Bis(adamantan-1-aminium) tetra-chloridozincate(II) 18-crown-6 monohydrate clathrate

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The structure of the title compound [systematic name: bis-(adamantan-1-aminium) tetrachloridozincate(II)–1,4,7,10,13,16-hexaoxacyclooctadecane–water (1/1/1)], $(C_{10}H_{18}N)_2[ZnCl_4]\cdot C_{12}H_{24}O_6\cdot H_2O$, consists of supramolecular rotator–stator assemblies and ribbons of hydrogen bonds parallel to [010]. The assemblies are composed of one protonated adamantan-1-aminium cation and one crown ether molecule (1,4,7,10,13,16-hexaoxacyclooctadecane) to give an overall $[(C_{10}H_{18}N)(18$-crown-6$)]^+$ cation. The $-NH_3^+$ group of the cation nests in the crown and links to the crown-ether O atoms through N—H···O hydrogen bonds. The 18-crown-6 ring adopts a pseudo-C_{3v} conformation. The second adamantan-1-aminium forms part of ribbons of adamantan-1-aminium–water–tetrachloridozincate units which are interconnected by O—H···Cl, N—H···O and N—H···Cl hydrogen bonds via three different continuous rings with $R_5^4(12)$, $R_4^3(10)$ and $R_3^3(8)$ motifs.

Comment

Crown ethers have attracted much attention due to their ability to form noncovalent and hydrogen-bonded complexes with ammonium cations in both the solid state and solution (Fender et al., 2002; Rieger et al., 2005). Both the size of the crown ether and the nature of the ammonium cation ($-NH_4^+$, RNH_3^+, etc.) can influence the stoichiometry and stability of these host–guest adducts. Through the intermolecular interactions between the host molecules and guest species, it is easy to realise high selectivity in ionic or molecular recognition (Sato et al., 2007; Akutagawa et al., 2008). 18-Crown-6 and its derivatives exhibit the highest affinity with organic ammonium cations RNH_3^+, with a 1:1 stoichiometry in most studies (Doxsee et al., 2000; Johnson et al., 2000; Buschmann et al., 2001). We now present the structure of the title compound, (I), containing an adduct of 18-crown-6 and an ammonium cation.

The asymmetric unit of (I) contains two adamantan-1-aminium cations, one 18-crown-6 ether molecule, one $[ZnCl_4]^{2-}$ anion and one water molecule (Fig. 1). Only one of the

two crystallographically independent adamantan-1-aminium cations joins the rotator–stator assembly with 18-crown-6, via hydrogen-bonding interaction (Fig. 2). The $-NH_3^+$ group of the cation interacts with the six crown ether O atoms through three short approximately linear N—H···O hydrogen bonds (Table 1) and three longer acute interactions [2.957 (4), 2.938 (4) and 2.958 (4) Å from N1 to atoms O1, O3 and O5, respectively].

(I)
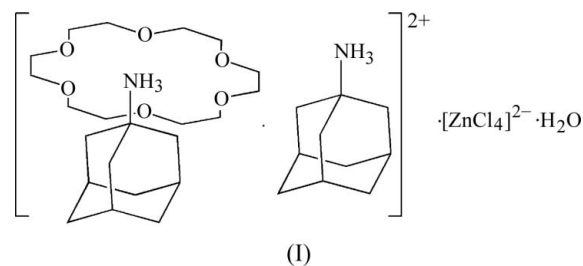
The conformation of the crown-ether ring (Table 1) and the hydrogen-bond geometry in this assembly closely resemble those in related adducts of 18-crown-6 and primary alkyl-ammonium salts (Henschel et al., 1997). The macrocycle adopts a conformation with approximate C_{3v} symmetry, with all O—C—C—O torsion angles being gauche and alternating in sign, and all C—O—C—C torsion angles being trans. The ether O atoms are nearly coplanar; O1, O3 and O5 are located below the mean O-atom plane [0.1798 (18), 0.1499 (18) and 0.1672 (19) Å, respectively] and O2, O4 and O6 are located above the plane [0.1635 (17), 0.1533 (18) and 0.1801 (18) Å, respectively]. The C—N bonds of the adamantan-1-aminium cation are almost perpendicular to the mean plane of the crown-ether O atoms. Atom N1 of the adamantan-1-aminium cation is 0.983 (3) Å out of the plane.

It is interesting that the second adamantan-1-aminium cation is not trapped by 18-crown-6 ether. The reason may lie in the $[ZnCl_4]^{2-}$ anions, which are relatively small {in contrast to the $[Ni(dmit)_2]^-$ (dmit is 2-thioxo-1,3-dithiole-4,5-dithiol-ate; Akutagawa et al., 2002) and $[PMo_{12}O_{40}]^{4-}$ (Akutagawa et
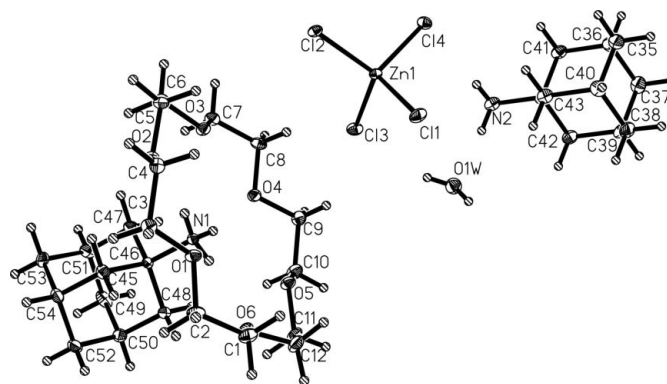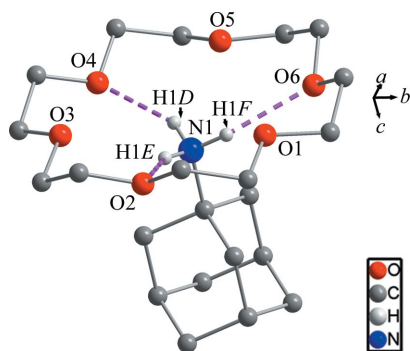

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

metal-organic compounds

Figure 2
The interactions between an adamantan-1-aminium cation and a crown ether molecule in (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen-bonding interactions have been omitted.

al., 2006) anions} for embedding large and structurally diverse supramolecular cations in the crystal lattice.

The [ZnCl$_4$]$^{2-}$ anions are present as counter-ions to the supramolecular [(C$_{10}$H$_{18}$N)(18-crown-6)]$^+$ and isolated adamantan-1-aminium cations, and hydrogen bond to both. The Zn^{II} centre adopts a tetrahedral coordination with four Cl$^-$ ions, which has been observed in many crystal structures (Jin *et al.*, 2005; Valkonen *et al.*, 2006). Generally, the Zn—Cl bond lengths and the Cl—Zn—Cl angles in a [ZnCl$_4$]$^{2-}$ anion are not equal (Wickleder, 2001; Albrecht *et al.*, 2003) but vary with the environment around the Cl atoms. In (I), as Cl1, Cl3 and Cl4 are involved in stronger and more numerous N—H···Cl hydrogen bonds than Cl2, the Zn1—Cl2 bonds are obviously shorter than all the other Zn—Cl bonds. The [ZnCl$_4$]$^{2-}$ anion shows typical Zn—Cl bond lengths [2.2354 (9)–2.3214 (10) Å] and the Cl—Zn—Cl angles range from 104.53 (4) to 115.96 (4)°. Owing to the obvious differences of the Zn—Cl distances and Cl—Zn—Cl angles, the coordination geometry of the Zn atom could be regarded as a distorted tetrahedron.

It has been reported that Cl ions coordinating to metal atom centres are good hydrogen-bond acceptors (Aullon *et al.*, 1998). In this structure, only one of the four chlorides (Cl2) of [ZnCl$_4$]$^{2-}$ fails to engage in hydrogen-bonding interactions (Table 2). The O—H···Cl, N—H···O and N—H···Cl hydrogen bonds between discrete tetrahedral tetrachloridozincate(II) anions, isolated adamantan-1-aminium cations and solvent water molecules result in a noteworthy one-dimensional ribbon-like structure along the *b* axis (Fig. 3). This ribbon motif (Fig. 3) is the dominant hydrogen-bonding motif (Hulme & Tocher, 2006) in the structure of (I). This structure propagates *via* two types of rings, *viz.* one of level four [$R_4^3(10)$] and one of level three [$R_3^3(8)$]. The $R_4^3(10)$ ring includes four hydrogen bonds, *viz.* N2—H2D···Cl4, N2—H2E···Cl1, O1W—H1WA···Cl4 and O1W—H1WB···Cl3. The second-order motif involves three hydrogen bonds, *viz.* N2—H2D···Cl4, N2—H2F···O1W and O1W—H1WB···Cl3. The discrete adamantan-1-aminium–crown ether units are located on both sides of the ribbon, forming possible C—H···Cl hydrogen bonds which would link all the units into a two-dimensional network.
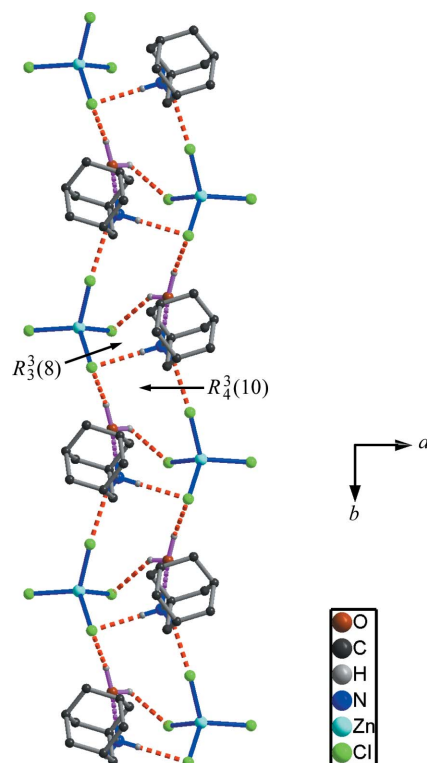
Figure 3
A ribbon motif of the hydrogen-bonded adamantan-1-aminium–water–tetrachloridozincate units. The graph-set notations for the three types of hydrogen-bonding patterns are $R_5^4(12)$, $R_4^3(10)$ and $R_3^3(8)$. Only those H atoms involved in hydrogen bonding are shown. Dashed lines indicate hydrogen-bonding interactions.

This study is also part of our systematic investigation of dielectric, ferroelectric and phase-transition materials (Ye *et al.*, 2009; Zhang *et al.*, 2009), including organic compounds, metal–organic coordination compounds and organic–inorganic hybrids. The measurement of the dielectric constant of (I) as a function of temperature showed that the permittivity is basically temperature-independent (dielectric constant of 6–7) below room temperature. Such a dielectric response suggests that this compound might not undergo a distinct structural phase transition in the lower temperature range. Similarly, in the range from room temperature to near its melting point (m.p. > 470 K), the dielectric constant increases smoothly from 7 to 17 as a function of temperature, and no dielectric anomaly was observed.

Experimental

Adamantan-1-aminium chloride (2 mmol, 0.375 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in methanol (40 ml). Zinc(II) dichloride (2 mmol, 0.272 g) was added to the solution, followed by concentrated hydrochloric acid (5 ml). Single crystals of (I) suitable for X-ray diffraction analysis were obtained *via* slow evaporation from the methanol solution at room temperature over two weeks. The crystals were colourless, of prismatic habit and of an average size of about 0.2 × 0.3 × 0.4 mm.

Dielectric studies (capacitance and dielectric-loss measurements) were performed on powder samples which had been pressed into

tablets, on the surfaces of which conducting carbon glue was deposited. An automatic impedance TongHui2828 Analyzer was used. In the measured temperature range (80–430 K), the title structure showed no dielectric anomaly.

Crystal data

$(C_{10}H_{18}N)_2[ZnCl_4]\cdot C_{12}H_{24}O_6\cdot H_2O$
$M_r = 794.03$
Orthorhombic, $Pbcn$
$a = 26.9702\,(12)$ Å
$b = 11.4912\,(7)$ Å
$c = 24.9646\,(18)$ Å

$V = 7737.0\,(8)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.96$ mm^{-1}
$T = 293$ K
$0.40 \times 0.30 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
  (*CrystalClear*; Rigaku, 2005)
  $T_{min} = 0.716$, $T_{max} = 0.826$

72972 measured reflections
7595 independent reflections
6098 reflections with $I > 2\sigma(I)$
$R_{int} = 0.094$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.134$
$S = 1.15$
7595 reflections
439 parameters
9 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected torsion angles (°).

C12—O6—C1—C2	171.3 (3)	C6—O3—C7—C8	172.0 (3)
C3—O1—C2—C1	−170.3 (3)	C9—O4—C8—C7	−176.6 (3)
O6—C1—C2—O1	−61.9 (4)	O3—C7—C8—O4	62.0 (4)
C2—O1—C3—C4	168.3 (3)	C8—O4—C9—C10	174.9 (3)
C5—O2—C4—C3	−177.9 (3)	C11—O5—C10—C9	−166.5 (3)
O1—C3—C4—O2	65.6 (4)	O4—C9—C10—O5	−62.3 (4)
C4—O2—C5—C6	174.2 (3)	C10—O5—C11—C12	170.1 (3)
C7—O3—C6—C5	−166.2 (3)	C1—O6—C12—C11	−175.9 (3)
O2—C5—C6—O3	−64.6 (4)	O5—C11—C12—O6	64.4 (4)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1WB⋯Cl3	0.85 (2)	2.57 (2)	3.312 (3)	146 (4)
N2—H2F⋯O1W	0.91 (3)	1.86 (3)	2.767 (5)	171 (5)
N2—H2D⋯Cl4	0.88 (3)	2.33 (3)	3.201 (4)	172 (5)
N1—H1E⋯O2	0.91 (3)	2.11 (3)	2.983 (4)	161 (4)
N1—H1D⋯O4	0.89 (3)	2.16 (3)	2.993 (4)	155 (5)
N1—H1F⋯O6	0.87 (3)	2.16 (3)	2.996 (4)	161 (5)
O1W—H1WA⋯Cl4^i	0.86 (2)	2.39 (2)	3.234 (3)	167 (4)
N2—H2E⋯Cl1^{ii}	0.89 (3)	2.38 (3)	3.233 (3)	160 (4)

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

All C-bound H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and allowed to ride on their parent C atoms,

with $U_{iso}(H) = 1.2U_{eq}(C)$. All N- and O-bound H atoms were discernible in the difference electron-density map. The positions of the N-bound H atoms were refined using a riding model, with N—H = 0.89 (3) Å and $U_{iso}(H) = 1.5U_{eq}(N)$. The coordinates of the water H atoms were refined with the restraint O—H = 0.84 (2) Å and $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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