystal, the molecules are stabilized by two N—H···O hydrogen bonds, to form columns along the *a* direction, which are further interconnected by O—H···Cl interactions into a three-dimensional network.

Comment

Carbonic anhydrase is a ubiquitous zinc enzyme which catalyses the reversible hydration of CO_2 with rates up to 10^7 times greater than that in the uncatalysed case (Silverman & Lindskog, 1988; Liang & Lipscomb, 1988; Christianson, 1991). In the active site, there is a zinc cation in a tetrahedral coordination geometry, surrounded by three imidazole ligands (His95, His96 and His119) and a water molecule (Eriksson *et al.*, 1988; Håkansson *et al.*, 1992). An important contribution to the detailed understanding of the catalytic acidity of the enzyme can be made *via* experimental investigations on suitable model systems. A vast number of various kinds of model complexes with a structural resemblance to the native enzyme have been synthesized and characterized with regard to their acidity toward carbonic anhydrase. Today, more and more model complexes of carbonic anhydrase appear in the literature (Makowska-Grzyska *et al.*, 2002; Bergquist *et al.*, 2002; Berreau *et al.*, 2001; Bräuer *et al.*, 2002; Chang *et al.*, 2002; Oste *et al.*, 2002; Sénèque *et al.*, 2001; Topol *et al.*, 2001; Xia *et al.*, 2001). In the title structure, (I), the Cl atoms, which are bonded to the tetrahedral Zn centre, can easily be detached, resulting in a model of carbonic anhydrase.



(I)

In the title compound, (I), the Zn^{II} atom is four-coordinated by two Cl atoms, and by one N atom and one O atom from the bidentate 2-[*N*-(2-hydroxyethylammonioethyl)iminomethyl]-phenolate ligand. This $ZnONCl_2$ coordination forms a distorted tetrahedral geometry, as usually observed in the structures of zinc complexes (McCleverty *et al.*, 1980), with angles subtended at the Zn atom of 96.1 (1)–113.5 (1)°.

The bond lengths in (I) (Table 1) are within normal ranges (Allen *et al.*, 1987). The ligand is a zwitterion with the negative and positive charges located at atoms O1 and N2, respectively. This is supported by the geometry of the ligand and unam-

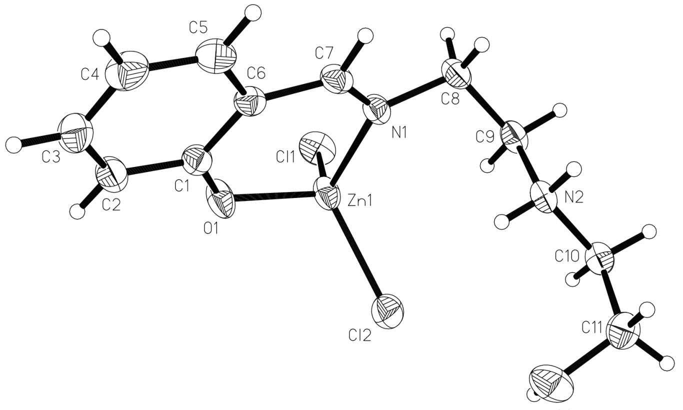


Figure 1
The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

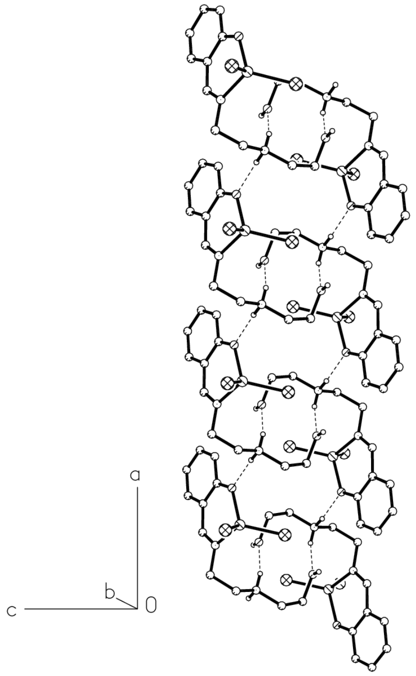


Figure 2
The packing of the title compound, viewed down the *b* axis, showing the molecular columns running along the *a* direction. H atoms attached to C atoms have been omitted for clarity. The dashed lines denote intermolecular N—H···O hydrogen bonds.

biguous location of the H atoms attached to atom N2. Atoms Zn1/O1/C1/C6/C7/N1 form a six-membered planar ring, with a maximum deviation of 0.047 (1) Å at atom O1. This plane is coplanar with the benzene ring, with a dihedral angle of 2.0 (1)°. Atoms C8, C9, C10, C11 and N2 of the 2-hydroxydiethylammonio substituent are coplanar and nearly orthogonal to the Zn1/O1/C1/C6/C7/N1 plane; the dihedral angle between these two planes is 87.9 (1)°.

In the crystal, the amino group acts as a donor to form N2—H1N2···O2^{ii} and N2—H2N2···O1^{iii} hydrogen bonds (Table 2). These hydrogen bonds interconnect the molecules into columns along the *a* direction (Fig. 2). The molecular columns are further interconnected into a three-dimensional network by O2—H2O···Cl1^{i} interactions (Table 2).

Experimental

Equimolar salicyldehyde (1 mmol, 122 mg) and 2-hydroxyaminoethylamine (1 mmol, 104 mg) were dissolved in anhydrous ethanol solution (5 ml) with stirring. To this solution, 244 mg (1 mmol) of $ZnCl_2·6H_2O$ in anhydrous ethanol solution (5 ml) was added. The resulting solution was allowed to evaporate slowly in air. After about half of the solvent had evaporated, colorless crystals of the title compound were deposited and were collected by filtration (yield 45%). Analysis calculated for $C_{11}H_{16}Cl_2N_2O_2Zn$: C 38.35, H 4.68, N 8.13, Cl 20.58%; found: C 38.50, H 4.72, N 8.03, Cl 20.89%.

Crystal data

$[ZnCl_2(C_{11}H_{16}N_2O_2)]$
$M_r = 344.53$
Triclinic, $P\overline{1}$
$a = 7.3217 (4)$ Å
$b = 8.6557 (4)$ Å
$c = 11.4876 (6)$ Å
$\alpha = 91.129 (1)°$
$\beta = 95.179 (1)°$
$\gamma = 108.674 (1)°$
$V = 685.97 (6)$ Å^3

$Z = 2$
$D_x = 1.668$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3563 reflections
$\theta = 2.5$–28.3°
$\mu = 2.17$ mm^{-1}
$T = 293 (2)$ K
Slab, pale yellow
0.50 × 0.34 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.410$, $T_{max} = 0.670$
3955 measured reflections

2865 independent reflections
2686 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.0°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -9 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.058$
$S = 1.06$
2865 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 0.2516P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.9488 (12)	O1—C1	1.319 (2)
Zn1—N1	2.0166 (13)	N1—C7	1.279 (2)
Zn1—Cl1	2.2313 (5)	N1—C8	1.466 (2)
Zn1—Cl2	2.2421 (5)		
O1—Zn1—N1	96.12 (5)	O1—Zn1—Cl2	110.77 (5)
O1—Zn1—Cl1	111.64 (4)	N1—Zn1—Cl2	113.54 (4)
N1—Zn1—Cl1	111.43 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···Cl1^{i}	0.90	2.77	3.469 (2)	135
N2—H1N2···O2^{ii}	0.85 (2)	2.26 (2)	2.987 (2)	143 (2)
N2—H2N2···O1^{iii}	0.89 (2)	1.90 (2)	2.747 (2)	160 (2)

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

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The H atoms attached to C and O atoms were fixed geometrically (C—H = 0.93–0.97 Å and O—H = 0.90 Å) and were treated as riding atoms, whereas the H atoms attached to N2 were located from a difference map and were refined isotropically. Owing to a large fraction of weak data at higher angles, the 2θ maximum was limited to 54°.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Bergquist, C., Koutcher, L., Vaught, A. L. & Parkin, G. (2002). *Inorg. Chem.* **41**, 625–627.

Berreau, L. M., Makowska-Grzyska, M. M. & Arif, A. M. (2001). *Inorg. Chem.* **40**, 2212–2213.

Bräuer, M., Pérez-Lustres, J. L., Weston, J. & Anders, E. (2002). *Inorg. Chem.* **41**, 1454–1463.

Chang, S., Karambelkar, V. V., Sommer, R. D., Rheingold, A. L. & Goldberg, D. P. (2002). *Inorg. Chem.* **41**, 239–248.

Christianson, D. W. (1991). *Adv. Protein Chem.* **42**, 281–355.

Eriksson, A. E., Jones, T. A. & Liljas, A. (1988). *Proteins*, **4**, 274–282.

Håkansson, M., Carlsson, L., Svensson, A. & Liljas, A. (1992). *J. Mol. Biol.* **227**, 1192–1204.

Liang, J. Y. & Lipscomb, W. N. (1988). *Biochemistry*, **27**, 8676–8682.

Makowska-Grzyska, M. M., Jeppson, P. C., Allred, R. A., Arif, A. M. & Berreau, L. M. (2002). *Inorg. Chem.* **41**, 4872–4887.

McCleverty, J. A., Morrison, N. J., Spencer, N., Ashworth. C. C., Bailey, N. A., Johnson, M. R., Smith, J. M. A., Tabbiner, B. A. & Taylor, C. R. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1945–1957.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Oste, L. A., Temminghoff, E. J. M., Lexmond, T. M. & van Riemsdijk, W. H. (2002). *Anal. Chem.* **74**, 856–862.

Sénèque, O., Rager, M.-N., Giorgi, M. & Reinaud, O. (2001). *J. Am. Chem. Soc.* **123**, 8442–8443.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Silverman, D. N. & Lindskog, S. (1988). *Acc. Chem. Res.* **21**, 30–36.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Topol, I. A., Nemukhin, A. V., Dobrogorskaya, Y. I. & Burt, S. K. (2001). *J. Phys. Chem. B*, **105**, 11341–11350.

Xia, J., Xu, Y., Li, S.-A., Sun, W.-Y., Yu, K.-B. & Tang, W.-X. (2001). *Inorg. Chem.* **40**, 2394–2401.

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