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# Aminosulfuric Acid: An Excellent Guest for Crown Ether Complexation. Crystal Structure of the 1 : 1 : 1 Molecular Complex between Aminosulfuric Acid, Water and 18,19-Benzo-1,16-Diaza-4,7,10,13-Tetraoxacycloeicosa-17,20-Dione

YURII A. SIMONOV* and MARINA S. FONARI
*Institute of Applied Physics of the Academy of Sciences of Moldova, Academicheskaya 5, Kishinev 277028, Moldova.*

JANUSZ LIPKOWSKI
*Institute of Physical Chemistry, Polish Academy of Sciences, 01-244 Warsaw, Poland.*

and

EDWARD V. GANIN
*Institute of Environmental and Human Protection at Odessa State University, Odessa 270100, Ukraine.*

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**Abstract.** The twenty-membered macrocycle, 18,19-benzo-1,16-diaza-4,7,10,13-tetraoxacycloeicosa-17,20-dione, $C_{18}H_{26}N_2O_6$ (**1**), aminosulfuric acid and water form a stoichiometric 1 : 1 : 1 inclusion compound. The crystal structure of $[\mathbf{1}\cdot NH_3^+SO_3^-]\cdot H_2O$ has been determined by X-ray crystallography. The crystal is monoclinic, space group $P2_1/c$, $a = 7.967(1)$, $b = 13.447(3)$, $c = 20.779(4)$ Å, $\beta = 90.20(2)$ Å; $Z = 4$. The final $R$-value is 0.0434 for 4638 unique reflections with $I > 2\sigma(I)$. The structure consists of the 1 : 1 molecular complexes between the crown host and aminosulfuric acid revealing hydrogen bonding with the ligand ether and carbonyl oxygen atoms. The complexes are united in the layer-like structure by NH···O host–guest and NH···O=C< host–host interactions. The water entity forms the second coordination sphere of the compound. Aminosulfuric acid exists in the complex as the zwitterion.

**Key words:** Host–guest complex structure, modified crown ethers, hydrogen bond, X-ray structure.

**Supplementary Data** relating to this publication have been deposited with the British Library as Supplementary Publication No. 82197 (33 pages) and include: the list of $F_{\mathrm{obs}}$, $F_{\mathrm{calc}}$, tables of anisotropic displacement parameters, and fractional atomic coordinates of hydrogen atoms.

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* Author for correspondence.

## 1. Introduction

The distinctive property of crown ethers is the formation of complexes with cations and uncharged molecules. Aminosulfuric acid, $NH_2SO_2OH$, appeared to us to be a suitable guest for crown ethers with different cavity sizes. Using X-ray techniques, we have investigated complexation in the crown ether – aminosulfuric acid system [1–4].

From the structural analysis it was deduced that the aminoacid exists in the solid state in the zwitterionic form. The interest in this molecule as a guest arises from its borderline position in the zwitterionic form between charged species (metal cations) and neutral organic molecules. Its nature allows one to separate two components of host–guest interactions: the usual $N—H\cdots O$ hydrogen bonds and electrostatic Coulombic interaction between the positively charged $NH_3^+$ end of the guest and the crown ether oxygens. In the complexes of aminosulfuric acid with 18-membered crown ethers (18-crown-6, isomers of dicyclohexano-18-crown-6) three $N—H\cdots O$ hydrogen bonds are formed [1,2].

In the benzo-18-crown-6 complex [2] we observed the tendency of one of these bonds to bifurcate due to the rigidity of the pyrocatechol fragment entering the macrocyclic ring.

15- and 12-membered crown ethers form dimers when complexing aminosulfuric acid [3,4]. Due to this phenomenon not all the guest H-atoms participate in the direct host–guest interactions. In the complex with 12-crown-4 only one H-atom of the zwitterionic guest interacts with the O- atoms of the ring [4]. We believe that in the last complex a system of Coulombic interactions is realized. This means that the complex is organized in a similar way to that observed in the host–guest compound formed between a benzene molecule and the modified dibenzo-18-crown-6 [5]. In these two series of complexes the host undergoes self-organization, resulting in a final conformation similar to that found in complexes with cations.

In modified crown ethers the NH or OH macrocycle H-donor groups are used for complexation. In this case the crown ether not only plays an acceptor role, as with Pedersen's crown ethers, but also a donor function in the H-bonds. The cavity sizes are also important for determining the number of guest molecules bound with the host.

The easily available 1 : 1 complex formed between the title crown and water was synthesized and its structure was determined by X-ray crystallography [6].

It was interesting to compare the crystal structures and complex organization for the title compound and the aquo complex of the same new host and the guests differing by the number of H-donor atoms taking part in host–guest interactions.

## 2. Experimental

### 2.1. PREPARATION OF COMPLEX

During the synthesis of the title crown ether [7] an aquo complex was formed with 1 : 1 stoichiometry. The hydrated form of **1** was maintained in the process of recrystallization of [**1**·$H_2O$] from a 1 : 1 acetone/hexane mixture. The hydrate [**1**·$H_2O$] (384 mg, 1 mmol) was dissolved in 20 mL of boiling methanol followed by addition of the aminosulfuric acid (97 mg, 1 mmol) in aqueous solution (5 mL). The solution was kept at room temperature and allowed to crystallize. Crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of methanol and benzene in 1 : 1 ratio. Colourless, transparent crystals of the complex [**1**·$NH_3SO_3$]·$H_2O$ were obtained. They are soluble in methanol, ethanol, acetone and insoluble in hexane, m.p. 166–168 °C (decomp.). *Anal. Calc.* for $C_{18}H_{31}N_3O_{10}S$ (%): C 44.90; H 6.49; N 8.73; S 6.66. *Found:* C 44.71; H 6.40; N 8.93; S 6.80.

### 2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

A summary of the data collection parameters for the complex at room temperature (293 K) is given in Table I, atomic fractional coordinates in Table II, and bond distances and angles in Table III. Preliminary examination and data collection for [**1**·$NH_3^+SO_3^-$]·$H_2O$ were performed with Cu$K_\alpha$ radiation on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least squares refinement, using a set of angles of 25 reflections in the range of $20 < \theta < 30°$. As a check on crystal stability three reflections were measured every 60 min. The structure was solved by using SHELXS-86 [8] and refined with SHELXL-93 programs [9]. The water molecule was found to occupy the vacancies in the unit cell. Its hydrogen atoms were not localized and the water O atom was refined isotropically. In the host molecule one oxyethylene fragment (—C(2)–C(3)—) is disordered and these atoms were refined in two positions with 80 and 20% occupancy (C(2*), C(3*)), respectively. The structure was refined by a full-matrix least squares method, using the anisotropic variant for non-H atoms and the isotropic one for the disordered C(2*), C(3*) and H atoms. The drawings were made by PLUTO in the CRYSRULLER [10] and ORTEP packages [11].

## 3. Discussion

### 3.1. HYDROGEN BONDING MODE

The molecular structure of the complex [**1**·$NH_3SO_3$]·$H_2O$ is shown in Figures 1a,b. In the host molecule two amide nitrogen atoms, together with the oxygen atoms, form the mixed set of the macrocycle heteroatoms. Analogously to the complexes described ealier, the guest entity enters the complex in the zwitterionic form. S—O distances are in the range 1.415(2)–1.429(2) Å. The positively charged $NH_3^+$ end of

TABLE I. Crystal data and summary of intensity data collection and structure refinement for complex [**1**·$NH_3SO_3$]·$H_2O$.

| | |
|---|---|
| Formula | $C_{18}H_{31}N_3O_{10}S$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Cell parameters | |
| $a$, Å | 7.967(1) |
| $b$, Å | 13.447(3) |
| $c$, Å | 20.779(4) |
| $\beta$, Å | 95.20(2) |
| $V$, Å$^3$ | 2216.9(7) |
| $Z$ | 4 |
| $D_{\text{calc}}$, g cm$^{-3}$ | 1.443(1) |
| Crystal form | Prism |
| Specimen dimensions, mm | 0.2 × 0.3 × 0.4 |
| $\theta$ range for data collection (°) | 3.92–76.48 |
| Diffractometer | CAD-4 |
| Radiation | $\text{Cu}K_\alpha$ ($\lambda = 1.54178$ Å) |
| $\mu$ (mm$^{-1}$) | 1.83 |
| $T$ (K) | 293 |
| Index ranges | $-10 \leq h \leq 10, 0 \leq k \leq 16, 0 \leq l \leq 26$ |
| Number of reflections | |
| Collected | 4772 |
| Independent | 4643 |
| Unique | 4638 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness of fit on $F^2$ | 1.041 |
| No. of variables | 410 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0401, wR2 = 0.1043$ |
| $\Delta\rho_{\text{min}}$ (e Å$^{-3}$) | −0.327 |
| $\Delta\rho_{\text{max}}$ (e Å$^{-3}$) | 0.360 |

the aminosulfuric acid entity is in the perching mode at 1.265 Å above the plane of these six (four oxygen and two nitrogen) atoms (Figure 2). It forms three H-bonds with O atoms of the host: N(1S)···O(4) = 3.059(5), N(1S)···O(10) = 2.944(4) Å and N(1S)···O(2) = 2.681(5). Two of these H-bonds (with O(4) and O(10)) are typical of classical crown ethers; they occur with oxygen atoms separated by the ethylene moiety and are in the range for those mentioned in the literature [12]. The third hydrogen bond is with the carbonyl oxygen atom (O(2)) and is a little shorter than the previous two. Their geometric parameters are given in Table IV. The nitrogen-to-oxygen distances to the remaining two crown oxygen atoms are: N(1S)···O(7) = 2.970(5), N(1S)···O(13) = 3.125(5) Å. Unlike this complex, the aquo complex of **1** is stabilized by two H-bonds with host O atoms: O(1W)···O(7) = 3.015(6), O(1W)···O(13) = 3.006(4) Å. A tripod-like arrangement was achieved

TABLE II. Atomic coordinates ($\times 10^4$) and $U$(eq) ($Å^2 \times 10^3$) for [1·$NH_3SO_3$]·$H_2O$. $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| S(1) | 1289(1) | 7939(1) | 5372(1) | 42(1) |
| N(1S) | 3071(2) | 7154(1) | 5384(1) | 36(1) |
| O(1S) | 1953(2) | 8792(1) | 5708(1) | 69(1) |
| O(2S) | 159(2) | 7353(1) | 5711(1) | 60(1) |
| O(3S) | 835(2) | 8053(2) | 4702(1) | 80(1) |
| O(1) | 5920(2) | 8587(1) | 7315(1) | 56(1) |
| O(2) | 4416(2) | 6867(1) | 6600(1) | 55(1) |
| N(1) | 7359(2) | 8259(1) | 6464(1) | 47(1) |
| C(2) | 6641(4) | 9172(2) | 6142(1) | 42(1) |
| C(2$^*$) | 7562(14) | 9125(7) | 6076(4) | 40(2) |
| C(3) | 7023(3) | 9235(2) | 5449(1) | 42(1) |
| C(3$^*$) | 5890(11) | 9188(6) | 6683(4) | 40(3) |
| O(4) | 5944(2) | 8540(1) | 5085(1) | 54(1) |
| C(5) | 6369(3) | 8579(2) | 4436(1) | 58(1) |
| C(6) | 4953(4) | 8177(2) | 4008(1) | 60(1) |
| O(7) | 4700(2) | 7167(1) | 4154(1) | 46(1) |
| C(8) | 3393(3) | 6737(2) | 3729(1) | 53(1) |
| C(9) | 3322(3) | 5651(2) | 3865(1) | 51(1) |
| O(10) | 2674(2) | 5478(1) | 4471(1) | 42(1) |
| C(11) | 2930(3) | 4466(1) | 4668(1) | 52(1) |
| C(12) | 1974(3) | 4248(1) | 5230(1) | 50(1) |
| O(13) | 2454(2) | 4926(1) | 5741(1) | 45(1) |
| C(14) | 1709(3) | 4644(2) | 6307(1) | 55(1) |
| C(15) | 1981(2) | 5435(2) | 6816(1) | 53(1) |
| N(16) | 3699(2) | 5490(1) | 7121(1) | 43(1) |
| C(17) | 4771(2) | 6210(1) | 7001(1) | 36(1) |
| C(18) | 6464(2) | 6226(1) | 7380(1) | 33(1) |
| C(19) | 7454(2) | 7081(1) | 7356(1) | 35(1) |
| C(20) | 6826(2) | 8026(1) | 7027(1) | 38(1) |
| C(21) | 9012(3) | 7121(2) | 7716(1) | 49(1) |
| C(22) | 9574(3) | 6329(2) | 8101(1) | 56(1) |
| C(23) | 8619(3) | 5484(2) | 8122(1) | 50(1) |
| C(24) | 7074(2) | 5427(1) | 7762(1) | 42(1) |
| O(1W)[#] | 2012(16) | 6804(10) | 2144(6) | 70(3) |

[#] O(1W) was refined in the isotropic approach.

by the water lone pair engagement in the H-bond with the amide N(1) atom, with the distance O(1W)···N(1) = 2.977(5) Å. The remaining two O(1W)···$O_{crown}$ contacts were: O(1W)···O(4) = 3.130(5) and O(1W)···O(10) = 3.197(6) Å. Unlike

TABLE III. Bond lengths [Å] and angles [deg] for [**1**·$NH_3SO_3$]·$H_2O$.

| Atoms | $d$, Å | Atoms | $d$ Å |
|---|---|---|---|
| S(1)—O(3S) | 1.415(2) | C(9)—O(10) | 1.423(2) |
| S(1)—O(1S) | 1.420(2) | O(10)—C(11) | 1.431(2) |
| S(1)—O(2S) | 1.429(2) | C(11)—C(12) | 1.480(3) |
| S(1)—N(1S) | 1.767(1) | C(12)—O(13) | 1.426(2) |
| O(1)—C(20) | 1.235(2) | O(13)—C(14) | 1.416(2) |
| O(2)—C(17) | 1.231(2) | C(14)—C(15) | 1.502(3) |
| N(1)—C(20) | 1.319(2) | C(15)—N(16) | 1.458(3) |
| N(1)—C(2) | 1.488(3) | N(16)—C(17) | 1.329(2) |
| N(1)—C(2*) | 1.434(9) | C(17)—C(18) | 1.499(2) |
| C(2)—C(3) | 1.501(3) | C(18)—C(24) | 1.396(2) |
| C(3)—O(4) | 1.439(3) | C(18)—C(19) | 1.399(2) |
| C(3*)—O(4) | 1.522(9) | C(19)—C(21) | 1.390(2) |
| O(4)—C(5) | 1.420(3) | C(19)—C(20) | 1.506(2) |
| C(5)—C(6) | 1.474(4) | C(21)—C(22) | 1.382(3) |
| C(6)—O(7) | 1.410(2) | C(22)—C(23) | 1.371(3) |
| O(7)—C(8) | 1.424(2) | C(23)—C(24) | 1.384(3) |
| C(8)—C(9) | 1.489(3) | | |

| Atoms | $\omega$, deg | Atoms | $\omega$, deg |
|---|---|---|---|
| O(3S)—S(1)—O(1S) | 116.5(1) | C(14)—O(13)—C(12) | 110.0(2) |
| O(3S)—S(1)—O(2S) | 115.4(1) | O(13)—C(14)—C(15) | 110.5(2) |
| O(1S)—S(1)—O(2S) | 115.2(1) | N(16)—C(15)—C(14) | 114.4(2) |
| O(3S)—S(1)—N(1S) | 102.25(8) | C(17)—N(16)—C(15) | 123.3(2) |
| O(1S)—S(1)—N(1S) | 102.26(9) | O(2)—C(17)—N(16) | 122.5(2) |
| O(2S)—S(1)—N(1S) | 101.80(8) | O(2)—C(17)—C(18) | 119.2(2) |
| C(20)—N(1)—C(2) | 116.9(2) | N(16)—C(17)—C(18) | 118.3(1) |
| C(2*)—C(3*)—O(4) | 108.8(7) | C(24)—C(18)—C(19) | 119.0(2) |
| N(1)—C(2*)—C(3*) | 102.2(7) | C(24)—C(18)—C(17) | 122.5(2) |
| N(1)—C(2)—C(3) | 112.0(2) | C(19)—C(18)—C(17) | 118.5(1) |
| O(4)—C(3)—C(2) | 107.7(2) | C(21)—C(19)—C(18) | 119.4(2) |
| C(5)—O(4)—C(3) | 107.1(2) | C(21)—C(19)—C(20) | 117.1(2) |
| O(4)—C(5)—C(6) | 108.9(2) | C(18)—C(19)—C(20) | 123.0(2) |
| O(7)—C(6)—C(5) | 109.9(2) | O(1)—C(20)—N(1) | 122.3(2) |
| C(6)—O(7)—C(8) | 111.6(2) | O(1)—C(20)—C(19) | 118.7(2) |
| O(7)—C(8)—C(9) | 108.6(2) | N(1)—C(20)—C(19) | 118.8(2) |
| O(10)—C(9)—C(8) | 110.5(2) | C(22)—C(21)—C(19) | 120.6(2) |
| C(9)—O(10)—C(11) | 110.8(1) | C(23)—C(22)—C(21) | 120.3(2) |
| O(10)—C(11)—C(12) | 110.1(2) | C(22)—C(23)—C(24) | 119.9(2) |
| O(13)—C(12)—C(11) | 109.7(2) | C(23)—C(24)—C(18) | 120.7(2) |

complexes with the pyridino crowns, in both these compounds the guest entities are not surrounded by an 18-membered-like environment because both (complex [**1**·$NH_3SO_3$]·$H_2O$) or one (complex [**1**·$H_2O$]) N atoms appeared to be out of the range of possible N···O contacts with N(1S)···N distances greater than 4 Å for the first complex and with a N(16)···O(1W) distance equal to 3.456(5) Å for the latter one. Thus, as mentioned above, the guest molecule interacts in the tripod-like mode with three host oxygen atoms (Table IV). Between the individual host–guest [H–G] complexes there are H-bonds in which host amide nitrogen atoms serve as H-donors. The H–G associates related by translation along the $x$ axis are joined by a weak hydrogen bond between the host amide group and the guest sulphuric group (N(1)···O(2S) = 3.088(4) Å) and a chain is formed in this direction. Another hydrogen bond, between the O(1) and N(16) atoms of the host amide groups equal to 2.820(5) Å, connects the H–G associates related by a screw axis giving rise to a layer-like structure. The H-bonded layers are approximately perpendicular to the '$z$' direction in the crystal. A similar N—H···O H-bond was found in the aquo complex of the title crown ether with an N···O distance equal to N(16)···O(25) = 3.007(6) Å. This H-bond unites the complexes in the zigzag-like chains.

The water molecule forms the second coordination sphere of the complex [H–G] and has three short contacts with it equal to O(1W)···O(1S) = 3.085(6), O(1W)···O(2) = 2.921(5) Å and O(1W)···O(1) = 3.146(5) Å. Disorder of the water molecule could be a reason that the water H atoms could not be localized.

The packing diagram of [**1**·$NH_3SO_3$]·$H_2O$ is illustrated in Figure 3. Schematically the structure might be presented in the following way:

—[ H—G] —[ H—G]—
/ /
$H_2O$ $H_2O$

—[ H—G] —[ H—G]—
/ /
$H_2O$ $H_2O$

### 3.2. HOST CONFORMATION AND GEOMETRY

The macrocyclic host (**1**) consists of a 20-membered heterocyclic cavity fused with the aromatic moiety. The ring conformation is described by the following set of torsion angles: $ag + aag - aag + aag - aag - g + aasg - a$ (their meanings are given in Table V). The C—C bonds apart from C(19)—C(20) (−105.2°) and C(18)—C(19) (6.9°) are in *gauche* conformations with torsion angle values of 56.3–75.1°, C—O torsion angles corresponding to *anti*-conformations have values in the range −159.9–177.7°. Three C—N torsion angles are in *trans*-conformations. One angle, C(15)—N(16) = 106.1°, has a *gauche*-conformation which, together with the neighbouring C(14)—C(15) *gauche*-bond, forms the angular $g + g$ fragment

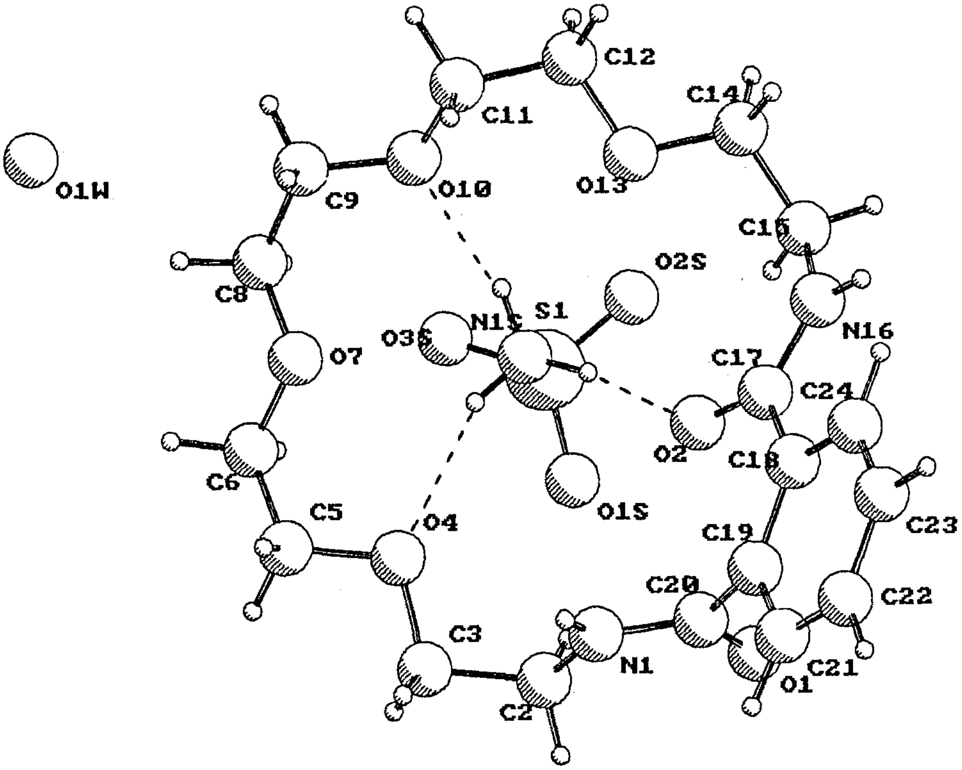

Fig. 1a. Structure of the complex [**1**·$NH_3SO_3$]·$H_2O$ in projection on the plane of the host heteroatoms and atomic numbering scheme. H-bonds are shown as dotted lines.

TABLE IV. H-bond distances and angles in complex [**1**·$NH_3SO_3$]·$H_2O$.

| H-donor (D) | H-acceptor (A) | R(D···A, Å) | R(H···A, Å) | Angle at H-atom | Symmetry code for (A) |
|---|---|---|---|---|---|
| N(1S) | O(2) | 2.681(5) | 1.76 | 171 | $x, y, z$ |
| N(1S) | O(4) | 3.059(5) | 2.24 | 159 | $x, y, z$ |
| N(1S) | O(10) | 2.944(4) | 2.05 | 163 | $x, y, z$ |
| N(1) | O(2S) | 3.088(4) | 2.32 | 127 | $1 + x, y, z$ |
| N(16) | O(1) | 2.820(5) | 2.02 | 153 | $1 - x, -0.5 + y, 1.5 - z$ |
| O(1W)* | O(1S) | 3.085(6) | – | – | $x, 1.5 - y, 0.5 + z$ |
| O(1W)* | O(2) | 2.912(5) | – | – | $x, -y, z$ |
| O(1W)* | O(1) | 3.146(5) | – | – | $-x, -y, -z$ |

* Water molecule H-atoms were not defined.

in the ring. The ring conformation differs somewhat from that in the complex with water, [**1**·$H_2O$], where the macroring is described by the following set of torsion angles: $ag + aag - aag + aag - aag - aaasg - a$. The differences in the ring conformations in these two structures are determined by the different amide group

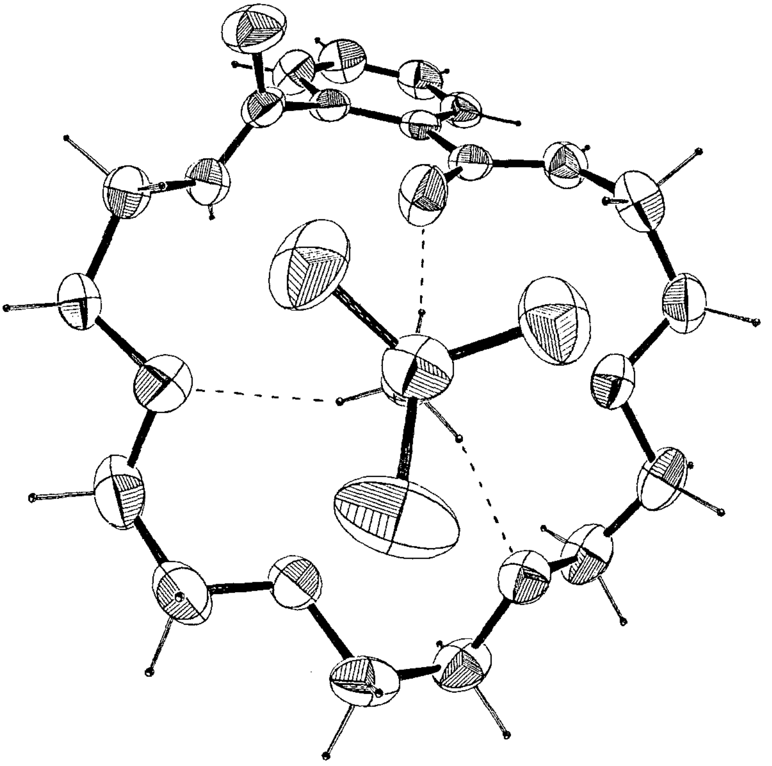

Fig. 1b. ORTEP plot of the [**1**·$NH_3SO_3$] entity in the complex [**1**·$NH_3SO_3$]·$H_2O$ with H-bond system indication.

orientations caused by the distinctive character of host–guest interaction in these two compounds.

The heteroatoms of the macrocyclic cavity deviate from the plane defined by all six of them by: N(1) −0.297 Å, O(4) 0.404 Å, O(7) −0.160 Å, O(10) −0.077 Å, O(13) 0.029 Å, N(16) 0.100 Å. The flat aromatic moiety forms a dihedral angle with this plane equal to 45.9°. Both diamide fragments are in *cis*-conformations with the torsion angles O—C—N—C equal to O(1)—C(20)—N(1)—C(2)= −7.9° and O(2)—C(17)—N(16)—C(15) = −3.1°, respectively.

The carbonyl O atom (O(2)) takes part in intramolecular >C=O· · ·C dipole–dipole interactions with the shortened >C=O· · ·C contact equal to 2.569(3) Å. Such contacts are common among the related crown ethers. For the same crown molecule in the complex [**1**·$H_2O$] its shortened >C=O· · ·C contact is equal to 2.862(4) Å. The average values of distances and angles for the title complex in comparison with the aquo complex [**1**·$H_2O$] are given in Table VI.

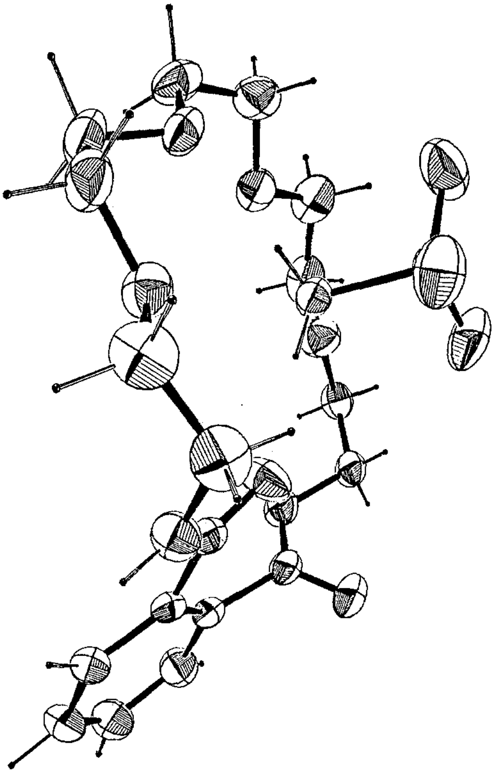

Fig. 2. ORTEP plot of the guest perching position in the complex [1·$NH_3SO_3$]·$H_2O$ (water molecule is omitted).

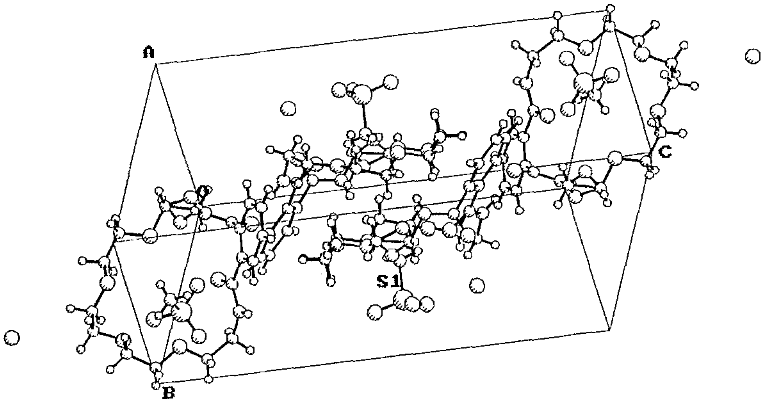

Fig. 3. Complex crystal packing.

TABLE V. Selected torsion angles (deg) in the heterocyclic framework in [**1**·$NH_3SO_3$]·$H_2O$ and [**1**·$H_2O$].

| Atoms | [**1**·$NH_3SO_3$]·$H_2O$ | [**1**·$H_2O$] |
|---|---|---|
| C(20)—N(1)—C(2)—C(3) | −166.9 | 141.7 |
| N(1)—C(2)—C(3)—O(4) | 75.1 | 70.7 |
| C (2)—C(3)—O(4)—C(5) | −177.7 | −177.2 |
| C(3)—O(4)—C(5)—C(6) | −159.9 | −176.8 |
| O(4)—C(5)—C(6)—O(7) | −63.3 | −62.3 |
| C(5)—C(6)—O(7)—C(8) | −177.2 | −169.8 |
| C(6)—O(7)—C(8)—C(9) | 174.0 | −177.8 |
| O(7)—C(8)—C(9)—O(10) | 70.9 | 74.9 |
| C(8)—C(9)—O(10)—C(11) | −167.7 | −174.4 |
| C(9)—O(10)—C(11)—C(12) | −169.2 | −179.6 |
| O(10)—C(11)—C(12)—O(13) | −56.3 | −61.4 |
| C(11)—C(12)—O(13)—C(14) | −172.5 | −176.3 |
| C(12)—O(13)—C(14)—C(15) | −171.2 | −174.2 |
| O(13)—C(14)—C(15)—N(16) | −73.4 | −61.3 |
| C(14)—C(15)—N(16)—C(17) | 106.1 | 151.4 |
| C(15)—N(16)—C(17)—C(18) | 175.8 | −178.6 |
| N(16)—C(17)—C(18)—C(19) | −166.9 | 145.2 |
| C(17)—C(18)—C(19)—C(20) | 6.9 | 7.3 |
| C(18)—C(19)—C(20)—N(1) | −105.2 | −69.7 |
| C(19)—C(20)-N(1)—C(2) | 177.1 | 176.4 |

TABLE VI. Bond distances and angles in [**1**·$H_3SO_3$]·$H_2O$ and [**1**·$H_2O$]

|  | [**1**·$H_3SO_3$]·$H_2O$ | [**1**·$H_2O$] |
|---|---|---|
|  | $d$, Å | $d$, Å |
| $Csp^3$—$Csp^3$ | 1.489(3) | 1.490(7) |
| $Csp^2$—$Csp^2$ | 1.388(3) | 1.386(6) |
| N—$Csp^3$ | 1.473(3) | 1.447(6) |
| N—$Csp^2$ | 1.324(2) | 1.324(5) |
|  | $\omega$, deg. | $\omega$ deg. |
| C—O—C | 113.2(2) | 112.1(3) |
| C—C—O | 109.8(2) | 109.5(4) |
| C—N—C | 120.1(2) | 121.3(4) |
| C—C—C | 120.0(2) | 120.0(4) |

## 3.3. CONCLUDING REMARKS

The data presented in this and previous papers [1–4] show that aminosulfuric acid forms stable complexes with the classical and modified crown ethers of different cavity sizes. In all cases when the macrocycle dimensions permit the formation of three H-bonds in the tripod-like mode, they play the major role in host–guest structure formation. If the host cavity sizes do not topologically match the guest $NH_3^+$ function, Coulombic forces define the structure.

The results for the complexes [**1**·$H_2O$] and [**1**·$NH_3SO_3$]·$H_2O$ reveal the host molecule's ability to self-organize during complexation. Depending on guest geometric peculiarities, the host adjusts its conformation with the different set of torsion angles along the heterocyclic framework. H-donor groups of (**1**) might be involved both in intramolecular and intermolecular H-bonds.

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