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Redetermination of chloro(triethanolaminato)zinc(II) at 150 K

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Key indicators

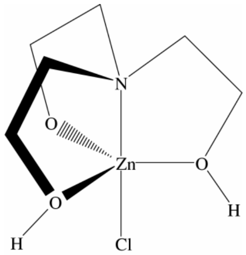
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.021
wR factor = 0.053
Data-to-parameter ratio = 17.8

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

The X-ray crystal structure of the title compound, $[ZnCl(C_6H_{14}NO_3)]$, was redetermined with a CCD area detector at 150 (2) K. The crystal appeared to be non-merohedrally twinned. Appropriate handling of the twinning, together with the low measurement temperature, allowed the localization and refinement of the H atoms, which was not possible with the film data from the literature [Follner (1972), *Acta Cryst.* B**28**, 157–160]. The precision of the other geometrical data has also significantly improved.

Comment

Triethanolamine is mostly encountered as a four-coordinating ligand with a few exceptions, in which the ligand is found to be three- (Topcu *et al.*, 2001) or even two-coordinating (Kapteijn *et al.*, 1997).



(I)

The crystal structure of the title compound, (I), was first described by Follner (1972), based on Weissenberg data. The author mentions a needle-shaped crystal form and a pseudo-monoclinic symmetry of the triclinic unit cell, but does not find any indication of twinning.

Compound (I) has a very low solubility in most solvents. We therefore prepared the crystals by gel crystallization from a tetramethoxysilane gel (Arend & Connelly, 1982). The crystals are needle-shaped and elongated along the *b* axis. All crystals appeared to be non-merohedrally twinned, with a twofold rotation around [010] as twin operation. A crystal with a small contribution of the second twin domain was chosen for the diffraction experiment. The refinement was performed with the HKLF 5 option of the *SHELXL*97 program (Herbst-Irmer & Sheldrick, 1998). The proper handling of the twinned data led to a significant decrease in the discrepancy factors; major peaks of residual electron density disappeared.

A molecular plot of (I) is depicted in Fig. 1. The Zn atom is five-coordinated by the three O atoms and the N atom of the triethanolamine ligand and by the Cl atom, and is situated 0.309 (1) Å below the O_3 plane of the triethanolamine ligand. The coordination geometry is intermediate between a trigonal

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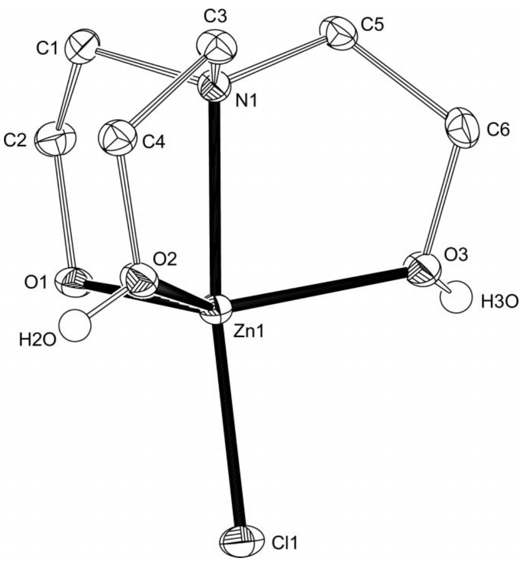

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. H atoms attached to C atoms have been omitted for clarity.

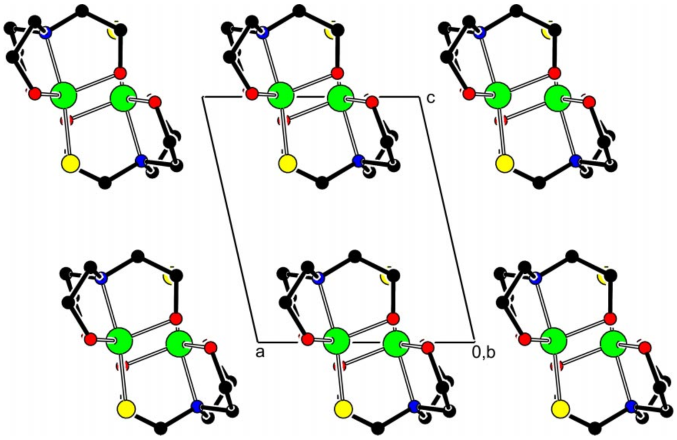

Figure 2
The packing of compound (I) in the crystal, viewed along the crystallographic *b* axis. The hydrogen-bonded chains run parallel to this direction. A twofold rotation around this direction is the twin operation.

bipyramid and a square pyramid. The τ descriptor (Addison *et al.*, 1984) has a value of 0.77, which is closer to a trigonal bipyramid ($\tau = 1$) than to a square pyramid ($\tau = 0$). This is consistent with the pseudorotation (Holmes, 1984), which is 0.23 on the pathway from trigonal bipyramid to square pyramid. It should be noted, that in the case of five-coordinated zinc compounds, a basal angle of 158° has to be used in the calculation of the pseudorotation (Vahrenkamp, 1999).

One of the three hydroxyl groups of the triethanolamine ligand is deprotonated, resulting in a short O1—Zn1 distance of 2.0014 (12) Å due to the negative charge on atom O1 (Table 1). The O2—Zn1 and O3—Zn1 distances of the neutral hydroxyl groups are correspondingly longer, with values of 2.1056 (13) and 2.0935 (13) Å, respectively. The hydroxyl H atoms point in opposite directions, thus increasing the O2—Zn1—O3 angle to 123.54 (5)°, while the other two O—Zn—O angles are significantly smaller than 120°. This distortion is also reflected in a tilt of Cl1 in the direction of O2 and O3, resulting in a Cl1—Zn1—N1 angle of 169.79 (4)°.

The deviation from perfect threefold symmetry can also be seen in the ring conformations. A ring-puckering analysis (Evans & Boeyens, 1989) of the three five-membered chelate rings results in coefficients of 86 and 84% for the envelope conformations of rings Zn1—O1—C2—C1—N1 and Zn1—O2—C4—C3—N1, respectively. Ring Zn1—O3—C6—C5—N1, however, has a coefficient of 64% for the twist conformation.

The compound forms two intermolecular hydrogen bonds, in which the deprotonated atom O1 is the acceptor and the neutral hydroxyl groups at atoms O2 and O3 are the donors (Table 2). This hydrogen bonding is the main reason for the arrangement of the hydroxyl H atoms in opposite directions and the resulting distortions of the coordination polyhedron. The hydrogen bonds lead to the formation of one-dimensional chains running parallel to the crystallographic *b* axis. A misarrangement of the chains is the most probable reason for the non-merohedral twinning, with a twofold rotation around the *b* axis as twin operation (Fig. 2).

Experimental

Crystals of (I) were obtained by gel crystallization (Arend & Connelly, 1982). 4.5 ml of an aqueous $ZnCl_2$ solution (1 molar) was stirred with 0.5 ml tetramethoxysilane until a clear solution was obtained. This solution was poured into test tubes and allowed to solidify for 12 h. Then an aqueous solution of triethanolamine (1 molar) was carefully put on top of the gel. After 24 h, crystals of suitable size were obtained.

Crystal data

$[ZnCl(C_6H_{14}NO_3)]$
$M_r = 249.00$
Triclinic, $P\overline{1}$
$a = 7.4014$ (9) Å
$b = 8.0163$ (6) Å
$c = 8.2906$ (12) Å
$\alpha = 89.413$ (9)°
$\beta = 77.541$ (9)°
$\gamma = 74.655$ (8)°
$V = 462.62$ (10) Å^3
$Z = 2$
$D_x = 1.788$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 3.4$–19.5°
$\mu = 2.91$ mm^{-1}
$T = 150$ (2) K
Needle, colourless
0.54 × 0.12 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: analytical (*PLATON*; Spek, 2002)
$T_{min} = 0.41$, $T_{max} = 0.85$
10000 measured reflections
2106 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 27.6°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.053$
$S = 1.08$
2106 reflections
118 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2 + 0.291P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.0014 (12)	Zn1—N1	2.1489 (14)
Zn1—O2	2.1056 (13)	Zn1—Cl1	2.2557 (6)
Zn1—O3	2.0935 (13)		
O1—Zn1—O3	115.10 (5)	O2—Zn1—N1	79.34 (5)
O1—Zn1—O2	114.74 (5)	O1—Zn1—Cl1	105.60 (4)
O3—Zn1—O2	123.54 (5)	O3—Zn1—Cl1	95.70 (4)
O1—Zn1—N1	84.55 (5)	O2—Zn1—Cl1	95.04 (4)
O3—Zn1—N1	80.63 (5)	N1—Zn1—Cl1	169.79 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O1^{i}	0.78 (3)	1.83 (3)	2.6156 (18)	174 (3)
O3—H3O···O1^{ii}	0.79 (3)	1.78 (3)	2.5678 (17)	175 (3)

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

X-ray intensities were obtained using two different orientation matrices. The HKLF 5 reflection file contains the non-overlapping reflections of the first twin domain and the overlapping reflections. The non-overlapping reflections of the second twin domain were disregarded. The twin fraction of the second domain refined to 0.0878 (19).

The direction cosines of all reflections were calculated with respect to the orientation matrix of the first twin domain. An analytical absorption correction was performed using the *ABST* routine of the program *PLATON* (Spek, 2002). Afterwards, equivalent reflections were merged using a locally written program.

Hydroxyl H atoms were refined freely with isotropic displacement parameters. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.99–1.00 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVAL*14 (Duisenberg, 1998); for structure solution: coordinates taken from the literature (Follner, 1972); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: manual editing of *SHELXL*97 CIF output.

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References

Addison, A. W., Nageswara Rao, T., Reedijk, J., van Rijn, J., Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Arend, H. & Connelly, J. J. (1982). *J. Cryst. Growth*, **56**, 642–644.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–95.
Duisenberg, A. J. M. (1998). PhD thesis, Utrecht University, The Netherlands.
Evans, D. G. & Boeyens, J. C. A. (1989). *Acta Cryst.* B**45**, 581–590.
Follner, H. (1972). *Acta Cryst.* B**28**, 157–160.
Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* B**54**, 443–449.
Holmes, R. R. (1984). *Prog. Inorg. Chem.* **32**, 119–235.
Kapteijn, G. M., Baesjou, P. J., Alsters, P. L., Grove, D. M., Smeets, W. J. J., Kooijman, H., Spek, A. L., van Koten, G. (1997). *Chem. Ber.* **130**, 35–44.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Utrecht University, The Netherlands.
Topcu, Y., Yilmaz, V. T. & Thöne, C. (2001). *Acta Cryst.* E**57**, m600–m602.
Vahrenkamp, H. (1999). *Acc. Chem. Res.* **32**, 589–596.