Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The hydrogen-bonded adduct 7,16-diazonia-18-crown-6–4-aminobenzenesulfonate–water (1/2/2)

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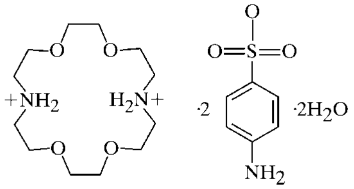
Received 2 January 2003
Accepted 15 January 2003
Online 31 January 2003

In the title hydrated adduct, 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(4-aminobenzenesulfonate) dihydrate, $C_{12}H_{28}N_2O_4^{2+}\cdot 2C_6H_6NO_3S^-\cdot 2H_2O$, formed between 7,16-diaza-18-crown-6 and the dihydrate of 4-aminobenzenesulfonic acid, the macrocyclic cations lie across centres of inversion in the orthorhombic space group *Pbca*. The anions alone form zigzag chains, and the cations and anions together form sheets that are linked *via* water molecules and anions to form a three-dimensional grid.

Comment

Nitrogen-containing crown ethers merit considerable attention for their host behaviour as receptors for anions and neutral organic molecules (Goldberg, 1984; Lehn, 1995; Vögtle & Weber, 1985). These receptors are capable of being included in the extended supramolecular networks formed by self-assembled organic molecules, rich in both hydrogen-donor and hydrogen-acceptor centres, with partial preservation or rearrangement of the hydrogen bonds which sustain the supramolecular architecture.

Diaza-18-crown-6 has attracted our attention as a suitable macrocycle to provide hydrogen-bonded frameworks. A search of the Cambridge Structural Database (CSD, April 2002 release; Allen, 2002) yielded a list of 17 entries covering complexes of 7,16-diazonia-18-crown-6 with different anions and water molecules with extended hydrogen-bonded architectures. The closest crown environment that includes both water molecules and anions in an inversion symmetry-related fashion is found in the 7,16-diazonia-18-crown-6 hydrates with tetrahydroxypentaborate (Chekhlov & Martynov, 1998), a 1,10-dioate derivative (Chekhlov, 2000) and hydrogen sulfate (Chekhlov, 1995). Another route for macrocyclic cation coordination also exists when the anions (formate, tartrate, hydrogen tartrate, sulfate) are bound directly to the macrocycle *via* hydrogen bonds, while the water molecules are not involved in direct contacts with the macrocycle but bridge the anions in the chains (Chekhlov, 1999; Chekhlov & Martynov, 1999*a*,*b*; Chekhlov, 1996). 7,16-Diaza-18-crown-6 and the dihydrate of 4-aminobenzenesulfonic acid form the title hydrated salt, (I), the structure of which is presented here.



(I)

The centrosymmetric formula unit of (I) is shown in Fig. 1. This salt crystallizes in space group *Pbca* with $Z = 4$. The macrocyclic cation adopts a C_i conformation and lies across a centre of inversion. The water molecule acts as a double donor, using O—H···O hydrogen bonds between the crown cation and the anion (Table 1), and as a single acceptor in N—H···O hydrogen bonds with the crown cation. The 4-aminobenzenesulfonate anion and the macrocyclic cation are arranged in a T-shaped mode, with the dihedral angle between the mean planes of the aromatic ring and the six-membered set of N and O atoms of the crown ether being 80.63 (6)°.

It is possible to identify one-component hydrogen-bonded zigzag chains built from the anions running along the [100] direction. The amino atom N11 of the anion at the original position forms a weak hydrogen bond with atom O11 of the anion at ($\frac{1}{2} + x$, y, $\frac{1}{2} - z$), with an N11···O11 distance of 3.052 (5) Å and the angle subtended at the H atom being 168 (3)°.

Each anion in the self-assembled chain interacts with the macrocyclic cation *via* the same atom O11, with an N1···O11 distance of 2.920 (3) Å [the angle subtended at the H atom is 175 (3)°]. The anionic chains and the cations attached to them generate sheets running parallel to the (101) plane (Fig. 2). These sheets are built from the centrosymmetric six-membered fused rings that combine two cations and four anions, each component being shared between two neighbouring rings.

The water molecules are located 1.702 (2) Å above and below the macrocyclic cavity and are bound to the macrocycle *via* the above-mentioned O—H···O and N—H···O hydrogen bonds (Table 1). The water molecule acts as a hydrogen-bond donor to sulfonate atom O12 of the anion related to that at the origin by a twofold screw axis, with an O1*W*···O12($\frac{3}{2} - x, y - \frac{1}{2}$, z) distance of 2.764 (3) Å [the angle subtended at the H atom is 161 (3)°], and functions as a bridge between adjacent sheets, consolidating them into a three-dimensional network. The architecture of (I) strictly resembles that of 7,16-diazonia-18-crown-6 bis(hydrogen sulfate) dihydrate (Chekhlov, 1995).

DOI: 10.1107/S010827010300129X

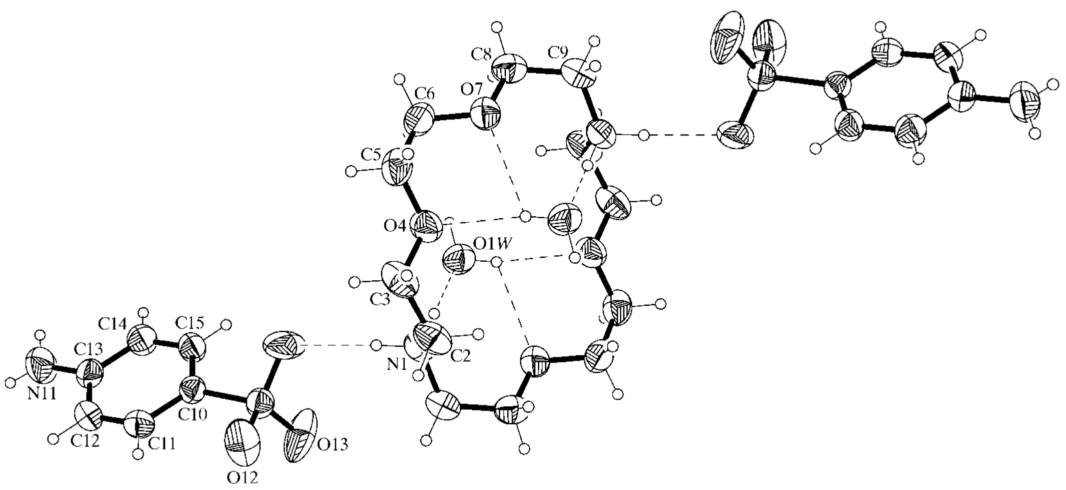


Figure 1

The structure of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the asymmetric unit is numbered. The minor site of the disordered SO_3 group has been omitted for clarity.

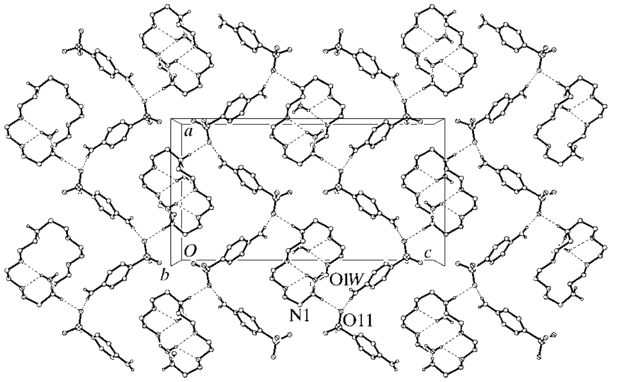


Figure 2

Part of the crystal structure of (I), showing the (101) sheets formed by the hydrogen-bonded anions and cations. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

For the preparation of the title compound, diaza-18-crown-6 (52.4 mg, 0.02 mmol) and 4-$H_2NC_6H_4SO_3H$ (83.6 mg, 0.04 mmol) were dissolved in a mixture of water (1.5 ml), methanol (2 ml) and *n*-butanol (4 ml). The resulting clear solution was reduced slowly in volume by evaporating the solvents at room temperature. Crystals of (I) [yield: 85% (110 mg); m.p. 498–500 K] suitable for X-ray analysis were selected directly from the analytical sample. Analysis, found: C 44.73, H 6.85, N 8.74%; $C_{24}H_{44}N_4O_{12}S_2$ requires: C 44.71, H 6.88, N 8.69%.

Crystal data

$C_{12}H_{28}N_2O_4^{2+}\cdot 2C_6H_6NO_3S^{-}\cdot 2H_2O$
$M_r = 644.75$
Orthorhombic, *Pbca*
$a = 12.319\ (2)$ Å
$b = 10.976\ (2)$ Å
$c = 22.826\ (4)$ Å
$V = 3086.4\ (9)$ Å^3
$Z = 4$
$D_x = 1.388$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5186 reflections
$\theta = 1.0$–$25.0°$
$\mu = 0.24$ mm^{-1}
$T = 293\ (2)$ K
Plate, white
$0.25 \times 0.15 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans
5052 measured reflections
2730 independent reflections
1821 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.2°$
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.118$
$S = 1.04$
2730 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.3407P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0081 (9)

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O11	0.94 (2)	1.99 (2)	2.920 (3)	175 (3)
N1—H1N···O11A	0.94 (2)	2.02 (3)	2.84 (2)	146 (3)
N1—H2N···O1W	0.95 (2)	1.84 (2)	2.778 (3)	170 (3)
O1W—H2W···O4$^{\rm i}$	0.83 (2)	2.11 (3)	2.933 (3)	170 (3)
O1W—H2W···O7$^{\rm i}$	0.83 (2)	2.39 (3)	2.848 (3)	115 (3)
O1W—H1W···O12$^{\rm ii}$	0.84 (2)	1.95 (2)	2.764 (3)	161 (3)
O1W—H1W···O12$A^{\rm ii}$	0.84 (2)	2.21 (4)	2.88 (2)	136 (3)
N11—H11N···O12$^{\rm iii}$	0.87 (3)	2.66 (3)	3.407 (5)	146 (3)
N11—H11N···O12$A^{\rm iii}$	0.87 (3)	1.84 (4)	2.682 (17)	162 (3)
N11—H12N···O11$^{\rm iv}$	0.82 (4)	2.25 (4)	3.052 (5)	168 (3)
N11—H12N···O11$A^{\rm iv}$	0.82 (4)	2.47 (4)	3.25 (2)	161 (3)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (iii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, y, \frac{1}{2}-z$.

Anisotropic displacement parameters were used for all non-H atoms except the O atoms of the minor site of the SO_3 group. This group was found to be disordered over two sites rotated about the C—S axis, with occupancy factors of 0.932 and 0.068. The major site was refined with anisotropic displacement parameters and the minor site was treated with SADI (*SHELXL*97; Sheldrick, 1997) restraints for three S—O distances and a group-value isotropic displacement parameter. The coordinates of the H atoms on atoms N1, N11 and O1*W* were determined from a difference map and were then allowed to refine isotropically subject to a DFIX (*SHELXL*97) restraint. All other H atoms were refined as riding, with C—H distances in the range 0.93–0.97 Å.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*III (Farrugia, 1997); software used to prepare material for publication: *SHELXS*97.

Financial support from the MRDA–CDRF (research grant MP2-3021) is gratefully acknowledged. The diffraction data were collected at the Department of Chemistry, Technion, Haifa, through the co-operation of Professor Menahem Kaftory, whom the authors would like to acknowledge.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1151). Services for accessing these data are described at the back of the journal.

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