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Absence of Hydronium Ion Formation in a Ternary Crown Ether·Mineral Acid·Water Complex: X-ray Crystal Structure of 1,8-Oxybis(ethyleneoxyethyleneoxy)-anthracene-9,10-dione·HNO_3·$3H_2O$

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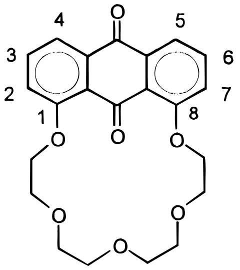
Introduction

Previous X-ray crystal structures of hydronium ion/18-crown-6 guest−host complexes reveal the H_3O^+ ion centered in the middle of the crown ether with all the polyether oxygens participating in hydrogen bonding to the hydronium ion.[1] 18-Crown-6, with approximate D_{3d} symmetry and optimum cross-ring oxygen−oxygen spacing, is ideally suited, in terms of cavity size and shape, for hosting H_3O^+. 1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione, **1**, is an analogue of the 18-crown-6 system, where one ether oxygen has been replaced by a carbonyl group of the anthraquinone. This molecule has been of particular interest as a redox-switchable crown ether that has a high affinity and selectivity for cations in its electrochemically reduced state, compared to its neutral form.[2,3] However, in **1**, the carbonyl of the anthraquinone diminishes the cavity size of the crown ether and reduces the symmetry of the polyether ring. Here we report the structure of 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione·HNO_3·$3H_2O$, **2**, where nitric acid, a strong mineral acid, does not form an hydronium ion or higher-order hydronium ion complex with the crown host in the crystalline state, even when cocrystallized with water. Nitric and sulfuric acid adducts, in this instance, join weak acid/crown ether examples that do not exhibit a leveling effect by water.



Experimental Procedures

1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione·HNO_3·$3H_2O$, 2. Slow evaporation of solvent from mixtures containing 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione, **1**,[2] and concentrated nitric acid in acetonitrile gave yellow needles of the title compound. The complex loses acid/solvent between 105 and 115 °C and melts at 155−157 °C, the melting point of **1**. ^1H NMR δ (300 MHz, DMSO-d_6): 7.73 (t, 2 H, $J_{2(4),3} = 7.7$ Hz, 3 and 6-H), 7.67 (dd, 2 H, $J_{2,3} = 7.6$ Hz, $J_{2,4} = 1.7$ Hz, 2 and 7-H), 7.50 (dd, 2 H, $J_{3,4} = 7.6$ Hz, $J_{2,4} = 1.7$ Hz, 4 and 5-H), 4.21−3.60 (m, 16 H, CH_2's), 3.94 (s, H_3O^+/H_2O). NMR chemical shifts are referenced to the residual proton resonance of the solvent. Elemental analyses calculated for $C_{22}H_{29}NO_{13}$: C, 51.26; H, 5.67; N, 2.72. Found: C, 51.77; H, 5.29; N, 2.66.

X-ray Data Collection, Structure Determination, and Refinement. A crystal of the compound (0.4 × 0.4 × 0.04 mm) was attached to a glass fiber and mounted on the Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from 35 reflections harvested from three sets of 30 frames. Final cell constants were calculated from a set of 2992 strong reflections from the actual data collection. A summary of data collection and refinement information is given in Table 1. The space group $P2_1/c$ was determined on the basis of systematic absences and intensity statistics.[4] A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the *E*-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All water protons were refined isotropically with isotropic displacement parameters fixed at 1.5 times the host oxygen. The covalent water bonds were restrained to have the same distances within 0.02 Å. All hydrogens are accounted for in this structure. Selected bond distance and angles are listed in Table 2.

Results and Discussion

The addition of a small amount of concentrated nitric acid to a solution of **1** in acetonitrile yields yellow, nonfluorescent needles after slow evaporation of solvent. Melting point determinations show that this material loses acid and solvent between 105 and 115 °C and subsequently melts at ∼155 °C, near the melting point of uncomplexed **1**.[2] Titration with strong base reveals that only 1 equiv of acid is present in this material.

X-ray crystallographic analysis reveals the asymmetric unit of this material contains the anthraquinone-containing crown ether, a nitric acid molecule, and three water molecules (**1**·HNO_3·$3H_2O$). The crown ether has approximate C_s symmetry as shown in Figure 1, and O−C−C−O torsion angles (range = 65.1−72.7°) alternate $\pm g$ (except for the aryl carbons which are synclinal), and all the C−O−C−C torsion angles (range = 162.9−179.6°) are *anti* in configuration. Within the macrocycle, bond distances and bond angles average O−C(alkyl) = 1.43 Å, O−C(aryl) = 1.36 Å, C(alkyl)−C(alkyl) = 1.50 Å, C(alkyl)−O−C(alkyl) = 112.4°, C(alkyl)−O−C(aryl) = 118.1°, O−C(alkyl)−C(alkyl) = 109.1°, and O−C(aryl)−C(aryl) = 118.0°. The two carbonyl C−O bonds, C(1)−O(1) and C(18)−O(7), are 1.214(5) and 1.234(5) Å, respectively, and the anthraquinone system is planar. Interatomic spacings of ether

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Table 1. Crystallographic Data for **1**·HNO_3·$3H_2O$

chemical formula	$C_{22}H_{29}NO_{13}$	formula weight	515.46
a	19.7151(14) Å	Space group	$P2_1/c$
b	16.4937(12) Å	T	173(2) K
c	7.5239(5) Å	λ	0.71073 Å
β	96.828(1)	$\rho_{obs.}$	1.409 g cm^{-3}
V	2429.2 (3) Å^3	μ	0.0117 cm^{-1}
Z	4	$R_1{}^{a}$	0.0761
		$R_w{}^{2\,b}$	0.1729

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w{}^2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$, where $w = q/\sigma^2(F_o{}^2) + (a*p)^2 + b*P$.

Table 2. Selected Bond Distances and Angles for **1**·HNO_3·$3H_2O$

Bond Distances			
C(1)−O(1)	1.214(5)	O(11)···O(1)	2.764(6)
C(18)−O(7)	1.234(5)	O(11)···O(4)	2.877(6)
N(21)−O(21)	1.173(6)	O(12)···O(3)	2.852(6)
N(21)−O(22)	1.309(6)	O(12)···O(13)	2.626(6)
N(21)−O(23)	1.184(6)	O(13)···O(5)	2.804(6)
		O(13)···O(22)	2.468(6)

Bond Angles	
O(21)−N(21)−O(22)	116.2(6)
O(21)−N(21)−O(23)	125.4(6)
O(22)−N(21)−O(23)	118.1(5)

oxygens across the macrocycle are 5.75 Å for O(2)···O(5) and 5.78 Å for O(3)···O(6), and are typical of 18-crown-6 cavity diameters.[5] Due to the presence of the carbonyl oxygen, O(1), within the polyether ring, the O(1)···O(4) interatomic distance of 4.65 Å decreases the cavity size by approximately 1.2 Å.

Of greatest interest is the hydrogen-bonded complex of the nitric acid, water molecules, and the crown ether. Two water molecules, O(12) and O(13), bridge two basic polyether oxygens, O(3) and O(5), in a daisy chain fashion, and O(13) is also hydrogen-bonded to the nitric acid (side view, Figure 1). This arrangement can be described as **1**·HNO_3·$2H_2O$, as opposed to $[H_5O_2\cdot\mathbf{1}]^+NO_3{}^-$, where the proton has been transferred to water. To support this case are unequal N−O bond distances in the nitric acid. The N−O(22) distance, the oxygen that participates in the hydrogen bond, is 1.309(6) Å, compared to the two other N−O double-bond distances that average 1.178(6) Å. These distances are very similar to other published nitric acid structures[6] that retain the acidic proton, and is different from a nitrate anion, where all N−O bond lengths are equal. The bond distance between the water molecule, O(13), and the nitric acid oxygen, O(22), is also short, equaling 2.468(6) Å, indicating that a particularly strong hydrogen bond has been formed between the acid and this water molecule.

In addition, numerous $H_5O_2{}^+$ complexes with crown ethers have been reported.[7,12] The average $H_2O\cdots H^+\cdots OH_2$ oxygen−oxygen contacts in these structures range from 2.42 to 2.43 Å with $O_{water}\cdots O_{ether}$ contacts of 2.60−2.74 Å. In the structure of **1**·HNO_3·$3H_2O$, the oxygen−oxygen contact (O(12)···O(13)) equals 2.626(6) Å, and $O_w\cdots O_{ether}$ contacts equal 2.804(6) Å for O(5)···O(13) and 2.852(6) Å for O(3)···O(12), all much longer compared to $H_5O_2{}^+$ hydronium ion complexes previously reported, implying considerably weaker hydrogen bondingoccurs between O(12) and O(13) and the polyether oxygens here.

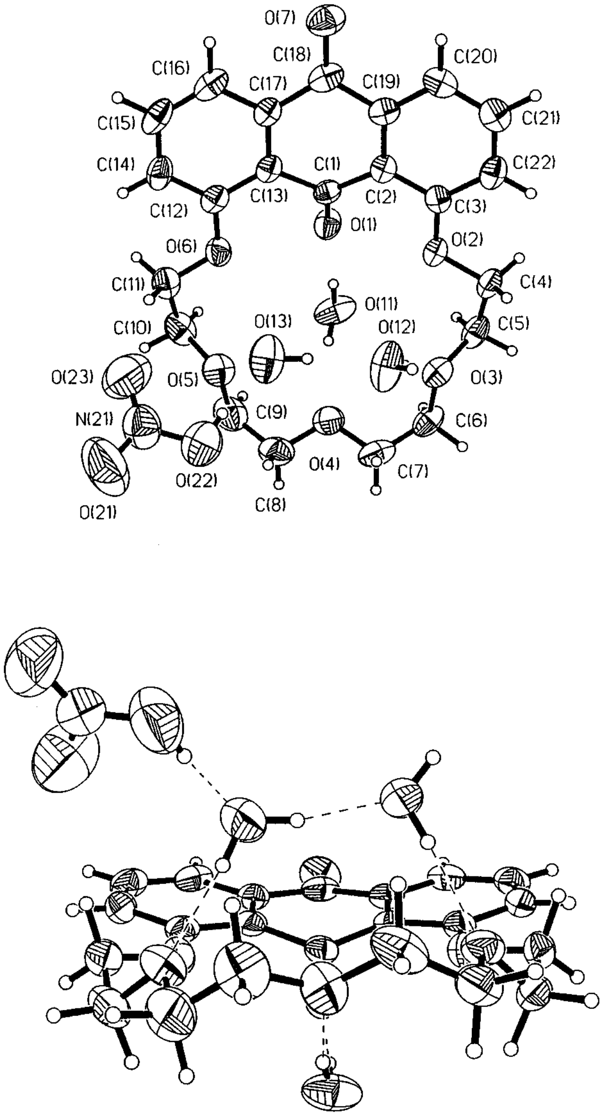

Figure 1. Thermal ellipsoid (50%) diagrams of the top and side views of **1**·HNO_3·$3H_2O$. In the side view diagram, O(12) and O(13) water molecules, together with the nitric acid, lie above the polyether ring and O(11) lies below.

One additional water molecule is also found on the opposite face of the crown ether, bridging O(1), the carbonyl oxygen in the ring, and O(4). O(1)···O(11) and O(4)···O(11) contacts are 2.764 and 2.877(6) Å, respectively. O(1), possibly due to this hydrogen-bonding interaction, has also been pulled out of the plane of the anthraquinone and the polyether ring by approximately 0.93 Å. Crown ether units within the crystal are separated by a hydrogen bond between the O(12) water molecule (above the polyether ring) and the O(11) water molecule (below the polyether ring of a neighboring complex).

To our knowledge, a polyether guest−host complex containing both a strong acid and water, where the acid proton has not been transferred to water, has not been previously observed. This conclusion is based on the extended series of bond lengths between heavy atoms in this structure including: unequal bond distances between nitrogen and oxygens in HNO_3, a short hydrogen bond between the nitric acid and the O(13) water molecule, a long oxygen−oxygen contact between the O(12) and O(13) water molecules, and long oxygen−oxygen contacts between O(12) and O(13) and the polyether oxygens of the ring,

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yielding **1**·HNO_3·$2H_2O$. These bond lengths are different from those expected for $[H_5O_2·\mathbf{1}]^+NO_3^-$, where N−O bond distances for nitrate would be the same, the contact between the nitrate ion and the organic cation would be longer, and bond distances associated with $H_5O_2^+$ would be significantly shorter, on the basis of reported results of other $H_5O_2^+$/crown ether structures.

Examples of weak acid/18-crown-6 guest−host complexes, where the acid retains the proton, have been reported, i.e. cyanoacetic acid ($CH_2(CN)COOH$, pK_a = 2.5[8]) and H_3PO_4 (pK_a = 2.1).[10] Although nitric acid is a much stronger acid (pK_a = −1.6),[11] its apparent inability to form a oxonium ion complex in this case is because of the restricted size of the crown ether cavity due to the carbonyl oxygen present inside the ring. The less basic carbonyl oxygen reduces the diameter of the ring by ~1.2 Å in one dimension, resulting in an asymmetric and crowded cavity for hydrogen bonding to occur for any pseudo-centered H_3O^+ guest. It is also of interest to point out that a higher order hydronium ion, such as $H_5O_2^+$, has not been formed in this case either. $H_5O_2^+$ has been observed to bridge 15-crown-5 rings that are too small to encapsulate H_3O^+ individually.[12] In **1**·HNO_3·$3H_2O$, proton transfer does not take place, and a unique bridging system of two water molecules (daisy chained) spans the crown ether on one side of the polyether ring. Daisy chains of water molecules bridging polyether rings have previously been observed.[10,13]

We have also determined the structure of the analogous sulfuric acid adduct of **1**.[14,15] The sulfate counter-ion appears severely disordered over two sites in this structure, and the protons could not be located; however, the anthraquinone and crown ether ring are almost identical in conformation to the nitric acid structure, indicating even sulfuric acid (pK_a = −3), a stronger mineral acid than nitric acid, most likely does not protonate water in this complex either. Also, we have not observed electrophilic substitution of the aromatic rings in **1** with either nitric acid or sulfuric acid or mixtures of the two, as is the case with anthraquinone itself and its many derivatives.

Whereas potassium ion (O_{ether}−K^+ distances average 2.8 Å)[5] is optimally suited for complexation with 18-crown-6, the structure of **1**·HNO_3·$3H_2O$ with a reduced cavity diameter provides an excellent fit for sodium ion (O_{ether}−Na^+ distances average 2.3−2.4 Å) within the macroring. This is supported by previous EPR and cyclic voltammetric studies of **1**.[2,3] However, due to the high spectral symmetry of the EPR spectrum of reduced **1** in the presence of Na^+,[2] a C_2 axis containing both carbonyl groups and any carbonyl-bound cation was proposed, indicating front and back sides of the anthraquinone are the same on the EPR timescale. Although complicated by crystal packing forces, the structure presented here has lower symmetry (C_s), with the mirror plane oriented perpendicular to the anthraquinone and containing both carbonyl groups. The polyether chain, then, must permit a certain degree of flexibility in conformations it adopts in solution and the solid-state.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, containing crystallographic data and details of the refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, torsion angles, and hydrogen positions for $C_{22}H_{29}NO_{13}$ and $C_{22}H_{26}O_9S_0$ are available. Access information is given on any current masthead page.

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(14) For the sulfuric acid adduct of **1** ($C_{22}H_{26}O_9S_0$): space group = $P2_1/c$; a = 20.1873(9) Å, b = 16.5852(8) Å, c = 7.4097(3) Å; B = 97.168(2)°; Z = 4; 4244 reflections with $I \geq 2\sigma(I)$, 280 parameters, R = 0.086, wR2 = 0.2071. The organic portion of the structure plus two water molecules, one on each side of the polyether ring, was determined easily. A sulfate anion was found in approximately one-half occupancy over two possible sites that are torsionally disordered and also probably occupied by solvent, leaving the position of the acid proton in question. Disordered atoms were removed, including the S atom using PLATON (see ref 15) and refined to achieve the final structure. Atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $C_{22}H_{26}O_9S_0$ are also available in the Supporting Information.

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