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# Unexpected IR Characteristics of Hydrogen Bonds in the 18-Crown-6-Ether Complex of the $\text{H}_3\text{O}^+$ Hydronium Ion. Can the Location of the Protons Be Specified?

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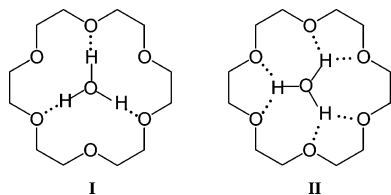
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The  $\nu_{\text{as}}(\text{COC})$  IR spectral signatures of polyethers in H-bonded hydronium ion complexes have been established in studies of  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  complexes with 15-crown-5, 18-crown-6, dibenzo-18-crown-6, and their open chain poly(ethylene glycol) analogues in 1,2-dichloroethane solutions. When experiment meets theory in the structure of the  $\text{H}_3\text{O}^+$ -18-crown-6 complex, there is disagreement. While DFT calculations at the BLYP/II//BLYP/6-31G\* level indicate a  $C_{3v}$  structure with three normal, static linear H bonds to alternate O atoms of the crown ether, IR spectroscopy in the  $\nu(\text{C}-\text{O}-\text{C})$  region indicates that all six O atoms are equivalent. A new type of low-barrier H-bonding involving rotational mobility of  $\text{H}_3\text{O}^+$  is proposed to rationalize the experimental observations.

## Introduction

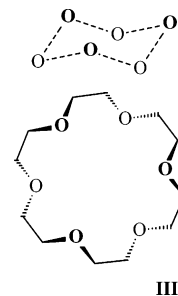
Crown ethers are very effective complexing agents for cations.<sup>1–3</sup> They show selectivity not only for metal cations, but also for hydronium ions,  $\text{H}(\text{H}_2\text{O})_n^+$ . For example, 18-crown-6 is selective for the simplest hydronium ion,  $\text{H}_3\text{O}^+$ , because the size of the polyether cavity and its  $D_{3d}$  conformation match the  $\text{H}_3\text{O}^+$  structure.<sup>4–6</sup> Larger crown ethers are well-suited for selectivity toward the  $\text{H}_5\text{O}_2^+$  (21–24 membered)<sup>6–8</sup> and  $\text{H}_7\text{O}_3^+$  ions (27–30 membered).<sup>6,8</sup> While single-crystal X-ray diffraction studies have confirmed these formulations, accurate structural information has been harder to obtain. In some structures, even the positions of the O atoms are not reliably determined, let alone the positions of the H atoms. The nature of the H-bonding remains debatable.

Perhaps the most interesting case is the  $\text{H}_3\text{O}^+$ -18-crown-6 complex. Early thermodynamic studies suggested an abnormally high binding enthalpy compared to other hydronium ion/crown ether complexes.<sup>9</sup> Cooperative H-bonding was suggested, including the possibility of bifurcated H bonds. Two limiting static structures can be envisaged: linear H bonds to three O atoms (**I**) or bifurcated H bonds to all six O atoms (**II**).



In many X-ray structures, there is an alternating pattern of inequivalent  $\text{O}_\text{W} \cdots \text{O}_\text{L}$  distances ( $\text{W} = \text{H}_3\text{O}^+$ ,  $\text{L} = \text{ligand}$ ), consistent with structure **I**.<sup>4,10,11</sup>  $\text{O}_\text{W}$  is ca. 0.3 Å above the plane of the three coordinating  $\text{O}_\text{L}$  atoms, reflecting the pyramidal nature of the  $\text{H}_3\text{O}^+$  ion. In some structures, depending upon the nature of the anion, the six  $\text{O}_\text{W} \cdots \text{O}_\text{L}$  distances appear to

become nearly equivalent (like the  $\text{K}^+$  complex) and the out-of-plane displacement of  $\text{O}_\text{W}$  decreases. A flattening of the  $\text{H}_3\text{O}^+$  ion is suggested.<sup>12,13</sup> It is sometimes difficult to tell whether there is real equivalence of the  $\text{O}_\text{W} \cdots \text{O}_\text{L}$  distances or whether it arises from disorder of the  $\text{H}_3\text{O}^+$  ion among the two sets of three O atoms.<sup>14,15</sup> As illustrated in **III**, the conformation of 18-crown-6 leads to one set of O atoms pointing up and the other pointing down and complexation can occur to either set.



The possibility of bifurcated H-bonding has also been mentioned.<sup>4,16</sup> Examples of bifurcated H bonds have been established for complexes of amines with cyclic ethers<sup>17–19</sup> and in ion pairs of dialkyl phosphates with  $\text{R}_3\text{NH}^+$ .<sup>20</sup>

Infrared spectroscopy is perhaps better suited than crystallography to probe the nature of the H-bonding in these complexes because many of the solid state structures suffer from crystallographic disorder and the H atoms are poorly located, if at all. IR has the additional advantage that it can be applied in the solution state as well as with both amorphous and crystalline solids. In an earlier publication,<sup>21</sup> IR spectroscopy was used to establish the formulations of  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  complexes with various crown ethers and their linear analogues, poly(ethylene glycol)s (PEGs). The bulky chlorinated cobalt(III) bis(dicarbollide) ion,  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_8\text{Cl}_3)_2]^-$  (CCD), was chosen to minimize perturbation of the cation via ion-pairing effects. In water-saturated 1,2-dichloroethane (DCE) solutions, only  $\text{H}_3\text{O}^+$  complexes are formed with 18-crown-6 and benzo-18-crown-6. Complexes of  $\text{H}_5\text{O}_2^+$  are formed with PEGs while complexes

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of both  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  ions were detected with 15-crown-5, depending on the concentration. Quantum mechanical calculations were used to clarify the nature of  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$  interaction with polyethers in a vacuum (i.e., in the absence of an anion). The results were consistent with linear H-bonding except in a few cases where some tendency toward partial bifurcation was indicated. The question of structure **I** vs **II** in  $\text{H}_3\text{O}^+\cdot 18\text{-crown-6}$  has recently been addressed by additional theory.<sup>22</sup> For an isolated cation in vacuo, linear H bonds are favored over bifurcated by ca. 4 kcal·mol<sup>-1</sup>.

We now present experimental IR spectroscopy data concerning the nature of H bonds in these complexes that challenge this conclusion and suggest a more sophisticated description of the H-bonding is needed. The findings have some conceptual relationship to short, strong, low-barrier (SSLB) H bonds in species such as  $\text{H}(\text{O donor})_2^+$  cations<sup>23,24</sup> where the H atom resides in a nearly flat-bottomed potential well, with a barrier separating two wells that is lower in energy than the first excited vibrational level. Thus, in some complexes  $\text{H}^+$  has an indeterminate position and must be addressed by a more complex theory.<sup>25</sup>

### Experimental Section

Chlorinated cobalt(III) bis(dicarbollide) (CCD) (90% in H-form and 10% in Na form) from Katchem, crown ethers 15-crown-5 and 18-crown-6 from Reaktiv-Servis (Moscow, Russia), poly(ethylene glycol)s PEG-400 and PEG-600 from Vekton (St. Petersburg, Russia) were used without additional purification. PEG-400 and PEG-600 contain mixtures of linear  $\text{HO}-\text{CH}_2-(\text{CH}_2-\text{O}-\text{CH}_2)_m-\text{CH}_2-\text{OH}$  molecules corresponding to average molecular masses of 400 and 600 au respectively. 1,2-Dichloroethane (DCE) of chemical purity grade was purified using standard methods. CCD was converted to 100% H-form by treating a DCE solution with 3 M  $\text{H}_2\text{SO}_4$  aqueous solution for a 5 min. Hydronium ion complexes were prepared as previously described.<sup>21</sup> The deuterated complex  $[\text{D}_3\text{O}^+\cdot 18\text{-crown-6}]\text{CCD}$  was obtained by mixing a DCE solution of  $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\text{CCD}$  with  $\text{D}_2\text{O}$ , monitoring with IR to determine full exchange.  $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$  was prepared as described previously<sup>26</sup> and converted to the  $\text{H}_3\text{O}^+\cdot 18\text{-crown-6}$  salt by similar methods used to prepare the CCD sample. IR spectra were recorded on a Bomem M-102 FTIR spectrometer (40 scans, resolution 4 cm<sup>-1</sup>) in the 920–4000 cm<sup>-1</sup> range using cells with  $\text{CaF}_2$  windows. Silicon windows were used for solid samples.

As previously described,<sup>21</sup> IR spectra of the complexes were obtained from measured data by sequential digital subtraction of the spectrum of the solvent, dissolved water and excess of free polyether (if any).

### Results

The frequency of the C–O–C asymmetric stretching vibrations of a polyether,  $\nu_{\text{as}}\text{COC}$ , decreases upon interaction of the O atoms with  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$  cations via hydrogen H bonds. When the interaction with the different O atoms is inequivalent,  $\nu_{\text{as}}(\text{COC})$  is split into two or more components in accordance with the number of inequivalent COC groups. Some of the COC groups may be nonbonded and therefore negligibly perturbed by the hydronium ion. To determine the ratio between different types of inequivalent COC groups, the integrated intensities  $I_{\text{COC}}$  of the corresponding  $\nu_{\text{as}}\text{COC}$  bands have been used. This is valid because the  $I_{\text{COC}}$  values per COC group are very similar for complexed and uncomplexed ligands (see Table 1). In other

**TABLE 1: Molar Intensities of the  $\nu_{\text{as}}(\text{COC})$  Bands in the IR Spectra of Solutions of Crown Ethers (L) in DCE as a Function of Their Concentration ( $C_L$ )**

L	$C_L$ (M)	$I_{\text{COC}}^a$	$I_{\text{COC}}/C_L^b$	$n^c$	$I_{\text{COC}}/C_L n^d$
15-crown-5	0.023	3.57	155.2	5	31.0
15-crown-5	0.1	15.87	158.7	5	31.7
18-crown-6	0.2045	38.47	188.12	6	31.3
18-crown-6	0.08	14.26	178.25	6	29.7
PEG-400	0.057	17.03	298.24	9	33.1
PEG-600	0.01	4.6	460.0	14	32.8

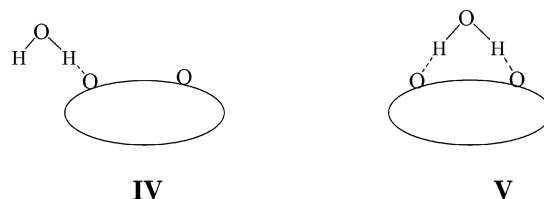
<sup>a</sup> Integrated intensity. <sup>b</sup> Molar intensity. <sup>c</sup> The number of COC groups in L. <sup>d</sup> Molar intensity per COC group.

words, for  $i$  different types of inequivalent  $\text{COC}^i$  groups, the proportion of each is close to the ratio  $I_{\text{COC}}^i/\Sigma I_{\text{COC}}^i$ .

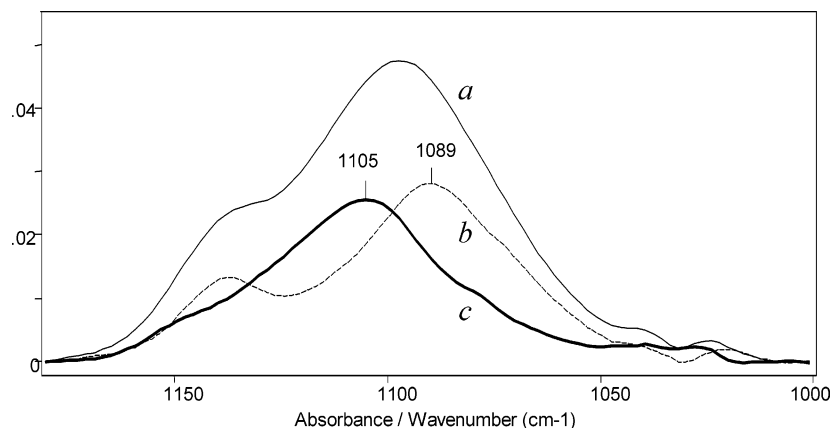
In PEG complexes, the  $\nu_{\text{as}}\text{COC}$  bands of bonded and nonbonded COC groups are broader and more strongly overlapping than those in crown ether complexes. To calculate the number of bonded and nonbonded PEG's COC groups, the bands must be segregated and their intensities measured. This task is complicated by the slightly different shape of the band from the nonbonded COC groups relative to those in uncomplexed PEG, presumably because of conformational transformations upon the complexation. To segregate overlapped  $\nu_{\text{as}}(\text{COC})$  bands, we recorded the spectra by varying the  $\text{H}(\text{H}_2\text{O})_n^+$ : PEG ratio from 1:1 to 2:1. The increasing acid concentration resulted in decreasing intensity (until zero) of the band of the nonbonded COC groups. The spectrum of the 2:1 solution contains the "pure" broad  $\nu_{\text{as}}(\text{COC})$  band of bonded COC groups, as well as the overlapping absorptions from the stretching vibrations of bonded COH groups. The aggregate band shapes are similar for PEG-400 and PEG-600 (Figure 1b). Subtracting these bands from the spectra of complexes with suitable coefficients leads to the bands of the nonbonded COC groups (Figure 1c). The molar intensities determine the proportion of these groups.

**Free Polyethers.** The IR spectra of 15-crown-5, 18-crown-6, and PEG-400 in anhydrous DCE solution differ mainly in the vibrations of the COC and  $\text{CH}_2$  groups, which are sensitive to changes in their conformation.<sup>3</sup> The  $\nu_{\text{as}}(\text{COC})$  frequencies decrease in the order 15-crown-5 > 18-crown-6 > PEG (Table 2), in line with the reduced ring strain. The half-width  $\Gamma_{1/2}$  of the  $\nu_{\text{as}}(\text{COC})$  band of 18-crown-6 is small, indicating the equivalency of all COC groups in this molecule. In 15-crown-5,  $\Gamma_{1/2}$  is slightly larger and the band shape is more complex, indicating that this molecule is conformationally less symmetrical. In PEG,  $\nu_{\text{as}}(\text{COC})$  and  $\nu(\text{COH})$  bands are overlapping and broad, suggesting a variety of conformers.

**Free Polyether Interactions with  $\text{H}_2\text{O}$ .** Spectra were studied in DCE saturated with water. In the case of 15-crown-5, two  $\nu(\text{OH})$  bands were observed at 3660(sharp) and 3501(broad) cm<sup>-1</sup>. These are ascribed to the free and bound O–H groups respectively, typical of  $\text{H}_2\text{O}$  molecules bound to crown ethers<sup>27</sup> or acyclic monoethers<sup>28,29</sup> in monodentate fashion (**IV**).



In the case of 18-crown-6, bands of type **IV** coordination are observed along with additional broad bands at 3580 and 3527 cm<sup>-1</sup>. These show similarities to those observed in  $\text{CCl}_4$



**Figure 1.** IR spectra in the  $\nu_{\text{as}}(\text{COC})$  frequency range of DCE solutions of (a) 0.05 M  $[\text{H}_5\text{O}_2^+\cdot\text{PEG-600}]$  CCD, (b) 0.05 M HCCD + 0.025 M PEG-600, (c) the difference  $a - b$  to reveal the  $\nu_{\text{as}}(\text{COC})$  band of the nonbonding COC groups.

**TABLE 2: Frequencies ( $\text{cm}^{-1}$ ) of  $\nu_{\text{as}}(\text{COC})$  Bands in the IR Spectra of Uncomplexed Polyethers and Their Complexes with Hydrated Protons in Wet DCE Solutions<sup>a</sup>**

L	uncomplexed		complexed L	
	L		$\text{H}_3\text{O}^+\cdot\text{L}$	$\text{H}_5\text{O}_2^+\cdot\text{L}_n$
PEG-400/600	1105			1090 (15)
15-crown-5	1128		1116 (12), 1084 (44)	1098 (30)
18-crown-6	1118		1095 (23)	
benzo-18-crown-6	1127		1094 (33), 1078 (49)	

<sup>a</sup> Shifts to lower frequency upon complexation are given in parentheses.

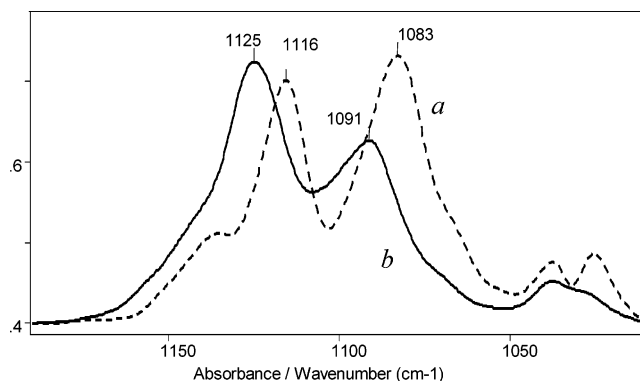
solution<sup>17</sup> and are ascribed to type **V** coordination. Type **IV** coordination dominates over **V** in DCE solution.

Spectra of PEG-400 display very intense absorption bands of H-bonded water molecules at 3440 and 1634  $\text{cm}^{-1}$ . From the intensity of  $\delta(\text{HOH})$  at 1634  $\text{cm}^{-1}$  and the coefficient of its molar absorption ( $\sim 37.4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ , calculated on the basis of published data<sup>30</sup>), the water content and molar ratio  $\text{H}_2\text{O}/\text{PEG} \approx 22.7$  were calculated. This suggests the formation of water clusters surrounded by the PEG molecules.

The stretching frequencies of the COC groups for all compounds are essentially insensitive to this H-bonding of  $\text{H}_2\text{O}$  molecules. Only the narrow  $\nu_{\text{as}}(\text{COC})$  band of 18-crown-6 is lowered by 1  $\text{cm}^{-1}$  in the presence of water. Deconvolution of the bands from free and H-bonded COC groups shows that the actual frequency decrease is 5  $\text{cm}^{-1}$ . For the polyether complexes with  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$ , discussed below, all shifts of  $\nu_{\text{as}}(\text{COC})$  bands to lower frequency significantly exceed those for hydrated polyethers. This establishes that the shifts do not arise simply from hydration effects.

**$\text{H}_5\text{O}_2^+$ /PEG Complexes in DCE.** PEG-400 and PEG-600 form nonhydrated 1:1 complexes with the  $\text{H}_5\text{O}_2^+$  cation whose first coordination sphere is filled by O atoms only from a PEG molecule. The absence of the typical stretching bands of the hydrated terminal OH groups of PEG molecules ( $\sim 3400 \text{ cm}^{-1}$ ) indicates that they are located at lower frequency, overlapped with the bands from the terminal OH groups of the  $\text{H}_5\text{O}_2^+$  ion. This indicates that the  $\text{H}_5\text{O}_2^+$  ion is H-bonded with the O atom of a COH group which in turn allows the COH group to H bond more strongly with the solvating water environment. This would shift  $\nu(\text{OH})$  of the COH group to  $< 3400 \text{ cm}^{-1}$ .

As shown in Figure 1a, the spectra of the  $\text{PEG}\cdot\text{H}_5\text{O}_2^+$  complexes contain one broad  $\nu(\text{COC})$  band whose frequency (1093  $\text{cm}^{-1}$ ) is slightly lower than that in the uncomplexed PEGs (1105  $\text{cm}^{-1}$ ). The calculated contribution of nonbonded COC groups to the total absorption is 21% for PEG-400 and 56.5%

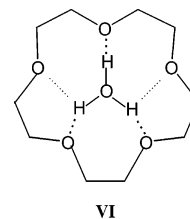


**Figure 2.** IR spectra in the  $\nu_{\text{as}}(\text{COC})$  frequency range of DCE solutions of (a)  $[\text{H}_3\text{O}^+\cdot 15\text{-crown-5}]$ CCD and (b)  $[\text{H}_5\text{O}_2^+\cdot 2(15\text{-crown-5})]$ CCD.

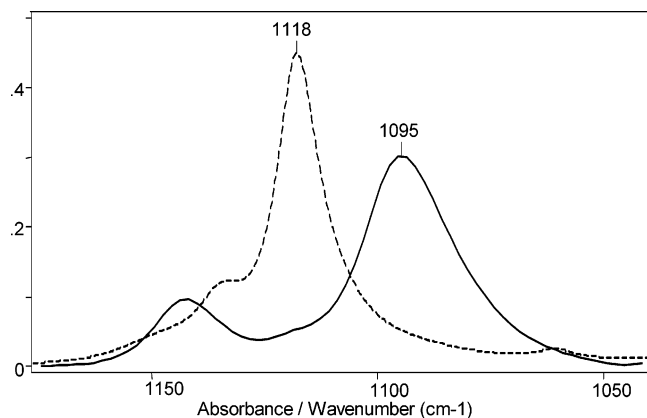
for PEG-600. This means that on the average, eight oxygen atoms of COC and COH groups of PEG interact with four peripheral hydrogen atoms of  $\text{H}_5\text{O}_2^+$  in these complexes.

**15-Crown-5 Complexes in DCE.** At fractional mole ratios of 15-crown-5 to acid, a 1:1 complex of the  $\text{H}_3\text{O}^+$  ion is formed. With excess polyether, a 2:1 complex of the  $\text{H}_5\text{O}_2^+$  ion is formed. All three protons of  $\text{H}_3\text{O}^+$  and four protons of  $\text{H}_5\text{O}_2^+$  form strong H bonds with the 15-crown-5 oxygen atoms.<sup>21</sup>

The spectrum of  $\text{H}_3\text{O}^+\cdot 15\text{-crown-5}$  has two intense bands in the  $\nu_{\text{as}}(\text{COC})$  frequency range from strongly bonded (1084  $\text{cm}^{-1}$ ) and weakly bonded (1116  $\text{cm}^{-1}$ ) COC groups (Figure 2a, Table 2). Their relative intensities are 3:2 indicating that three of the five ether oxygen atoms form strong hydrogen bonds with  $\text{H}_3\text{O}^+$  and two engage these H bonds in partial bifurcation (**VI**).

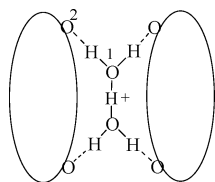


The spectrum of  $\text{H}_5\text{O}_2^+\cdot 2(15\text{-crown-5})$  also has two intense  $\nu_{\text{as}}(\text{COC})$  bands. The lower frequency one (1091  $\text{cm}^{-1}$ ) corresponds to COC groups bonded to protons of  $\text{H}_5\text{O}_2^+$ , whereas the higher frequency one (1125  $\text{cm}^{-1}$ ) coincides with that of uncomplexed 15-crown-5 and corresponds to nonbonded COC groups (Figure 2b, Table 2). The integrated intensity of the 1091  $\text{cm}^{-1}$  band contributes ca. 40% to the total intensity which means that only two of the five COC groups of 15-crown-5



**Figure 3.**  $\nu_{\text{as}}(\text{COC})$  band of  $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\text{CCD}$  in 0.06 M DCE solution at 25 °C (solid line). The spectrum of noncomplexed 18-crown-6 (dotted line) is given for comparison. Note that the band at about 1145  $\text{cm}^{-1}$ , belonging to one of bending  $\text{CH}_2$  vibrations, is observed in IR spectra of the free ligands (15-crown-5, 18-crown-6, benzo-18-crown-6, and PEG-400), their complexes with  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  (Figures 1, 2, 4, and 5) as well as in complex  $\text{K}^+\cdot 18\text{-crown-6}$  (at 1148  $\text{cm}^{-1}$ ).

interact with the  $\text{H}_5\text{O}_2^+$  ion. This suggests structure **VII** where the  $\text{H}_5\text{O}_2^+$  cation bridges two 15-crown-5 molecules forming strong H bonds with two oxygens of each ligand. Similar



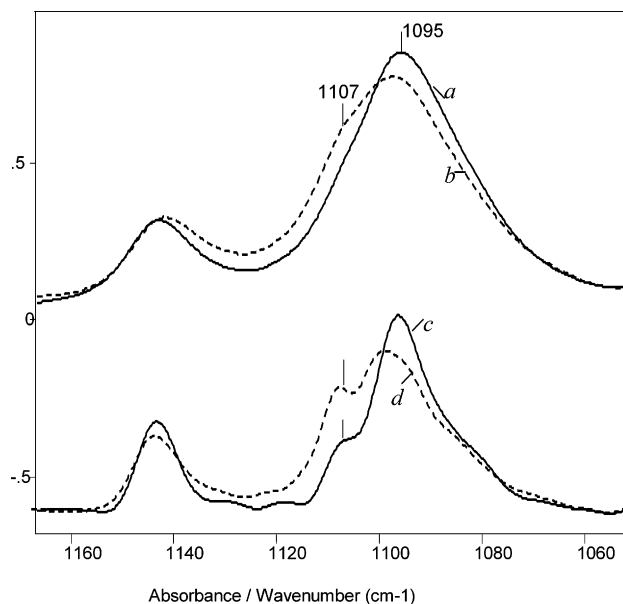
**VII**

coordination patterns have been observed in the solid-state structure of  $\text{H}_5\text{O}_2^+\cdot 2(12\text{-crown-4})$ .<sup>31</sup>

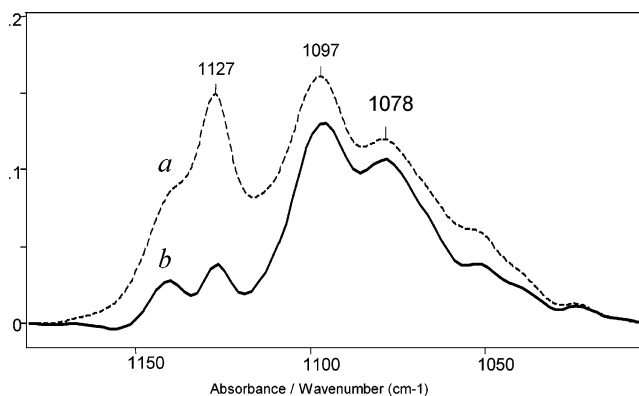
**$\text{H}_3\text{O}^+\cdot 18\text{-Crown-6}$  in DCE.** The IR spectrum of  $\text{H}_3\text{O}^+\cdot 18\text{-crown-6}$  contains only one  $\nu_{\text{as}}(\text{COC})$  band at 1095  $\text{cm}^{-1}$ , corresponding to COC groups interacting with the hydrated proton (Figure 3). A similar spectrum with one  $\nu_{\text{as}}(\text{COC})$  band at 1108  $\text{cm}^{-1}$  is observed in the  $\text{K}^+\cdot 18\text{-crown-6}$  complex. This is in accord with X-ray data that show all six O atoms of 18-crown-6 interacting equivalently with  $\text{K}^+$ . Such equivalency for the  $C_{3v}$   $\text{H}_3\text{O}^+$  cation is unexpected.

With decreasing temperature from 25 to 17 °C, the shape of this band changes only slightly. Upon deuteration, i.e., in  $\text{D}_3\text{O}^+\cdot 18\text{-crown-6}$ , a shoulder at 1107  $\text{cm}^{-1}$  is revealed (Figure 4). The use of spectral Fourier self-deconvolution techniques allowed this shoulder to be observed with confidence in both  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  spectra. Its presence suggests that some portion of the sample has a nonsymmetrical structure. The intensity of this band corresponds to ca. 14% of the  $\text{H}_3\text{O}^+$  sample and ca. 36% of the  $\text{D}_3\text{O}^+$  sample.

**$\text{H}_3\text{O}^+\cdot \text{Benzo-18-crown-6}$  in DCE.** The IR spectrum of  $\text{H}_3\text{O}^+\cdot \text{benzo-18-crown-6}$  differs from that of  $\text{H}_3\text{O}^+\cdot 18\text{-crown-6}$  by showing three  $\nu_{\text{as}}(\text{COC})$  bands (Figure 5). The band at 1127  $\text{cm}^{-1}$  arising from nonbonded COC groups has about half the intensity of that of free benzo-18-crown-6. Therefore, the bands at 1097 and 1079  $\text{cm}^{-1}$  are assigned to COC groups that are inequivalently bonded to the  $\text{H}_3\text{O}^+$  cation. They have the expected relative intensities of 2:1, respectively. The data are consistent with the benzo group breaking symmetry in a structure of type **I**.



**Figure 4.**  $\nu_{\text{as}}(\text{COC})$  bands of  $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\text{CCD}$  (a, c) and  $[\text{D}_3\text{O}^+\cdot 18\text{-crown-6}]\text{CCD}$  (b, d) for 0.04 M DCE solutions at 17 °C. Spectra c and d are the results of Fourier self-deconvolution of the initial spectra a and b, respectively.



**Figure 5.** IR spectra in the  $\nu_{\text{as}}(\text{COC})$  frequency range of  $[\text{H}_3\text{O}^+\cdot \text{benzo-18-crown-6}]\text{CCD}$  in 0.05 M DCE solution (a) initial spectrum and (b) spectrum after subtraction of the spectrum of free benzo-18-crown-6 (0.05 M DCE solution) with a coefficient of 0.5.

**$\text{H}_3\text{O}^+\cdot 18\text{-Crown-6}$  in Solid State.** The thin film of the  $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\text{[CCD]}$  salt was obtained by evaporating drops of a DCE solution onto a silicon window. The IR spectrum coincides with that obtained in DCE solution indicating that the film is amorphous. Similar results were obtained with  $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\text{[CHB}_{11}\text{H}_5\text{Cl}_6]$  for freshly evaporated samples except that after several hours the sample became visually opaque and a new set of  $\nu_{\text{as}}(\text{COC})$  bands evolved. This indicated a phase transformation of amorphous to crystalline. The single  $\nu_{\text{as}}(\text{COC})$  band at 1090  $\text{cm}^{-1}$  in the amorphous/solution state decreased in intensity and a pair of equal-intensity new bands grew in at 1103 and 1078  $\text{cm}^{-1}$ . The splitting indicates that the crystal lattice induces a lowering of symmetry of the complex cation, consistent with three  $\text{O}_L$  atoms interacting more strongly with  $\text{H}_3\text{O}^+$  than the other three. The difference in frequency between the 1078  $\text{cm}^{-1}$  band and that of the free ligand ( $\Delta = 40 \text{ cm}^{-1}$ ) is nearly twice as much as that for the amorphous/solution state ( $\Delta = 23 \text{ cm}^{-1}$ ) indicating a near doubling of strength of the H-bond. This is consistent with a structure having three linear  $\text{O}_w\text{-H}\cdots\text{O}_L$  interactions in the crystalline state. However, a  $\Delta = 15 \text{ cm}^{-1}$  value for the 1103  $\text{cm}^{-1}$  band indicates that the



**TABLE 3: Comparison of Calculation and Experiment for the Characteristic Stretching Vibrations ( $\text{cm}^{-1}$ ) and  $\text{O}_W \cdots \text{O}_L$  Distances (Å) of the  $\text{H}_3\text{O}^+ \cdot 18\text{-Crown-6}$  Cation<sup>a</sup>**

	COC group	calculated <sup>b</sup>	crystalline $\text{BF}_4^-$ salt <sup>c</sup>		CCD or $\text{CHB}_{11}\text{H}_5\text{Cl}_6^-$ salt	
			+25 °C	-195 °C	in DCE soln	solid
$\text{O}_W \cdots \text{O}_L$	nonbonded	2.87		<i>d</i>		<i>d</i>
	bonded	2.76	2.68–2.73			
$\nu_{\text{as}}(\text{H}_3\text{O}^+)$		2873	2850	2700	2770	2770
$\nu_{\text{as}}(\text{COC})$	nonbonded	1112				
	bonded	1057 (55)	1090 (28)	1097 (21) 1080 (38)	1095 (23)	1092 <sup>e</sup> 1103 (15) <sup>f</sup> 1078 (40) <sup>f</sup>

<sup>a</sup> The difference in  $\nu_{\text{as}}(\text{COC})$  frequency of the complex and the free ligand (1118  $\text{cm}^{-1}$ ) is given in parentheses. <sup>b</sup> Reference 22. <sup>c</sup> Reference 15. <sup>d</sup> No data available. <sup>e</sup> Amorphous.

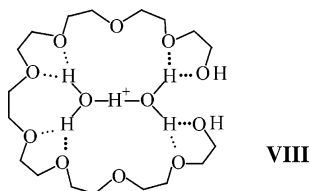
“nonbonded”  $\text{O}_L$  oxygen atoms experience secondary interactions from the H-bonding.

Despite these changes in the spectra of the crown ether portion of the complex, the spectrum of  $\text{H}_3\text{O}^+$  ion itself changes very little. Within experimental error, the O–H stretching and bending vibrations coincide. This indicates that the binding energy of  $\text{H}_3\text{O}^+$  to the crown ether is the same in the symmetrical and unsymmetrical forms of the complex.

## Discussion

The IR spectra of  $\text{H}_5\text{O}_2^+$  complexes with PEGs and 15-crown-5 ligands provide benchmarks for interpreting the more unusual IR spectrum of the  $\text{H}_3\text{O}^+$  complex with 18-crown-6.

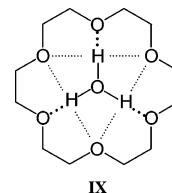
**$\text{H}_5\text{O}_2^+$  Complexes in DCE.** Although the  $\text{H}_5\text{O}_2^+ \cdot \text{PEG}$  complexes are 1:1 and the  $\text{H}_5\text{O}_2^+ \cdot 2(15\text{-crown-5})$  complex is 1:2, the stretching frequencies of the terminal O–H of the  $\text{H}_5\text{O}_2^+$  cation are practically coincident (3000–3100  $\text{cm}^{-1}$ ). Thus, the  $\text{H}_5\text{O}_2^+$  cation experiences a similar overall strength of ligand interactions in both situations. On the other hand, from the intensities of the  $\nu(\text{COC})$  bands for bonded and nonbonded C–O–C groups, it was deduced that *eight* O atoms from PEG interact with the cation while only *four* O atoms from two 15-crown-5 ligands are involved. This is precisely reflected in a halving of the interaction strength at the COC groups in PEG relative to 15-crown-5: the differences in frequencies ( $\Delta$ ) between the free and complexed COC groups are 15 and 30  $\text{cm}^{-1}$  respectively (Table 2). It follows therefore that the H bonds with PEG are bifurcated (**VIII**) whereas those to the two 15-crown-5 ligands are linear (**VII**).



**$\text{H}_3\text{O}^+$  Complexes in DCE.** The stretching frequencies of O–H vibrations of  $\text{H}_3\text{O}^+$  cation in the 15-crown-6 and 18-crown-6 complexes are almost the same (ca. 2770  $\text{cm}^{-1}$ ) while that for the benzo-18-crown-6 complex is higher (2880  $\text{cm}^{-1}$ ). This means that the overall strength of the  $\text{H}_3\text{O}^+$  interaction with  $\text{O}_L$  atoms is somewhat weaker in the benzo crown ether. If the H bonds in all three complexes were of the same type (e.g., linear), then the  $\nu(\text{O–H})$  frequencies should correlate with the strength of their interaction with the COC groups, as measured by the values of  $\Delta\nu(\text{COC})$  (Table 3). In reality, the difference between free and bound ligand follow the order benzo-18-crown-6 greatest ( $\Delta = 49 \text{ cm}^{-1}$ ), 15-crown-5 slightly weaker ( $\Delta = 40 \text{ cm}^{-1}$ ), and 18-crown-6 half as weak again ( $\Delta = 23 \text{ cm}^{-1}$ ). Thus, the nature of H-bonding in the 18-crown-6

complex must be quite different from those in the benzo analogue or the 15-crown-5 ligand. Since normal, linear H bonds have been deduced for the latter two complexes, and since the interaction strength per  $\text{O}_L$  is halved in the former, one might be tempted to propose bifurcated H bonds of type **II** in 18-crown-6 complex. However, as discussed below, the alternative possibility of indeterminate locations for the H atoms must also be considered. We note that chemical equivalence of the six  $\text{O}_L$  atoms of the crown ether is a necessary condition for equivalence of  $\nu(\text{COC})$  in the IR spectrum. Disturbing this equivalency by the introduction of a benzo group into 18-crown-6 causes a change to the three linear H bonds as indicated by the distinct splitting of  $\nu(\text{COC})$ . As discussed next, a similar effect can be produced in the solid state by anion and lattice asymmetry effects.

**Solution vs Solid-State Structure for  $\text{H}_3\text{O}^+ \cdot 18\text{-Crown-6}$ .** The unexpected feature of the  $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$  complex in solution is the equivalence of the six COC groups. This is retained in the amorphous solid state as long as the anion is large and weakly ion-pairing, which is why carborane anions<sup>32</sup> were chosen for the present study. In the crystalline state, however, two  $\nu(\text{COC})$  frequencies are observed. The difference in  $\nu(\text{COC})$  frequency ( $\Delta$ ) between the free ligand and the complex in solution (or amorphous state) is only 23  $\text{cm}^{-1}$ , whereas that of the crystalline material is nearly twice this value (40  $\text{cm}^{-1}$ ). This is consistent with the crystalline structure having three linear  $\text{O}_W\text{–H} \cdots \text{O}_L$  interactions. The remaining three atoms ( $\text{O}_L'$ ) are not completely free, however. Their finite  $\Delta$  value (15  $\text{cm}^{-1}$ ) indicates that they are also under the electrostatic influence of the  $\text{H}_3\text{O}^+$  ion and are therefore also involved in some degree of H-bonding. These secondary interactions are probably the result of the trifurcated interaction indicated in structure **IX**.



Despite the variation in  $\nu_{\text{as}}(\text{COC})$  in the ligand portion of the cationic complex, the IR spectrum of the complexed  $\text{H}_3\text{O}^+$  ion itself changes very little. Within experimental error, the O–H stretching and bending vibrations coincide between the amorphous and crystalline states. This indicates that the binding energy of  $\text{H}_3\text{O}^+$  to the crown ether is the same in the symmetrical and unsymmetrical forms of the complex.

A transformation from higher to lower symmetry has been observed in the phase change of solid  $[\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}][\text{BF}_4^-]$  when the temperature is decreased from +25 to -195 °C.<sup>34</sup>

The room-temperature spectrum shows a somewhat broad  $\nu_{\text{as}}(\text{COC})$  band at  $1090\text{ cm}^{-1}$  whereas the low-temperature spectrum splits into two distinct components at  $1097$  and  $1080\text{ cm}^{-1}$  (Table 3) accompanied by some distortion of the symmetry of the  $\text{BF}_4^-$  anion. The near equivalence of all six  $\text{O}_L$  atoms in the room-temperature structure may be reflected in the crystal structure where the  $\text{O}_W \cdots \text{O}_L$  distances span the small range  $2.68\text{--}2.73\text{ \AA}$ .<sup>12</sup>

Usually the lattice asymmetry combines with the electrostatic effects of the counterion to favor splitting the  $\text{O}_W \cdots \text{O}_L$  distances into three shorter and three longer,<sup>10,33,34</sup> or even something more complex. In the  $\text{GaCl}_4^-$  salt, for example, there are four practically coincident  $\text{O}_W \cdots \text{O}_L$  distances at  $2.75\text{ \AA}$  along with one shorter ( $2.67\text{ \AA}$ ) and one longer ( $2.81\text{ \AA}$ ).<sup>35</sup> When both the counterion influence and the lattice distortion is weak (e.g., in the  $\text{AsF}_6^-$ ,  $\text{I}_7^-$ , and  $\text{BF}_4^-$  salts<sup>12–14</sup> all six  $\text{O}_W \cdots \text{O}_L$  distances appear to become nearly equivalent.

**Comparison of Experiment and Theory.** To date, all calculations on the structures of  $\text{H}_5\text{O}_2^+$  and  $\text{H}_3\text{O}^+$  complexes with polyethers have favored linear (or nearly linear) H-bonding.<sup>21,22</sup> This is in agreement with the present experimental work only for the  $\text{H}_3\text{O}^+ \cdot 15\text{-crown-5}$ ,  $\text{H}_3\text{O}^+ \cdot \text{benzo-18-crown-6}$ , and  $\text{H}_5\text{O}_2^+ \cdot 2(15\text{-crown-5})$  cations. For the  $\text{H}_5\text{O}_2^+ \cdot \text{PEG}$  complexes, SCF-MI calculations at the  $6\text{-13G}^*$  level argue for partial interaction with the noncoordinated O atoms but even this is a poor match with the IR data which show the protons of  $\text{H}_5\text{O}_2^+$  interact more or less equivalently with pairs of  $\text{O}_L$  atoms in bifurcated H bonds. Higher level calculations have been performed on the  $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$  complex but the lowest energy structure always has three classical linear H bonds. While this is in qualitative agreement with selected crystal structure data, it is inconsistent with the IR data in solution or the amorphous state that show essential equivalence of all six  $\text{O}_L$  atoms. The conflict is all the more dramatic because it occurs where comparisons should be most valid, i.e., when the influence of the anion and environmental asymmetry have been minimized in the experimental data, and are absent in the calculation.

With DFT calculations at the BLYP/II//BLYP/6-31G\* level, the optimized structure of  $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$  has three short  $\text{O}_W \cdots \text{O}_L$  distances of  $2.76\text{ \AA}$  corresponding to linear H bonds and three longer “nonbonding” distances of  $2.87\text{ \AA}$ .<sup>22</sup> The IR spectrum calculated for this structure has two  $\nu(\text{COC})$  bands at  $1057$  and  $1112\text{ cm}^{-1}$  corresponding to the H-bonded  $\text{O}_L$  and nonbonded  $\text{O}_L$  atoms, respectively. Thus, the calculated structure (in the absence of counterion) more closely resembles the structure obtained under the distorting influence of the crystal lattice and counterion. This is difficult to reconcile. Moreover, the splitting of  $\nu(\text{COC})$  in the calculated structure ( $55\text{ cm}^{-1}$ ) is more than three times that of the corresponding experimental value for the  $\text{BF}_4^-$  salt ( $17\text{ cm}^{-1}$ ), and more than twice that of the crystalline CCD salt ( $25\text{ cm}^{-1}$ ). Thus, on a more quantitative basis, the calculated structure is quite far from experimental data. One of the closest experimental approaches to linear H bonds appears to be the  $\text{ZnCl}_4^{2-}$  salt because the difference between the two sets of  $\text{O}_W \cdots \text{O}_L$  distances is largest.<sup>34</sup> The average short distance is  $2.614\text{ \AA}$ , considerably shorter than the calculated distance.

## Conclusion

IR spectroscopy on the nature of the H-bonding in hydronium ion complexes with polyethers leaves little doubt that the intrinsic structure of the  $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$  cation has essentially equivalent interactions of the three protons with all

six crown ether O atoms. Theory is unable to reproduce this result. Small symmetry-lowering influences such as the introduction of a benzo substituent to the ligand, electrostatic effects of the anion, or the incorporation of salts into an asymmetric crystal lattice lead to asymmetric structures where a description of the cation in terms of three “normal” linear H bonds becomes valid. Currently applied theory reproduces this result but *without* the external symmetry-lowering perturbation.

There are two possible explanations for our experimental data. The first is a static structure with bifurcated H bonds (structure **III**). This would satisfy the requirement of equivalency of  $\nu(\text{COC})$ . However, if this were the case, it is difficult to understand why theory consistently finds bifurcated H-bonding higher in energy than linear. The second explanation, which we favor, is based on our recent experience with short, strong, low-barrier (SSLB) H bonds in cations of the type  $\text{H}(\text{O-donor})_2^+$ , where the protons have indeterminate positions between the O atoms.<sup>23,24</sup> We propose that the protons in  $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$  reside on a ring-shaped potential surface with six minima corresponding to six linear H bonds but with barrier heights separating these minima of similar or less than the rotational/vibrational energy levels populated at room temperature. Under this proposal, the question of linear vs bifurcated H bonds in a static structure begins to lose its meaning. A low barrier to rotational ratcheting of the  $\text{H}_3\text{O}^+$  ion makes all six ligand O atoms equivalent and rationalizes the somewhat broadened nature of the  $\nu(\text{COC})$  band. The shoulder appearing under certain conditions on the high-frequency side may correspond to a small population of molecules with a finite barrier. The increase in the relative intensity of this shoulder upon deuteration of the hydronium ion is consistent with this proposal. The precise nature of the proton motion that leads to COC bond equivalency provides a new challenge for theory.

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