On the basis of the intermolecular distances, the crystal structure is stabilized by van der Waals interactions only. Enantiomeric disorder is sufficient to create a statistical centre of inversion, whereas the rotational disorder was not anticipated.

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Bis(hydronium dichloropicrate)–1,4,7,10,13,16-Hexaoxacyclooctadecane Complex, $2[H_3O^+.C_6(NO_2)_3Cl_2O^-].(CH_2CH_2O)_6$

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Abstract. $M_r = 896{\cdot}35$, monoclinic, $P2_1/a$, $a = 8{\cdot}369\,(3)$, $b = 25{\cdot}538\,(6)$, $c = 9{\cdot}562\,(2)$ Å, $\beta = 110{\cdot}12\,(2)°$, $Z = 2$, $V/Z = 959{\cdot}5\,(8)$ Å^3, $D_x = 1{\cdot}551\,(1)$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 4{\cdot}06$ cm^{-1}, $F(000) = 920$, $T = 297\,(2)$ K, $R = 0{\cdot}056$ for 1618 reflections. The complex is centrosymmetric with the two hydronium ions weakly hydrogen bonded to O atoms of the crown ether (18-crown-6) and strongly hydrogen bonded to a dichloropicrate anion. The hydronium-ion positions are disordered. There are no unusual bond distances or angles.

Introduction. In the course of studying possible analytical uses of crown ethers (Kolthoff, Wang & Chantooni, 1983; Chantooni, Wang & Kolthoff, 1984) the title compound was prepared. A study of the binding of the two hydronium ions to the 18-crown-6 was the objective of this paper.

Experimental. The compound was prepared in water by precipitation of dichloropicric acid with an equivalent of hexaoxacyclooctadecane (18-crown-6). Crystals suitable for the diffraction experiments were obtained. D_m not measured. Crystal $0{\cdot}1 \times 0{\cdot}15 \times 0{\cdot}4$ mm cut from a larger crystal and coated with a thin layer of epoxy cement to prevent loss of water. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. 22 reflections with $11° < \theta < 16°$ to determine the cell parameters. Systematic extinctions ($0k0$, k odd; $h0l$, h odd) uniquely determined space group $P2_1/a$. Data collected in the range $0° < \theta < 25°$ for one quadrant (ranges: h, 0 to 9; k, 0 to 30; l, -11 to 11). 3369 unique reflections measured; 1618 with $I > \sigma(I)$ used in the calculations. Three check reflections measured every 5000 s of exposure time showed no systematic change with time. No absorption corrections; ψ scans were run, max. variation in intensity 4%. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined with full-matrix least-squares refinement of F's. Secondary-extinction coefficient $1{\cdot}23\,(3) \times 10^{-7}$ included in the refinement. Methylene H atoms placed at idealized positions with fixed isotropic thermal parameters and not refined. Hydronium H atoms could not be located, presumably due to the disorder, and were not included. All remaining atoms given anisotropic thermal parameters. The O of a hydronium ion was found to be distributed over two positions and was included with partial occupancy at each position such that the total occupancy was $1{\cdot}00$; the occupancy was $0{\cdot}55\,(2)$ for OW(1), $0{\cdot}45\,(2)$ for OW(2). Refinement converged

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Table 1. *Atomic coordinates, e.s.d.'s and equivalent isotropic thermal parameters*

$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$

	x	y	z	B_{eq}(Å^2)
Cl(3)	0·1597 (2)	0·29586 (7)	0·4398 (1)	5·9
Cl(5)	0·1904 (2)	0·19082 (5)	0·9346 (2)	5·0
O(1)	0·2551 (5)	0·3865 (1)	0·9393 (3)	5·1
O(2*A*)	0·3218 (6)	0·4075 (2)	0·6090 (6)	17·5
O(2*B*)	0·0784 (7)	0·4179 (2)	0·5982 (7)	12·9
O(4*A*)	0·3149 (5)	0·1822 (2)	0·6182 (5)	9·7
O(4*B*)	0·0508 (5)	0·1784 (2)	0·5687 (5)	8·7
O(6*A*)	0·1109 (5)	0·3017 (2)	0·1078 (4)	8·2
O(6*B*)	0·3778 (5)	0·2918 (2)	0·1714 (4)	7·3
O(3*C*)	0·0768 (5)	0·0523 (1)	0·2635 (4)	5·4
O(6*C*)	0·2556 (4)	0·0808 (1)	0·0667 (4)	5·2
O(9*C*)	0·2347 (4)	0·0064 (1)	−0·1565 (4)	5·0
O*W*(1)	0·3183 (9)	0·4741 (2)	0·8915 (7)	6·1
O*W*(2)	0·4281 (9)	0·4552 (3)	0·8838 (8)	4·5
N(2)	0·2039 (6)	0·3919 (2)	0·6262 (5)	5·9
N(4)	0·1837 (5)	0·1997 (2)	0·6211 (5)	4·8
N(6)	0·2389 (5)	0·2963 (2)	1·0808 (4)	4·4
C(1*R*)	0·2327 (6)	0·3436 (2)	0·8578 (5)	3·7
C(2*R*)	0·2106 (6)	0·3419 (2)	0·7061 (5)	3·7
C(3*R*)	0·1926 (6)	0·2961 (2)	0·6267 (5)	3·7
C(4*R*)	0·1924 (6)	0·2495 (2)	0·7000 (5)	3·4
C(5*R*)	0·2031 (6)	0·2485 (2)	0·8482 (5)	3·6
C(6*R*)	0·2243 (6)	0·2954 (2)	0·9220 (5)	3·5
C(1*C*)	−0·1555 (8)	0·0114 (2)	0·3043 (6)	6·3
C(2*C*)	−0·0663 (8)	0·0611 (2)	0·3060 (6)	5·6
C(4*C*)	0·1754 (8)	0·0989 (2)	0·2765 (7)	6·5
C(5*C*)	0·3180 (8)	0·0887 (3)	0·2203 (7)	6·8
C(7*C*)	0·3898 (7)	0·0703 (2)	0·0107 (8)	6·6
C(8*C*)	0·3154 (7)	0·0555 (2)	−0·1474 (7)	6·9

with $wR = 0·059$ and $S = 1·674$; $w = 1/\sigma^2(F)$ calculated from $\sigma^2(I) = \sigma^2(I_c) + (0·04I)^2$, where $\sigma(I_c)$ is the standard deviation in I based on the counting statistics alone. In the final cycle of refinement $(\Delta/\sigma)_{max} = 0·12$ for positional parameters and 0·34 for thermal parameters. Extreme variation from zero on final difference Fourier synthesis 0·177 e Å^{-3}. The three largest peaks were in the neighborhood of the $NO_2(2)$ group. These peaks plus the unusually large thermal motion of the O(2*A*) and O(2*B*) atoms suggest that this group is also disordered, rather than just vibrating with a large amplitude; attempts to refine the O atoms in disordered positions, however, gave no improvement in the results. The next six highest peaks were in the neighborhood of O*W*(1) and O*W*(2). One of these was 1·1 Å from O(1) and 1·3 Å from O*W*(1) with an O(1)—peak—O*W*(1) angle of 157°, and a second was 1·2 Å from O(1) and 1·3 Å from O*W*(2) with an O(1)—peak—O*W*(2) angle of 158°. Since these were only two of six similar peaks and in the presence of disorder, it did not seem warranted to try to refine them nor to attach any particular significance to the distances. Atomic scattering factors and anomalous-dispersion corrections for all atoms from *International Tables for X-ray Crystallography* (1974). All computer programs from the Enraf–Nonius *Structure Determination Package*, described by Frenz (1978).

Discussion. The final positional parameters and the equivalent isotropic thermal parameters are given in Table 1.* The molecular ensemble of two dichloropicrate ions, one crown ether, and two hydronium ions is located at a crystallographic center of symmetry. Fig. 1 shows a complete crown ether (without H atoms), one dichloropicrate ion, and one hydronium ion (in its two disordered positions) along with the labeling of the atoms. Fig. 2 shows the complete ensemble in stereoscopic projection; the ellipsoids are drawn with 50% probability boundaries.

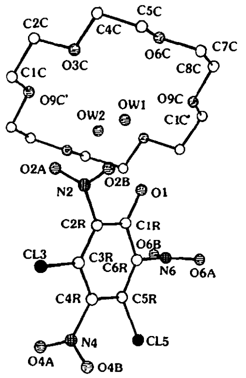

Fig. 1. Atom labeling. One asymmetric unit plus the symmetry-related remainder of the crown-ether ring are shown in the same orientation as in the lower half of Fig. 2. H atoms are omitted for clarity.

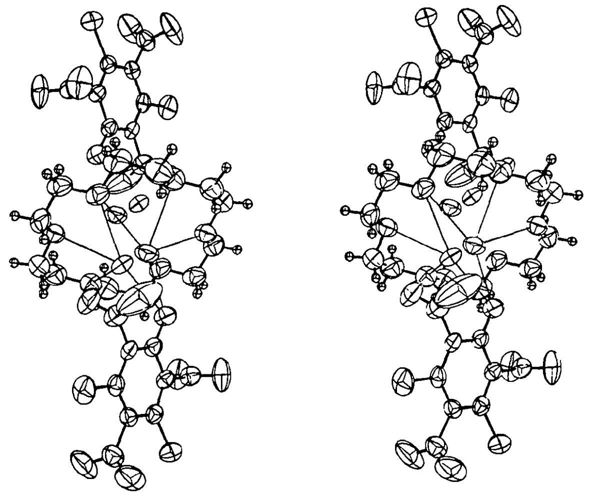

Fig. 2. Stereodrawing of $C_6H_{12}O_2.(H_3O^+.PiCl_2^-)_2$ showing the thermal ellipsoids, the assumed H-atom positions, and the hydrogen bonds (light line) between the picrate O atom, the hydronium ions in both disordered positions, and the crown-ether O atoms.

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* Tables of H-atom parameters, anisotropic thermal parameters, torsion angles in the crown ether, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39468 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°) *with e.s.d.'s*

C(1C)—C(2C)	1·471 (7)	C(2R)—N(2)	1·479 (6)
C(2C)—O(3C)	1·409 (6)	C(4R)—N(4)	1·468 (5)
O(3C)—C(4C)	1·428 (6)	C(6R)—N(6)	1·482 (5)
C(4C)—C(5C)	1·491 (7)	N(2)—O(2A)	1·127 (6)
C(5C)—O(6C)	1·394 (6)	N(2)—O(2B)	1·194 (6)
O(6C)—C(7C)	1·425 (6)	N(4)—O(4A)	1·194 (5)
C(7C)—C(8C)	1·473 (8)	N(4)—O(4B)	1·184 (4)
C(8C)—O(9C)	1·413 (6)	N(6)—O(6A)	1·193 (5)
O(9C)—C(1C′)	1·413 (6)	N(6)—O(6B)	1·192 (5)
C(1R)—C(2R)	1·399 (5)	O(1)···OW(1)	2·378 (7)
C(2R)—C(3R)	1·374 (6)	O(1)···OW(2)	2·497 (7)
C(3R)—C(4R)	1·383 (6)		
C(4R)—C(5R)	1·389 (6)		
C(5R)—C(6R)	1·372 (6)	OW(1)···O(3C)	2·803 (7)
C(6R)—C(1R)	1·386 (6)	OW(1)···O(6C)	2·854 (7)
		OW(1)···O(9C)	2·841 (7)
C(1R)—O(1)	1·321 (5)		
C(3R)—Cl(3)	1·713 (4)	OW(2)···O(3C)	2·845 (7)
C(5R)—Cl(5)	1·709 (4)	OW(2)···O(6C′)	2·850 (9)
		OW(2)···O(9C′)	2·894 (8)
O(9C′)—C(1C)—C(2C)	110·5 (5)		
C(1C)—C(2C)—O(3C)	109·8 (4)	C(1R)—O(1)···OW(1)	131·5 (6)
C(2C)—O(3C)—C(4C)	111·5 (4)	C(1R)—O(1)···OW(2)	116·3 (6)
O(3C)—C(4C)—C(5C)	109·5 (4)	O(1)···OW(1)···O(3C)	154·6 (6)
C(4C)—C(5C)—O(6C)	110·5 (5)	O(1)···OW(1)···O(6C)	142·9 (6)
C(5C)—O(6C)—C(7C)	111·4 (5)	O(1)···OW(1)···O(9C)	89·3 (6)
O(6C)—C(7C)—C(8C)	108·9 (5)		
		O(1)···OW(2)···O(3C)	145·5 (6)
C(7C)—C(8C)—O(9C)	108·4 (5)	O(1)···OW(2)···O(6C′)	98·7 (7)
C(8C)—O(9C)—C(1C′)	113·3 (4)	O(1)···OW(2)···O(9C′)	152·9 (7)
C(6R)—C(1R)—C(2R)	115·1 (4)	O(2A)—N(2)—O(2B)	121·2 (6)
C(1R)—C(2R)—C(3R)	123·3 (4)	O(4A)—N(4)—O(4B)	123·8 (5)
C(2R)—C(3R)—C(4R)	118·2 (4)	O(6A)—N(6)—O(6B)	125·3 (5)
C(3R)—C(4R)—C(5R)	121·5 (4)		
C(4R)—C(5R)—C(6R)	117·4 (4)	C(2R)—C(1R)—O(1)	125·3 (4)
C(5R)—C(6R)—C(1R)	124·4 (4)	C(6R)—C(1R)—O(1)	119·6 (4)

Interatomic distances and angles are given in Table 2. The crown ether occurs in the approximate D_{3d} conformation previously found, for example, in the KNCS, RbNCS, and CsNCS complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974) with normal bond distances and angles; the torsion angles are all close to 69° about the C—C bonds and near 180° about the C—O bonds. The dichloropicrate ion also has normal bond distances and angles. In particular, the large deviations from 120° found in the ring angles are just those to be expected from the substituents on the ring (Norrestam & Schepper, 1978, 1981; Domenicano & Murray-Rust, 1979; Murray-Rust, 1982).

The details of the bonding between the crown ether, hydronium ions and dichloropicrate ions, which were the reason for undertaking the structure determination, are confused by the disorder. The broad outline appears to be clear, however. Dichloropicric acid is a relatively strong acid with K_a near 1. Virtually complete transfer of the proton from the acid to the water can be assumed. Each H_3O^+ ion forms a strong hydrogen bond with the phenolate oxygen of an adjacent dichloropicrate ion, as indicated by the short O(1)···O*W*(1) and O(1)···O*W*(2) distances 2·38 (1) and 2·50 (1) Å, respectively. The remaining two H atoms on an H_3O^+ then form weaker hydrogen bonds to O atoms in the crown ether. Each of the two O*W* positions is 2·8–2·9 Å from three of the crown ether O atoms, and none of the O(1)···O*W*···O(*C*) angles is close to tetrahedral. Although we have refined the structure as if there were two positions for each hydronium ion, it seems more likely that there is a series of positions for the hydronium ion where it is strongly bound to the O(1) atom and weakly bound to two of the ring O atoms. This range of possibilities cannot be sorted out from the anisotropic motion of the hydronium O atom. Two other recently determined structures should be compared to this one. In a complex of a tetracarboxy-18-crown-6 ether with H_3OCl (Behr, Dumas & Moras, 1982) the Cl^- ion does not hydrogen bond to the H_3O^+, leaving the latter free to form three stronger hydrogen bonds (distances ~2·7 Å) to the crown ether. Instead, Cl^- is hydrogen bonded to the carboxyl groups. In the complex of 18-crown-6 ether with 4,4′-biphenyldiol and water (Grossie, Watson, Vögtle & Müller, 1982) a structure similar to that reported here occurs with each crown ether ring bound to two water molecules which are bound in turn to OH groups of the phenyl rings. The difference is that this structure is ordered. The hydrogen bond to the phenol is weaker (longer, 2·67 Å) than ours, presumably with the $H_2O\cdots HO$ arrangement rather than $H_3O^+\cdots O^-$, and the hydrogen bonds to the crown ether also appear weaker (longer, 2·9 Å).

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Note added in proof: Watson, Galloy, Grossie, Vögtle & Müller (1984) have reported the structures of six complexes of neutral molecules with 18-crown-6. One of these, the complex with 3-nitrophenol, is structurally similar to the complex reported here. The 2:1 3-nitrophenol–18-crown-6 diaqua complex is essentially that between 3-nitrophenol and hydrated 18-crown-6. There is, however, no disorder and the phenol hydrogen can be seen attached to the phenol.

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Structure of the Antitumour Agent *m*-AMSA (Amsacrine), $C_{21}H_{19}N_3O_3S$, as the Free Base

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Abstract. $M_r = 393{\cdot}5$, monoclinic, $P2_1/c$, $a = 11{\cdot}176\ (3)$, $b = 21{\cdot}142\ (4)$, $c = 8{\cdot}794\ (3)$ Å, $\beta = 112{\cdot}29\ (2)°$, $U = 1922$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ g cm^{-3} (*cf.* 1·39 g cm^{-3} for HCl salt), Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}01$ cm^{-1}, $F(000) = 824$, $T = 256$ K, $R = 0{\cdot}041$ using 1478 reflections. In the acridine moiety the four outer C atoms are displaced to the same side, with the two central atoms displaced in the opposite direction. The phenyl ring is more nearly planar. The molecular geometry is compared with that of the HCl salt and other derivatives.

Introduction. The antitumour agent 4′-(9-acridinylamino)-3′-methoxymethanesulphonanilide (*m*-AMSA)† has shown dramatic activity against some tumours in clinical trials (Legha *et al.*, 1978; Von Hoff *et al.*, 1978). Its mode of action has been the subject of extensive investigations and it is known to react with DNA (Waring, 1976; Gormley, Sethi & Cysyk, 1978; Deaven, Oka & Tobey, 1978). As a class the 9-anilinoacridines are intercalating agents although their biological activity depends critically on substitution requiring, especially, electron-releasing substituents at the aniline 1′-position. The exact significance of the total substituent requirement is not, however, known. We report the structure of *m*-AMSA itself for comparison with the hydrochlorides of AMSA (which although active lacks the 3′-methoxy group) (Hall, Swann & Waters, 1974) and *m*-AMSA and with the methanesulphonate salt of the 2-methoxy substituent of AMSA (Karle, Cysyk & Karle, 1980).

Experimental. Crystals grown as orange, diamond-shaped plates by slow evaporation from methanol. D_m not measured. CAD-4 diffractometer, Mo $K\alpha$ radiation. 3675 reflections collected, 1478 with $I > 3\sigma(I)$ used; $\omega/2\theta$ mode, *hkl* range 0–12, 0–24, $\overline{10}$–10, θ limit 25°; scan range $\theta = (0{\cdot}80 + 0{\cdot}35\tan\theta)°$ was extended by 25% on either side of the peak to record backgrounds; scan speed chosen to return a constant $\sigma(I)$ of $0{\cdot}02I$ with a maximum scan time set at 100 s. Three standard reflections recorded every 3600 s and three orientation-control reflections after every 100 measurements: no significant changes in standards or controls. Standard deviations determined from counting statistics but $\sigma(F_o^2) = [\sigma^2(I) + (fI)^2]^{1/2}/\mathrm{Lp}$ with a modifying factor, $f_{,} = 0{\cdot}04$. Weights $1/\sigma^2(F_o)$, *i.e.* $4F_o^2/\sigma^2(F_o^2)$, applied in later least-squares minimization of $\sum w(|F_o| - |F_c|)^2$. Crystal: rectangular plate, developed in $\{001\}$, dimensions $0{\cdot}34 \times 0{\cdot}42 \times 0{\cdot}11$ mm. Absorption corrections not applied. Systematic absences *h*0*l* (*l* odd) and 0*k*0 (*k* odd). Structure solved with the phase-determining program *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement [calculations with Enraf–Nonius *SDP* package and with a program derived from *ORFLS* (Busing, Martin & Levy, 1962)] of 253 variables of atomic positions (excluding H atoms) and anisotropic temperature parameters (not H atoms) brought R to 0·041 and R_w to 0·048. Atom scattering factors and anomalous-dispersion coefficients from Cromer & Waber (1974) and Cromer (1974). E.s.d. of an observation of unit weight 1·432; $(\Delta/\sigma)_{\max} = 0{\cdot}3$. Final $\Delta\rho$ map showed no residual density. No correction for secondary extinction.

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† The compound is now known as amsacrine but the older nomenclature is retained here because of the comparisons made with other AMSA derivatives.

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