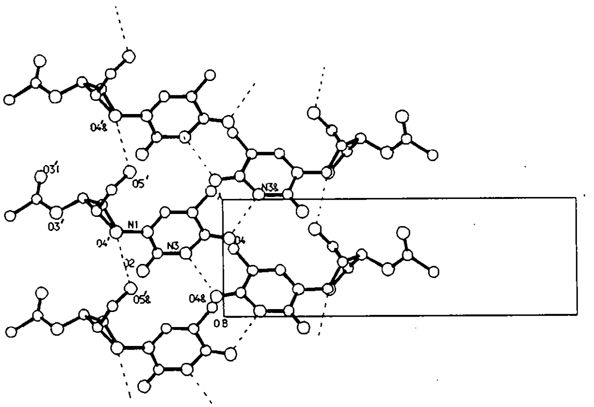

Fig. 2. The stacking in the title compound, showing the hydrogen-bonding scheme.

are linked along **a** by a hydrogen bond between O(4′) and O(5′):

O(4′)···O(5′) (1 + *x*, *y*, *z*) 2·819 (4) Å
O(4′)···H(5′3) (1 + *x*, *y*, *z*) 2·21 (3) Å.

Thus there are regions of bases and of sugar groups packing along **a**, as shown.

There are no other significant close contacts between the molecules in the structure. This goes against the strong trend in other acetylated pyrimidine and purine nucleosides for the C=O moiety of an acetyl group to stack above the base ring of a neighbouring molecule (Wilson, 1985). However, the interaction in 3′,5′-di-*O*-acetylthymidine was the weakest of those found in the earlier work and while the 3′-acetyl group was involved it is not particularly surprising that in the less sterically congested mono-substituted title compound the interaction no longer plays a significant role. It has been found that in nucleoside structures the mono-acetylated compounds show less propensity to display this interaction.

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Ammonium Chloride Complexes with 18-Crown-6

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Abstract. (I): $2C_{12}H_{24}O_6.2NH_4^+.Cl^-.PF_6^-.0{\cdot}9CH_2Cl_2$, $M_r = 821{\cdot}6$, monoclinic, $P2_1/n$, $a = 8{\cdot}460\ (2)$, $b = 22{\cdot}852\ (7)$, $c = 21{\cdot}604\ (4)$ Å, $\beta = 92{\cdot}77\ (1)°$, $V = 4172\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 3{\cdot}09$ mm^{-1}, $F(000) = 1752$, room temperature, $R = 0{\cdot}114$ for 2127 observed reflections with $|F_o| > 3\sigma(|F_o|)$. (II): $C_{12}H_{24}O_6.NH_4^+.Cl^-.2H_2O$, $M_r = 353{\cdot}8$, orthorhombic, $Pnam$ (equivalent positions, $-x, -y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$), $a = 9{\cdot}751\ (1)$, $b = 12{\cdot}844\ (1)$, $c = 14{\cdot}972\ (2)$ Å, $V = 1875\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\mathrm{Co}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 2{\cdot}13$ mm^{-1}, $F(000) = 768$, room

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temperature, $R = 0{\cdot}074$ for 1059 observed reflections with $|F_o| > 3\sigma(|F_o|)$. In complexes (I) and (II), the 18-crown-6 (18C6) ring adopts the conventional all-*gauche* conformation with the NH_4^+ cations hydrogen-bonded in a perching arrangement to the nearer triangle of macrocyclic O atoms. In the dimeric complex (I), a Cl^- anion acts as a hydrogen-bonding bridge between two $[NH_4.18C6]^+$ ions. In the polymeric complex (II), the Cl^- anions and the H_2O molecules form a continuous hydrogen-bonded chain with each Cl^- anion forming a hydrogen bond to an $[NH_4.18C6]^+$ ion.

Introduction. The aliphatic α,ω-diamines, $H_2N(CH_2)_n$-NH_2 ($n = 2$–6), are important industrial chemicals with a wide range of applications (*Kirk-Othmer Encyclopedia of Chemical Technology,* 1979). The lowest member ($n = 1$) of the homologous series, H_2NCH_2-NH_2, has only been prepared (Knudsen, 1914) as its di-salts, $^+H_3NCH_2NH_3^+.2X^-$, by the action of an excess of strong acid on $CH_2(NHCHO)_2$ at low temperatures:

$$CH_2(NHCHO)_2 + 2HX + 2H_2O \rightarrow CH_2(NH_2)_2.2HX + 2HCO_2H$$

where $X = $ Cl, NO_3, HSO_4, *etc.* The methylenediammonium salts are white crystalline solids. They have received almost no attention since their discovery because they hydrolyse spontaneously on standing in air at ambient temperature:

$$CH_2(NH_2)_2.2HCl + H_2O \rightarrow HCHO + 2NH_4Cl.$$

In an attempt to isolate a stable methylenediammonium salt, we treated the bishydrochloride with 18-crown-6 (18C6) in dry dimethyl sulfoxide in the presence of tetramethylammonium hexafluorophosphate:

$$CH_2(NH_2)_2.2HCl + 2Me_4NPF_6 + (18C6)_2 \rightarrow [18C6.H_3NCH_2NH_3.18C6][PF_6]_2 + 2Me_4NCl.$$

Unfortunately, we were unable to prevent hydrolysis, and isolation of the 2:1 complex evaded us. However, two 1:1 crystalline complexes, (I) and (II), of NH_4^+ ions with 18C6 were isolated. This communication describes the X-ray structural investigations of these two complexes.

Experimental. Tetramethylammonium hexafluorophosphate (100 mg), 18-crown-6 (60 mg), and methylenediamine bishydrochloride (30 mg) (Knudsen, 1914) were stirred under nitrogen in dry dimethyl sulfoxide (5 cm^3) at room temperature for 16 h. The solvent was removed and the solid residue was extracted with dichloromethane. This extract was concentrated to afford a white solid which was redissolved in dichloromethane (0·5 cm^3) and layered with *n*-pentane. This resulted in the formation of two distinctly different crystalline products, (I) as rhombic plates and (II) as small octahedra; both proved adequate for single-crystal X-ray analysis. Crystal (I) 0·23 × 0·18 × 0·08, crystal (II) 0·18 × 0·15 × 0·15 mm. Refined unit-cell parameters by centring (I) 15 reflections with $13{\cdot}6 \le \theta \le 23{\cdot}3°$ and (II) 18 reflections with $18{\cdot}2 \le \theta \le 29{\cdot}1°$. Nicolet $R3m$ diffractometer. For (I) 4657 reflections measured ($\theta \le 50°$), 4294 independent, $R_{\rm int}$ 0·031 and for (II) 1322 independent reflections ($\theta \le 58°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. For (I) 2127 $[|F_o| > 3\sigma(|F_o|)]$ considered observed, index range h −8/8, k 0/22, l 0/21 and for (II) 1059 $[|F_o| > 3\sigma(|F_o|)]$ considered observed, index range h 0/10, k 0/13, l 0/16; two check reflections every 50 reflections, no decomposition, 5% variation for (I) and 7% for (II); data brought to uniform scales, Lorentz and polarization corrections, no absorption or extinction corrections. Structures solved by direct methods, non-hydrogen atoms refined anisotropically; positions of ammonium H atoms from ΔF maps, groups initially idealized and then refined subject to N—H and H···H distance constraints (N—H = 0·96 Å). All methylene H-atom positions calculated (C—H = 0·96 Å), assigned isotropic thermal parameters $U({\rm H}) = 1{\cdot}2U_{\rm eq}({\rm C})$, allowed to ride on parent C atoms. In (I) CH_2Cl_2 included in asymmetric unit, refined with estimated occupancy 0·9. In (II) H_2O included in asymmetric unit, unit occupancy, H-atom positions not located. Refinement using F magnitudes by block-cascade full-matrix least squares. For (I) $R = 0{\cdot}114$, $wR = 0{\cdot}109$ $[w^{-1} = \sigma^2(F) + 0{\cdot}0012F^2]$; S(figure of merit) = 1·16; 466 refined parameters, $(\Delta/\sigma)_{\max} = 0{\cdot}23$; residual electron density in difference map within −0·39 and +0·54 e Å^{-3}; high R factor due to disorder/large anisotropy in both CH_2Cl_2 and PF_6^- groups. For (II) $R = 0{\cdot}074$, $wR = 0{\cdot}086$ $[w^{-1} = \sigma^2(F) + 0{\cdot}0023F^2]$; $S = 1{\cdot}66$; 114 refined parameters, $(\Delta/\sigma)_{\max} = 0{\cdot}01$; residual electron density in difference map within −0·25 and +0·46 e Å^{-3}; slightly high R factor due to significant anisotropy of some of the methylene C atoms and the solvate H_2O molecule; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computation carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. Table 1* lists the fractional coordinates of the non-hydrogen atoms and Table 2 the bond lengths and angles for (I). The structure of (I) is illustrated in Fig. 1 which includes the atomic numbering scheme. Clearly, the crystalline complex (I) contains two independent macrocycles (*A* and *B*), each of which adopts the conventional all-*gauche* conformation with pseudo D_{3d} symmetry (Goldberg, 1980; Wipff, Weiner

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44918 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times$ 10^3) *for* (I)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	4274 (10)	3116 (4)	3389 (4)	69 (3)
C(2)	4156 (20)	3747 (7)	3509 (8)	105 (4)
C(3)	2427 (17)	3904 (7)	3476 (7)	84 (3)
O(4)	1696 (12)	3625 (4)	3964 (4)	83 (3)
C(5)	78 (18)	3795 (8)	3999 (7)	106 (4)
C(6)	−537 (20)	3512 (7)	4522 (7)	107 (4)
O(7)	−582 (11)	2893 (5)	4426 (4)	73 (3)
C(8)	−1268 (18)	2575 (7)	4917 (7)	92 (3)
C(9)	−1072 (17)	1941 (7)	4840 (7)	83 (3)
O(10)	483 (11)	1747 (5)	4888 (4)	83 (3)
C(11)	702 (17)	1132 (6)	4834 (7)	78 (3)
C(12)	2432 (19)	1013 (7)	4885 (7)	97 (3)
O(13)	3116 (12)	1268 (4)	4380 (4)	70 (3)
C(14)	4772 (17)	1112 (7)	4335 (9)	92 (3)
C(15)	5384 (17)	1395 (7)	3786 (8)	89 (3)
O(16)	5341 (11)	1993 (4)	3837 (4)	74 (3)
C(17)	5978 (17)	2285 (7)	3305 (6)	84 (3)
C(18)	5856 (16)	2914 (7)	3420 (7)	83 (3)
O(19)	4302 (10)	4048 (5)	7977 (4)	73 (3)
C(20)	4261 (22)	4663 (7)	7826 (10)	125 (4)
C(21)	2690 (22)	4857 (8)	7856 (9)	132 (4)
O(22)	1705 (12)	4592 (4)	7362 (5)	87 (3)
C(23)	95 (18)	4766 (7)	7360 (7)	85 (3)
C(24)	−837 (19)	4476 (7)	6845 (8)	83 (3)
O(25)	−746 (10)	3873 (4)	6957 (4)	63 (3)
C(26)	−1668 (17)	3587 (8)	6495 (7)	78 (3)
C(27)	−1614 (16)	2950 (8)	6608 (7)	89 (3)
O(28)	−15 (11)	2735 (4)	6528 (4)	63 (3)
C(29)	151 (17)	2123 (6)	6593 (7)	78 (3)
C(30)	1850 (19)	1945 (7)	6547 (7)	91 (3)
O(31)	2701 (11)	2190 (4)	7046 (4)	68 (3)
C(32)	4361 (19)	2056 (6)	7045 (7)	79 (3)
C(33)	5197 (16)	2323 (7)	7613 (7)	82 (3)
O(34)	5168 (11)	2936 (4)	7578 (4)	69 (3)
C(35)	5922 (17)	3236 (7)	8113 (6)	82 (3)
C(36)	5804 (18)	3855 (7)	7994 (7)	86 (3)
N(1)	2937 (11)	2552 (5)	4530 (4)	56 (3)
N(2)	2685 (6)	3481 (4)	6833 (4)	49 (3)
Cl	4517 (5)	3305 (2)	5588 (2)	81 (2)
P(1)	6995 (5)	700 (2)	6263 (2)	63 (2)
F(1)	6790 (13)	1345 (4)	6059 (5)	131 (3)
F(2)	7177 (12)	46 (4)	6411 (5)	126 (3)
F(3)	8828 (11)	761 (4)	6249 (6)	125 (3)
F(4)	5167 (11)	647 (5)	6288 (6)	148 (3)
F(5)	6899 (16)	547 (5)	5550 (5)	153 (3)
F(6)	7127 (17)	861 (6)	6940 (5)	180 (3)
C(37)	7730 (35)	328 (8)	267 (9)	198 (4)
Cl(1)	8156 (11)	63 (4)	990 (3)	195 (3)
Cl(2)	7476 (13)	−152 (4)	−250 (4)	235 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (I)

O(1)—C(2)	1·469 (18)	O(1)—C(18)	1·415 (17)
C(2)—C(3)	1·505 (22)	C(3)—O(4)	1·401 (18)
O(4)—C(5)	1·429 (19)	C(5)—C(6)	1·422 (24)
C(6)—O(7)	1·429 (20)	O(7)—C(8)	1·431 (18)
C(8)—C(9)	1·468 (23)	C(9)—O(10)	1·387 (18)
O(10)—C(11)	1·422 (17)	C(11)—C(12)	1·488 (22)
C(12)—O(13)	1·388 (18)	O(13)—C(14)	1·454 (18)
C(14)—C(15)	1·468 (25)	C(15)—O(16)	1·372 (20)
O(16)—C(17)	1·456 (17)	C(17)—C(18)	1·462 (24)
O(19)—C(20)	1·444 (20)	O(19)—C(36)	1·345 (18)
C(20)—C(21)	1·405 (26)	C(21)—O(22)	1·455 (21)
O(22)—C(23)	1·419 (18)	C(23)—C(24)	1·489 (22)
C(24)—O(25)	1·402 (18)	O(25)—C(26)	1·397 (18)
C(26)—C(27)	1·475 (25)	C(27)—O(28)	1·458 (17)
O(28)—C(29)	1·412 (17)	C(29)—C(30)	1·501 (21)
C(30)—O(31)	1·384 (18)	O(31)—C(32)	1·437 (19)
C(32)—C(33)	1·515 (21)	C(33)—O(34)	1·404 (19)
O(34)—C(35)	1·465 (17)	C(35)—C(36)	1·438 (23)
P(1)—F(1)	1·546 (10)	P(1)—F(2)	1·535 (10)
P(1)—F(3)	1·559 (10)	P(1)—F(4)	1·555 (10)
P(1)—F(5)	1·578 (11)	P(1)—F(6)	1·506 (11)
C(37)—Cl(1)	1·699 (21)	C(37)—Cl(2)	1·573 (21)

C(2)—O(1)—C(18)	112·6 (11)	O(1)—C(2)—C(3)	107·4 (12)
C(2)—C(3)—O(4)	108·6 (12)	C(3)—O(4)—C(5)	112·1 (11)
O(4)—C(5)—C(6)	107·9 (13)	C(5)—C(6)—O(7)	110·0 (14)
C(6)—O(7)—C(8)	113·8 (11)	O(7)—C(8)—C(9)	111·5 (12)
C(8)—C(9)—O(10)	114·8 (13)	C(9)—O(10)—C(11)	115·9 (11)
O(10)—C(11)—C(12)	107·9 (12)	C(11)—C(12)—O(13)	108·1 (12)
C(12)—O(13)—C(14)	112·9 (11)	O(13)—C(14)—C(15)	109·0 (12)
C(14)—C(15)—O(16)	111·2 (14)	C(15)—O(16)—C(17)	112·4 (12)
O(16)—C(17)—C(18)	106·5 (11)	O(1)—C(18)—C(17)	112·8 (12)
C(20)—O(19)—C(36)	109·8 (12)	O(19)—C(20)—C(21)	108·0 (15)
C(20)—C(21)—O(22)	110·1 (16)	C(21)—O(22)—C(23)	113·6 (12)
O(22)—C(23)—C(24)	110·5 (13)	C(23)—C(24)—O(25)	106·7 (12)
C(24)—O(25)—C(26)	108·2 (11)	O(25)—C(26)—C(27)	109·3 (12)
C(26)—C(27)—O(28)	109·6 (12)	C(27)—O(28)—C(29)	114·3 (11)
O(28)—C(29)—C(30)	110·7 (12)	C(29)—C(30)—O(31)	107·6 (12)
C(30)—O(31)—C(32)	112·6 (11)	O(31)—C(32)—C(33)	109·4 (12)
C(32)—C(33)—O(34)	110·6 (12)	C(33)—O(34)—C(35)	114·8 (11)
O(34)—C(35)—C(36)	107·2 (12)	O(19)—C(36)—C(35)	112·6 (13)
F(1)—P(1)—F(2)	175·4 (7)	F(1)—P(1)—F(3)	90·4 (6)
F(2)—P(1)—F(3)	90·1 (6)	F(1)—P(1)—F(4)	89·2 (6)
F(2)—P(1)—F(4)	90·4 (6)	F(3)—P(1)—F(4)	179·0 (6)
F(1)—P(1)—F(5)	86·1 (6)	F(2)—P(1)—F(5)	89·3 (6)
F(3)—P(1)—F(5)	90·2 (7)	F(4)—P(1)—F(5)	90·7 (7)
F(1)—P(1)—F(6)	92·6 (7)	F(2)—P(1)—F(6)	91·9 (7)
F(3)—P(1)—F(6)	88·3 (7)	F(4)—P(1)—F(6)	90·8 (8)
F(5)—P(1)—F(6)	178·1 (7)	Cl(1)—C(37)—Cl(2)	114·9 (12)

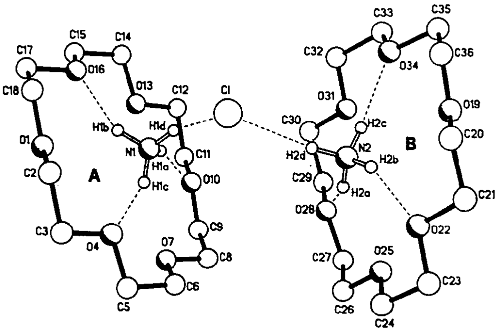

Fig. 1. Ball-and-stick representation of the structure of (I) showing the atomic numbering scheme. Hydrogen bonds are indicated by dashed lines.

& Kollman, 1982). The torsional angles lie in the range 62–70 (1)° for |O—C—C—O| and 172–180 (1)° for |C—C—O—C|. Macrocycles *A* and *B* are linked *via* hydrogen bonds that involve the Cl^- anion and the two NH_4^+ cations, both of which assume three-point binding geometries in a so-called perching arrangement (Cram & Trueblood, 1981; Trueblood, Knobler, Lawrence & Stevens, 1982). Upper triangles of O atoms, which can be identified as O(4), O(10), and O(16) in macrocycle *A*, and O(22), O(28), and O(34) in macrocycle *B*, form [N^+—H···O] hydrogen bonds with N^+···O distances of 2·91 (1), 2·91 (1) and 2·88 (1) Å respectively for *A* and 2·92 (1), 2·90 (1) and 2·87 (1) Å respectively for *B*. The corresponding N—H—O angles at H(1*c*), H(1*a*) and H(1*b*) in *A* are 151, 155 and 151° respectively, and at H(2*b*), H(2*a*) and H(2*c*) in *B* are 152, 148 and 146° respectively. The angles between the COC planes and the HO vectors are 19, 25 and 29° respectively for H(1*c*), H(1*a*) and H(1*b*) in *A* and 20, 24 and 29° respectively for H(2*b*), H(2*a*) and H(2*c*) in *B*. Other hydrogen-bond distances are 3·11 (1) and 3·19 (1) Å for N(1) and N(2) respectively to the Cl^- anion. The

Table 3. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (II)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	4647 (4)	2171 (3)	7500	66 (1)
C(2)	3847 (5)	2161 (4)	8285 (3)	79 (2)
C(3)	4773 (5)	2201 (4)	9083 (3)	78 (2)
O(4)	5525 (3)	1266 (2)	9132 (2)	65 (1)
C(5)	6338 (4)	1209 (4)	9920 (3)	78 (2)
C(6)	7181 (5)	248 (5)	9884 (3)	85 (2)
O(7)	8158 (3)	354 (2)	9184 (2)	73 (1)
C(8)	8994 (6)	−549 (4)	9057 (4)	91 (2)
C(9)	9909 (5)	−364 (4)	8279 (4)	92 (2)
O(10)	9102 (4)	−382 (3)	7500	82 (2)
N	6211 (4)	158 (4)	7500	57 (2)
Cl	3691 (2)	−1497 (2)	7500	90 (1)
O(11)	6385 (4)	−2211 (4)	8623 (3)	134 (2)

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (II)

O(1)–C(2)	1·410 (5)		
C(2)–C(3)	1·499 (7)	C(3)–O(4)	1·408 (6)
O(4)–C(5)	1·424 (5)	C(5)–C(6)	1·483 (8)
C(6)–O(7)	1·424 (6)	O(7)–C(8)	1·430 (6)
C(8)–C(9)	1·487 (8)	C(9)–O(10)	1·407 (6)
C(2)–O(1)–C(2′)*	112·9 (5)	O(1)–C(2)–C(3)	109·3 (4)
C(2)–C(3)–O(4)	109·0 (4)	C(3)–O(4)–C(5)	112·1 (3)
O(4)–C(5)–C(6)	108·8 (4)	C(5)–C(6)–O(7)	108·6 (4)
C(6)–O(7)–C(8)	113·7 (4)	O(7)–C(8)–C(9)	108·5 (4)
C(8)–C(9)–O(10)	108·1 (4)	C(9)–O(10)–C(9′)*	111·9 (5)

* C(2′) and C(9′) are related to C(2) and C(9) by the symmetry operation $x, y, 1\frac{1}{2}-z$.

corresponding N—H—Cl angles are 158 and 162° at H(1*d*) and H(2*d*) respectively. The H(1*d*)···Cl···H(2*d*) angle is 122°. The nitrogen atom N(1) lies 0·96 (1) Å from the mean plane of the six O atoms in macrocycle *A* while the nitrogen atom N(2) lies 1·01 (1) Å from the mean plane of the six O atoms in macrocycle *B*, *cf.* the displacement of 0·84 Å for the N atom from the mean plane of the macrocyclic O atoms in [NH_4.18C6.2H_2O][Br] (Nagano, Kobayashi & Sasaki, 1978). The angle between the normals to the mean planes of the six O atoms in macrocycles *A* and *B* of (I) is 119°. The PF_6^- anion is not involved in any intermolecular interactions other than van der Waals. The shortest intermolecular contact between this anion and the complex is 3·37 (1) Å to C(14). Similarly, the shortest contact to the included CH_2Cl_2 molecule is 3·36 (1) Å between one of its Cl atoms and O(22) on macrocycle *B*.

Table 3 lists the fractional atomic coordinates of the non-hydrogen atoms and Table 4 the bond lengths and angles for (II). The structure of (II), which is illustrated in Fig. 2 along with the atomic numbering scheme, is isostructural with that already described in the literature (Nagano *et al.*, 1978) for [NH_4.18C6.2H_2O][Br]. The Cl, N and two ether oxygen atoms [O(1) and O(10)] lie in a crystallographic mirror plane. In complexing with the NH_4^+ cation, the 18C6 macrocycle once again adopts (Fig. 2) its conventional all-*gauche* conformation with pseudo D_{3d} symmetry (Goldberg, 1980; Wipff *et al.*, 1982) with a perching arrangement (Cram & Trueblood, 1981; Trueblood *et al.*, 1982) for the cation. The torsion angles lie in the range 67–70 (1)° for |O—C—C—O| and 171–179 (1)° for |C—C—O—C|. An upper triangle of O atoms which can be identified as O(4), O(4′) and O(10) form [N^+—H···O] hydrogen bonds with N^+···O distances of 2·91 (1), 2·91 (1) and 2·90 (1) Å respectively. The N—H—O angles at H(*a*′), H(*a*) and H(*b*) are all 169°. The angles between the COC planes and the HO vectors are 25, 25 and 12° for H(*a*′), H(*a*) and H(*b*) respectively. The N atom is displaced 1·07 Å from the mean plane of the six macrocyclic oxygen atoms. An investigation of the role played by the Cl^- anions and the H_2O molecules in the structure of (II) reveals a feature previously not alluded to in the reported structure (Nagano *et al.*, 1978) of [NH_4.18C6.2H_2O]-[Br]. Fig. 3 illustrates the important function of the Cl^- anions and the H_2O molecules which combine to form an elegant polymeric chain of hydrogen bonds that link

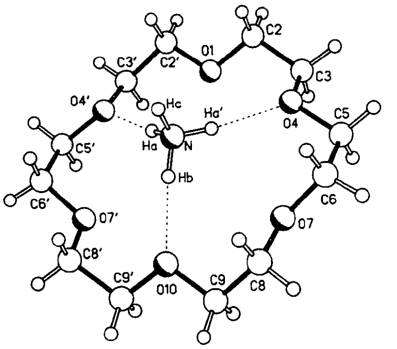

Fig. 2. Ball-and-stick representation of the structure of (II) showing the atomic numbering scheme. Hydrogen bonds are indicated by dashed lines.

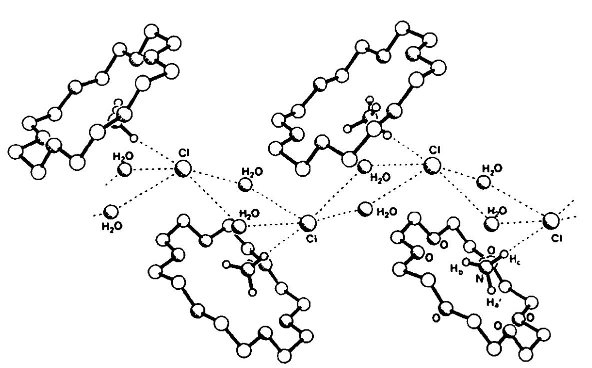

Fig. 3. The structure of (II) showing the polymeric hydrogen-bonded chains involving the NH_4^+ cations, the Cl^- anions and the H_2O molecules. Hydrogen bonds are indicated by dashed lines.

crystallographically glide-related $[NH_4.18C6]^+$ ions along the **a** direction in the crystal. Hydrogen-bond distances are: 3·25 (1) Å for $N^+\cdots Cl$, with an $N^+—H(c)\cdots Cl$ angle of 168°, and 3·25 (1) and 3·26 (1) Å respectively for $Cl^-\cdots OH_2$ and $Cl'^-\cdots OH_2$. The distance between the O atoms of the water molecules H_2O and H_2O' is 3·36 (1) Å.

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Structure of 1α,3α-Trimethylene-2′,5-epoxyandrostane-3β,17β-diol 17-Propionate Methanol Solvate (1/0·5)

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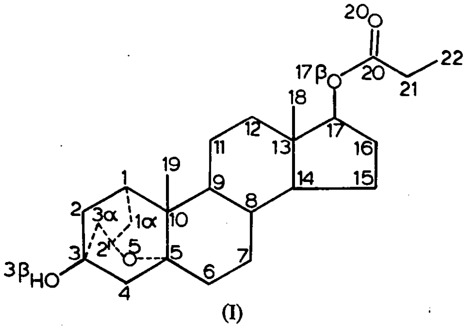
Abstract. $C_{25}H_{38}O_4.0\cdot5CH_4O$, $M_r = 418\cdot6$, monoclinic, $P2_1$, $a = 19\cdot8504$ (20), $b = 7\cdot3909$ (4), $c = 15\cdot7998$ (18) Å, $\beta = 93\cdot09$ (2)°, $V = 2314\cdot7$ (8) Å^3, $Z = 4$, $D_x = 1\cdot201$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 0\cdot604$ mm^{-1}, $F(000) = 916$, $T = 295$ K, $R = 0\cdot056$ for 4946 unique observed reflections. The crystallographic asymmetric unit contains two steroid molecules and a molecule of methanol. All six-membered rings for both molecules have chair conformations. The *D* ring has a 13β-envelope conformation in molecule 1 and a 13β,14α-half-chair conformation in molecule 2. The most significant differences between the crystallographically independent steroids are in the orientation of the H atoms of the C(3) hydroxyl groups and the conformations of the propionate side chains. When the crystallographically observed molecules are subjected to energy minimization their respective hydroxyl H-atom orientations are retained, but the *D* rings of both molecules refine to a common 13β,14α-half-chair conformation and a significantly different orientation of the C(17) propionate side chain is generated. A comparison with other C(17)-ester-bearing steroids suggests that the energy minimization fails to simulate fully all intramolecular interactions.

Introduction. The title compound (I) is a product of the Michael addition reaction of ethyl acetoacetate and 3-oxoandrosta-1,4,6-trien-17β-yl propionate. Although UV, IR, ^{1}H NMR, and mass spectroscopy spectra were consistent with an oxaadamantane structure, a strained structure with a β-side addition could not be ruled out. This is the first oxaadamantane steroid for which the crystal structure has been determined.



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