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Diaquachlorozinc(II)–18-crown-6–water (1/1/1)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.065
Data-to-parameter ratio = 14.9

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

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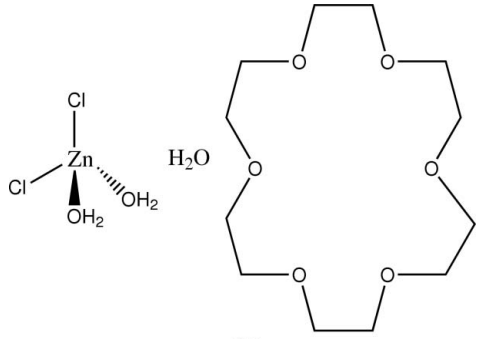
The structure of the title compound, $[ZnCl_2(H_2O)_2]\cdot C_{12}H_{24}O_6\cdot H_2O$, contains the Zn atom with tetrahedral geometry and two coordinated water molecules linked to two 18-crown-6 macrocycles (residing on inversion centres) by O—H···O interactions. A water molecule of crystallization further links the metal salt and one of the crown ether macrocycles.

Comment

In this paper, we report the synthesis and crystal structure of an intermediate in the 18-crown-6 ether-mediated solubilization of zinc chloride salts, namely $[ZnCl_2(H_2O)_2]\cdot$(18-crown-6)$\cdot H_2O$, (I).



(I)

Doxsee and co-workers have reported the preparation and single-crystal structures of several zinc complexes of crown ethers (Bel'sky *et al.*, 1989; Doxsee *et al.*, 1994; Junk *et al.*, 1998). Most of these structures exhibit varying degrees of encapsulation of the Zn ion by the crown ether with direct $Zn—O_{ether}$ coordination, while few represent supramolecular interactions between the Zn species and the crown ether. The title compound, (I), comprises three components: the $ZnCl_2(H_2O)_2$, crown ether and water solvent molecules, held together by O—H···O hydrogen bonds.

Compound (I) contains the $ZnCl_2(H_2O)_2$ complex, two unique half-molecules of 18-crown-6 ether (residing on inversion centres with different conformations) and one water molecule in the crystallographic asymmetric unit. The Zn atom has tetrahedral coordination and is bonded to two Cl and two H_2O molecules. The mean Zn—Cl and Zn—O bond lengths are 2.211 (1) and 1.999 (2) Å, respectively, and are similar to literature values, (Dejehet *et al.*, 1986; Richardson *et al.*, 2002). Both crown ether molecules (crown *A* containing O1, O2 and O3; crown *B* containing O4, O5 and O6) have approximate D_{3d} symmetry. All O atoms in crown *A* form O—

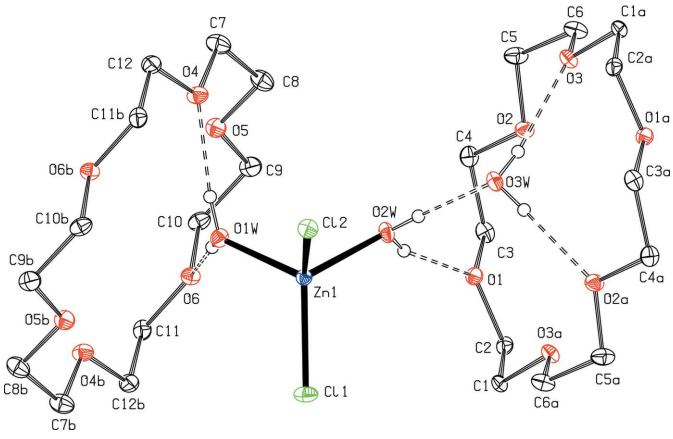


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. The H atoms attached to C have been omitted for clarity. Dashed lines indicate hydrogen bonds.

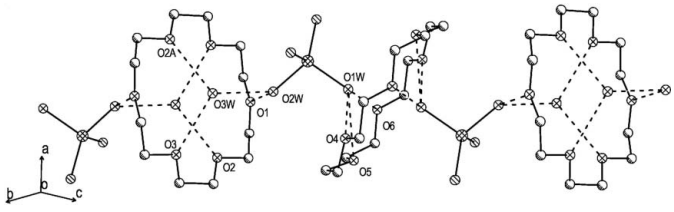


Figure 2
One-dimensional chain of (I) showing the $O_{water}—H\cdots O_{crown}$ hydrogen bonds (dashed lines). H atoms have been omitted.

$H\cdots O_{crown}$ hydrogen bonds with adjacent coordinated water O2*W* and uncoordinated water O3*W*, with average O···O distances of 2.840 (2) Å: the O2*W*···O3*W* distance is 2.628 (2) Å. All O atoms in crown B merely have interactions with adjacent coordinated water O1*W*, with average O···O distances of 2.854 (2) Å (Table 2). Thus, the hydrogen bonds link the crown ethers and Zn complex into a one-dimensional chain extending along the [01$\bar{1}$] direction (Fig. 2).

The synthesis of (I) is detailed below. When $ZnCl_2\cdot H_2O$ replaces $ZnCl_2\cdot 2H_2O$ in a similar reaction procedure, a new compound $ZnCl_2$(18-crown-6)$\cdot H_2O$ with less water content is obtained, in which 18-crown-6 is coordinated to the Zn atom *via* one O atom (Chenevert *et al.*, 1990); when anhydrous $ZnCl_2$ was reacted with 18-crown-6 instead of $ZnCl_2\cdot 2H_2O$, an anhydrous white precipitate, $(ZnCl_2)_2$(18-crown-6), formed (Chenevert *et al.*, 1990). Obviously, the content of water in the $ZnCl_2$/18-crown-6/THF reaction system is an important factor affecting the final products; the lower the water content in the reactants, the less water content in the products.

Experimental

$ZnCl_2\cdot 2H_2O$ (35 mg, 0.2 mmol) and 18-crown-6 (53 mg, 0.2 mmol) were added to 10 ml of THF, and this reaction mixture was stirred at 333 K for 6 h. After filtration, the resulting filtrate was reduced to 5 ml in a small tube, which was loaded into a large vial containing 5 ml of diethyl ether. The large vial was sealed and left undisturbed at room temperature, and colorless crystals of (I) were obtained in 6 d. Yield: 60%. Calculated for $C_{12}H_{30}O_9Cl_2Zn$: C 31.70, H 6.65%; found: C 31.1, H 6.37%.

Crystal data

$[ZnCl_2(H_2O)_2]\cdot C_{12}H_{24}O_6\cdot H_2O$
M_r = 454.63
Triclinic, $P\bar{1}$
a = 8.412 (3) Å
b = 9.885 (3) Å
c = 12.812 (4) Å
α = 87.047 (9)°
β = 76.819 (7)°
γ = 84.039 (8)°
V = 1031.4 (6) Å^3
Z = 2
D_x = 1.464 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.49 mm^{-1}
T = 293 (2) K
Prism, colorless
0.20 × 0.20 × 0.08 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
T_{min} = 0.843, T_{max} = 1.00
(expected range = 0.749–0.888)
6636 measured reflections
3600 independent reflections
3144 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.065
S = 1.01
3600 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O1*W*	1.9796 (16)	Zn1—Cl2	2.2113 (8)
Zn1—O2*W*	2.0173 (16)	Zn1—Cl1	2.2114 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H14*B*···O4	0.81 (3)	1.98 (3)	2.781 (2)	173 (3)
O1*W*—H14*A*···O6	0.75 (3)	2.08 (3)	2.822 (3)	178 (3)
O2*W*—H15*A*···O1	0.77 (3)	2.05 (3)	2.792 (2)	162 (3)
O2*W*—H15*B*···O3*W*	0.80 (3)	1.83 (3)	2.628 (3)	176 (3)
O3*W*—H13*A*···O2^{i}	0.79 (3)	2.09 (3)	2.867 (2)	169 (2)
O3*W*—H13*B*···O3	0.79 (3)	2.08 (3)	2.861 (2)	167 (2)

Symmetry code: (i) $-x+1, -y+2, -z+1$.

The water H atoms were located in a difference Fourier map, and freely refined with isotropic displacement parameters; the O—H distances are give in Table 2. All H atoms attached to C were allowed to ride on their respective parent atoms with C—H distances of 0.97 Å, and were included in the refinement with isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *PLATON*

(Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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