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Propane-1,3-diaminium tetrachloridozincate(II) 18-crown-6 clathrate

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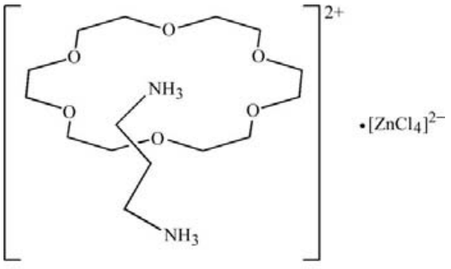
The reaction of propane-1,3-diamine hydrochloride, 18-crown-6 and zinc(II) chloride in methanol solution yields the title complex salt [systematic name: propane-1,3-diaminium tetrachloridozincate(II)–1,4,7,10,13,16-hexaoxacyclooctadecane (1/1)], $(C_3H_{12}N_2)[ZnCl_4]\cdot C_{12}H_{24}O_6$, with an unusual supramolecular structure. The diprotonated propane-1,3-diaminium cation forms an unexpected 1:1 supramolecular rotator–stator complex with the crown ether, *viz.* $[C_3H_{12}N_2(\text{18-crown-6})]^{2+}$, in which one of the $-NH_3^+$ substituents nests in the crown and interacts through N—H···O hydrogen bonding. The other $-NH_3^+$ group interacts with the $[ZnCl_4]^{2-}$ anion *via* N—H···Cl hydrogen bonding, forming cation–crown–anion ribbons parallel to [010].

Comment

There is currently a great deal of interest in crown ethers because of their ability to form noncovalent, hydrogen-bonding complexes with ammonium cations both in the solid state and in solution (Fender *et al.*, 2002; Kryatova *et al.*, 2004). Not only the size of the crown ether, but also the nature of the ammonium cation (NH_4^+, RNH_3^+, $R_2NH_2^+$, *etc.*) can influence the stoichiometry and stability of these host–guest complexes. The host molecules combine with the guest species by intermolecular interaction, and if the host molecule possesses some specific sites that can bind by chelate effect, it is easy to realize high selectivity in ion or molecular recognitions. 18-Crown-6 has a high affinity for RNH_3^+ cations and studies have invariably shown a 1:1 stoichiometry in complexes of 18-crown-6 and its derivatives with RNH_3^+ cations (Doxsee *et al.*, 2000; Johnson *et al.*, 2000; Buschmann *et al.*, 2001). By contrast, alkylidenediammonium cations, $^+H_3N\text{–}R\text{–}NH_3^+$, typically form complexes in a 1:2 stoichiometry in which each dication is sandwiched by two crowns (Akutagawa *et al.*, 2002, 2006). In the present study, a reaction of propane-1,3-diaminium cations, 18-crown-6 and tetrachloridozincate(II) has produced a complex, (I), with an unexpected 1:1 stoichiometry between the dication and crown ether.

The asymmetric unit of (I) is composed of one unique $[C_3H_{12}N_2(\text{18-crown-6})]^{2+}$ cation and one $[ZnCl_4]^{2-}$ anion (Fig. 1). A supramolecular rotator–stator structure is thus assembled between the diprotonated propane-1,3-diaminium cations and 18-crown-6 molecules by hydrogen bonding. One $-NH_3^+$ group interacts with the six O atoms of one crown ether molecule through three short, approximately linear, N—H···O hydrogen bonds and three longer more acutely angular interactions (Table 1). The conformation of the macrocycle and the hydrogen-bond geometry in the complex cation closely resemble those in related adducts between 18-crown-6 and primary alkylammonium salts (Henschel *et al.*, 1997). The symmetry of the macrocycle approximates to D_{3d}. The ether O atoms are nearly coplanar, with O1, O2 and O5 displaced *ca* 0.2 Å above the plane and O3, O4 and O6 displaced below the plane by roughly the same distances. Atom N1 of the propane-1,3-diaminium cation is 0.832 (3) Å out of this best plane of O atoms.



(I)

The supramolecular $[C_3H_{12}N_2(\text{18-crown-6})]^{2+}$ cation is paired in this structure with the relatively compact $[ZnCl_4]^{2-}$ anion. The Zn^{II} ion adopts a modestly flattened tetrahedral coordination by four Cl^- ions which has been seen in many crystal structures (Jin *et al.*, 2005; Valkonen *et al.*, 2006). The $[ZnCl_4]^{2-}$ anion possesses typical Zn—Cl bond lengths [2.2323 (9)–2.3267 (9) Å], while the Cl—Zn—Cl angles [99.00 (4)–117.67 (3)°] indicate some distortion from a regular tetrahedron.

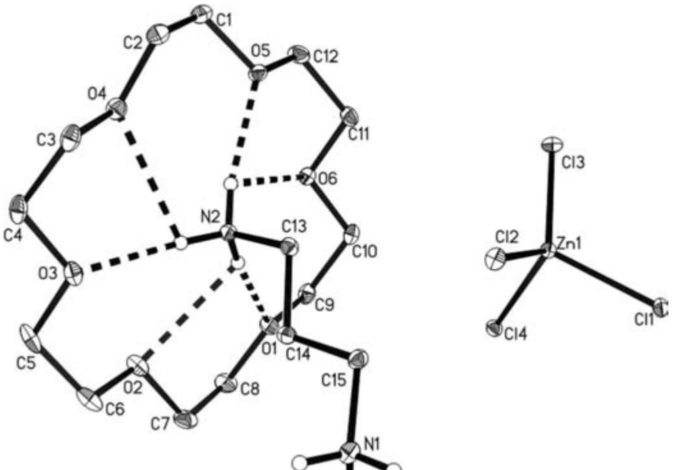


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

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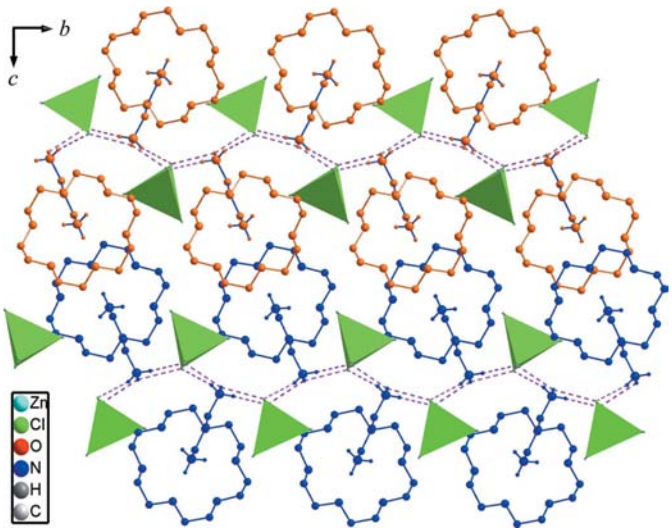

Figure 2
The structure of a layer of diaminium–crown–anion ribbons crosslinked by hydrogen bonds to $[ZnCl_4]^{2-}$ anions, viewed along the *a* axis. Dotted lines indicate hydrogen bonding.

It has been shown that Cl^- ions coordinated to metal centres are good hydrogen-bond acceptors (Aullon *et al.*, 1998). Two of the four Cl atoms of $[ZnCl_4]^{2-}$ are engaged in hydrogen bonding to the H atoms on the other $–NH_3^+$ group of two different neighbouring dications (Table 1). These interactions between discrete $[ZnCl_4]^{2-}$ anions and $[C_3H_{12}N_2\text{-}(18\text{-crown-}6)]^{2+}$ cations result in a novel one-dimensional ribbon-like structure running in the *b* direction (Fig. 2). These ribbons stack in the *c* direction into *bc* pseudo-sheets.

No similar complexes with a 1:1 $[NH_3–R–NH_3]^{2+}$/(18-crown-6) stoichiometry have been reported. Most diaminium–18-crown-6 complexes have a sandwich-type structure with a 1:2 stoichiometry, *e.g.* $[NH_3–R–NH_3]^{2+}[(18\text{-crown-}6)_2]$ (Akutagawa *et al.*, 2002, 2006). It was thus interesting that the propane-1,3-diaminium dication was not combined with the 18-crown-6 ether forming a similar sandwich-type $[C_3H_{12}N_2\text{-}(18\text{-crown-}6)_2]$ complex. 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-dithiolate; Akutagawa *et al.*, 2002) and $[PMo_{12}O_{40}]^{4-}$ (Akutagawa *et al.*, 2006) anions, for embedding large and structurally diverse supramolecular cations in the crystal lattice. The $[ZnCl_4]^{2-}$ anions also offer better hydrogen-bond acceptors to the N atoms of the unincluded $–NH_3^+$ group. Such a feature would further support the observed behaviour.

Experimental

$NH_2–C_3H_6–NH_2\cdot 2HCl$ (2 mmol, 0.294 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in methanol. Zinc(II) chloride (2 mmol, 0.272 g) in concentrated hydrochloric acid medium was added to the mixture. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solution at room temperature over a period of 2 weeks. The crystals were colourless prismatic with an average size of 0.2 × 0.3 × 0.4 mm.

The compound powder was characterized by X-ray powder diffraction at room temperature and the pattern calculated from the single-crystal X-ray data was in good agreement with the observed pattern with regard to the peak positions, with some difference in peak intensities.

Dielectric studies (capacitance and dielectric loss measurements) were performed using an automatic impedance TongHui2828 Analyzer on powder samples that were pressed into tablets on the surfaces of which a conducting carbon glue was deposited. Dielectric permittivity of the compound was tested to systematically investigate the possibility of ferroelectric phase transitions (Ye *et al.*, 2009; Zhang *et al.*, 2009). In the measured temperature range from 80 to 400 K (m.p. > 420 K), the temperature dependence of the relative permittivity at 1 MHz varied smoothly from 3.2 to 4.0 in the title compound. No dielectric anomaly was observed, suggesting that this compound should not be a real ferroelectric or that no distinct phase transition occurred within the measured temperature range.

Crystal data

$(C_3H_{12}N_2)[ZnCl_4]\cdot C_{12}H_{24}O_6$
$M_r = 547.65$
Orthorhombic, $P2_12_12_1$
$a = 9.134$ (3) Å
$b = 9.862$ (3) Å
$c = 27.810$ (8) Å
$V = 2505.1$ (13) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.44$ mm^{-1}
$T = 93$ K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{\min} = 0.602$, $T_{\max} = 0.750$
24776 measured reflections
5729 independent reflections
5432 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.095$
$S = 1.11$
5729 reflections
253 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.003 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*C*···O1	0.89	2.00	2.884 (3)	173
N2—H2*C*···O2	0.89	2.56	2.991 (3)	111
N2—H2*B*···O3	0.89	2.01	2.894 (4)	174
N2—H2*B*···O4	0.89	2.55	2.942 (3)	107
N2—H2*A*···O5	0.89	2.00	2.860 (3)	161
N2—H2*A*···O6	0.89	2.57	2.994 (4)	110
N1—H1*C*···Cl4$^{\rm i}$	0.89	2.35	3.233 (3)	174
N1—H1*A*···Cl4$^{\rm ii}$	0.89	2.79	3.315 (3)	120
N1—H1*A*···Cl1$^{\rm i}$	0.89	2.95	3.370 (3)	111
N1—H1*B*···Cl1$^{\rm ii}$	0.89	2.36	3.215 (3)	162

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

All methylene H atoms were placed in geometrically idealized positions and allowed to ride on their attached C atoms, with C—H = 0.97 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). All aminium H atoms were placed in geometrically idealized positions and refined using a riding model, with N—H = 0.89 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(N). The methyl and aminium groups were allowed to rotate, but not to tilt.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3249). Services for accessing these data are described at the back of the journal.

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