1236 *J. Phys. Chem. A* **2007,** *111,* 1236−1244

Infrared Hole Burning of Crown Ether 18-c-6 Ammonium Ion Complexes

Christopher Endicott and Herbert L. Strauss*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received: September 8, 2006; In Final Form: December 6, 2006

Crystals of the complexes of 18-crown-6 with a number of ammonium salts (bromide, chloride, two forms of iodide, nitrate) and with amminetrifluoroboron have been prepared, analyzed with X-ray diffraction, and then investigated by infrared hole burning. The complexes all have similar hydrogen-bonding arrangements between the crown ether ring and the ammonium nitrogen. Hole burning of the infrared bands at low temperature identifies the N−D hydrogen bonds of the compounds that have been doped with a small amount of deuterium. The patterns of N−D bands from different complexes are often quite overlapped, with a few notable exceptions. The hole burning reveals a wide variety of phenomena, including monotonic decay and kinetic interchange among the holes and antiholes, a variety similar to that observed in previous hole-burning experiments.

1. Introduction

A characteristic property of the crown ethers is their ability to form complexes selectively with various ionic species, such as alkali-metal and alkaline-earth-metal cations. The different crown ethers have different "cavity" sizes and can be chosen to bind most strongly with a given cation.[1−3] The stability of these complexes depends on the size of the ion with respect to the cavity size of the crown ether, the charge of the ion, the conformation of the ring, and the solvent. Here we consider complexes of the representative molecule of this series, the 18-c-6 crown ether (1,4,7,10,13,16-hexaoxacyclooctadecane, $C_{12}H_{24}O_6$). The noncomplexed ring, which has a center of inversion, is composed of three successive nonequivalent $-OCH_2CH_2O-$ units. All of the bonds are *gauche*, creating a roughly planar molecule, with four of the six oxygens facing the inside cavity of the ring. The potassium cation forms the tightest complex with the 18-c-6 ring cavity,[2] so it might be expected that the ammonium ion will form a stable complex as well, as ammonium has an "ionic radius" close to that of potassium. The binding does indeed turn out to be stable. The counterion and the presence of any included solvent molecules (for example, water) in the crystal structure can alter the hydrogen bonding to the ammonium ion as well as modify the simple idea of an ionic cavity holding the cation.

We have crystallized 18-c-6 with a series of ammonium salts and investigated these by X-ray diffraction. We have substituted the crystals with a small amount of deuterium (∼2%) and systematically obtained the infrared spectrum in the hydrogen (deuterium) bond stretching region. We have then used infrared lasers to "hole burn" the N−D stretching bands.

Such hole burning has been shown previously[4] to identify the absorption bands arising from the hydrogen-bonded hydrogens (deuteriums). The spectral holes and the accompanying antiholes arise by the internal rotation of the nitrogen moiety changing the position of the N−D band, thus identifying the bands that belong to a specific nitrogen and providing information on the dynamics of the reorientation of the nitrogen-containing group. The compounds we have previously investigated include numerous ammonium salts as well as compounds containing the NH_3^+ moiety such as amino acid salts.[5] Another noteworthy complex is between ammonia and a substituted borane[6] in which the ammonia is hydrogen bonded to three oxygen atoms of the borane and the fourth coordinating position is occupied by a nitrogen−boron bond.

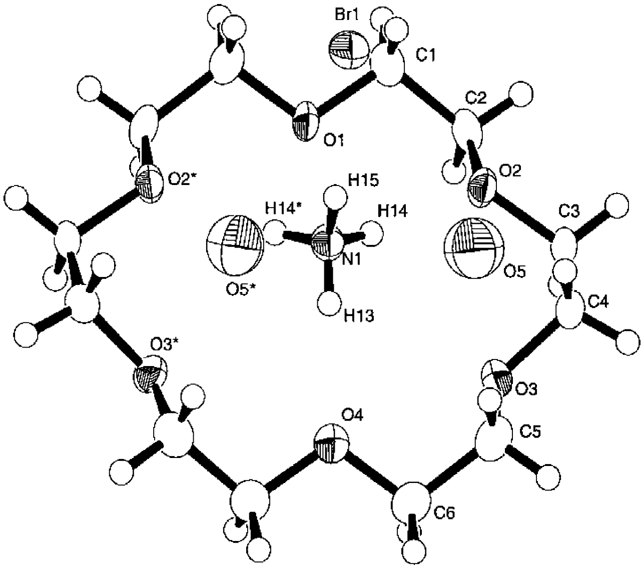

Figure 1. X-ray crystal structure of the 18-c-6 ammonium bromide complex at 118 K. The P_{nam} space group for this complex is identical with the room-temperature structure. There is a mirror plane that runs through O1, O4, N1, H13, H15, and Br1. There are hydrogen bonds between N1 and O2, O2*, O4, and Br1. The hydrogen atoms of the water molecules (O5 and O5*) were not located and are not shown.

In each of the 18-c-6 complexes, such as the ammonium bromide complex illustrated in Figure 1, three of the hydrogens of the ammonium group are directly hydrogen bonded to three of the oxygens on the inside of the crown ether ring. For ammonium ion complexes, the fourth ammonium hydrogen is hydrogen bonded to the counterion. The crown ether ring retains the *all-gauche* conformation, with three of the oxygens slightly above and three slightly below the mean plane of the ring. The ammonium group adopts a perching position onto one side of the ring, hydrogen bonding with the three closest oxygens that are on the same side of the ring. The nitrogen of the ammonium

10.1021/jp0658795 CCC: $37.00

group is located about 1.0 Å from the mean plane of the ring, although this distance varies among complexes with different counterions. For most of the ammonium crown ether complexes, the ammonium group sits in a localized C_s or C_1 site and the conformation of the ring has approximately D_{3d} symmetry.

We studied the series of 18-c-6 ammonium ion complexes with bromine, chlorine, iodine, and nitrate counterions as well as the complex with aminotrifluoroborane. We find that each of these complexes is capable of being hole burned and that there are similarities in the N−D stretching band regions of their infrared spectra, as well as in their resulting hole-burning patterns. The crystals were checked by X-ray diffraction. It turns out that some of the compounds crystallized in different forms depending on the solvent molecules included in the crystal. However, the basic ammonium crown ether geometry remains. The details of the hole burning differ markedly for the different complexes and indeed for the different crystal forms of the same complex.

The frequencies of the infrared bands of an A−H···B hydrogen bond correlate with the A−B distance, and this correlation allows an assignment of the bands to a specific hydrogen bond.[4,7] Many of the infrared bands are overlapped, and the hole burning allows us to untangle the various component bands. In some of the crystals we study here, the distances are so close to one another that the bands overlap and the assignment remains uncertain. Most of the hydrogen bonds have oxygen as the B atom, but some of the hydrogen bonds have a halogen as the B atom. For these cases, the correlation with the other hydrogen bond distances is not well established, which adds additional uncertainty to the assignment.

2. Experimental Details

The 18-c-6 and ammonium ion complexes with halogen counterions were prepared using several different methods, following previous studies whenever possible.[8,9] The complex of 18-c-6 with ammonium bromide was prepared by dissolving 0.2000 g of 18-c-6 (0.75 mmol) and 0.0735 g of NH_4Br (0.75 mmol) in 6 drops of water. To make the deuterated ammonium samples, a 2% (by volume) solution of D_2O in H_2O was used to dissolve the compounds. The solution was left overnight and then dried under vacuum. The remaining white powder was then dissolved in CH_2Cl_2, and a comparable amount of *n*-pentane was carefully layered on top. The mixture was put in a room-temperature water bath to slow the evaporation of the solvent. After several days, the layers had mixed and clear crystals had formed that were large enough for analysis.

The 18-c-6 complexes with ammonium chloride and ammonium iodide were prepared in the same way as the 18-c-6 ammonium bromide sample. The samples were both made with 0.2000 g of 18-c-6 (0.75 mmol) and either 0.0398 g of NH_4Cl (0.75 mmol) or 0.1073 g of NH_4I (0.75 mmol). The ammonium iodide crystals tended to grow rather easily, sometimes within an hour, but the ammonium chloride crystals grew very slowly.

We found that a second crystal type of the 18-c-6 ammonium iodide complex could be prepared using more water. This was done by dissolving 0.2552 g of 18-c-6 (0.96 mmol) and 0.1400 g of NH_4I (0.96 mmol) in 26 drops of water. This solution was left to slowly evaporate at room temperature for several days, after which clear needle-like crystals had grown. It should be noted that this solution was not dried under vacuum or layered with any other precipitating solvent.

The preparation of the 18-c-6 ammonium nitrate complex followed the procedure given by K. M. Doxsee et al. by dissolving 0.0665 g of 18-c-6 (0.25 mmol) and 0.0201 g of NH_4NO_3 (0.25 mmol) in 3 mL of chloroform.[9] To get the NH_4NO_3 to completely dissolve, the mixed reactions were placed in a standard sonic bath overnight. Once dissolved, a comparable amount of either benzene or diethyl ether was layered on top, and the mixture was allowed to slowly evaporate over several days. By selecting either benzene or diethyl ether as the crystallization solvent, slightly different crystal structures could be made. When using benzene, the crystal complex does not contain any water molecules, but when diethyl ether is used, the complex becomes a monohydrate. Introducing deuterium into the ammonium ion proved to be difficult for these samples. Many attempts that tried using various mixtures of $CDCl_3$ in $CHCl_3$ to dissolve the compounds failed to introduce any deuterium, and even using a previously deuterated and dried NH_4NO_3 sample as a starting reagent turned out to be unsuccessful. The only method that appeared to work properly was to add a single drop of D_2O into the dissolved NH_4NO_3 mixture, and this led to the monohydrated crystal structure. The aminotrifluoroborane and the complex of 18-c-6 with BF_3NH_3 were prepared following the procedures of Colquhoun et al.[10]

All of the chemicals used in these preparations were commercially available and were used as they came. For each of these samples, the deuterium concentrations were kept low enough to ensure that there was at most only one deuterium atom per ammonium ion.

Crystals of each of these samples were left in their respective solutions until needed, since they tended to dry quickly when left in the air. Single crystals were used when large enough ones were available; otherwise, several small crystals were used instead. Each crystal was patted dry, crushed, and mulled in mineral oil. Mineral oil was used due to its transparency in the N−D stretching region. The mull was then placed between two CaF_2 windows and put into the sample holder of the cryostat. Spectra were recorded over the range of 2000−4000 cm^{-1} with 1 cm^{-1} resolution using an InSb detector. Each sample was allowed to come to thermal equilibrium at low temperatures before the hole-burning experiment was performed, which was verified by waiting for any spectral changes to become negligible over the time scale of the irradiations. The hole burning was accomplished with a difference-frequency laser[11] used to provide about 80 mW/cm^2. We estimate that the bandwidth of the difference frequency laser is about 1 cm^{-1}. The samples were irradiated for 10 min at each frequency unless otherwise noted. Also effective for hole burning was overnight irradiation using the spectrometer Nernst Glower as a broad-band source.

3. Results: 18-c-6 Ammonium Bromide Complex

The room-temperature crystal structure of the 18-c-6 ammonium bromide complex, $C_{12}H_{24}O_6 \cdot NH_4Br \cdot 2H_2O$, has been known since 1978.[8] The crystal is orthorhombic, with a space group of P_{nam} (No. 62) and $Z = 4$. Our crystal, examined at 118 K, had a nearly identical structure, which is illustrated in Figure 1. The X-ray data show that the ammonium ion is located at a C_s site between the crown ether ring and the bromine anion as expected. There are two crystallographically equivalent water molecules in an asymmetric unit. The water molecules seem to hydrogen bond only with the bromine anions and not with the ammonium ions or the crown ether rings.

The ammonium ion hydrogens were located in a difference Fourier map, but the water hydrogens appeared disordered and were not included in the final refinement. The low-temperature X-ray analysis is in Appendix S1 in the Supporting Information, and Table 1 gives the hydrogen-bonding information for the 18-c-6 ammonium bromide complex. The infrared spectra of

TABLE 1: Hydrogen-Bonding Data for the 18-c-6 Ammonium Bromide Complex

A−H···X[a]	A···X[b] (Å)	N−H[b] (Å)	N−H···X[b] (deg)	infrared bands (cm^{-1})	
N1−H13···O4	2.858	0.88	174.21	**I**, 2326	**II**, 2343
N1−H14···O2	2.889	0.88	165.11	**I**, 2208	**II**, 2230
N1−H14*···O2*	2.889	0.88	165.11		
N1−H15···Br1	3.398	1.00	161.56	**I**, 2260	**II**, 2295
O5−H···Br1	3.344			2515−2565	
O5−H···Br1′	3.348				
O5*−H···Br1	3.344				
O5*−H···Br1′	3.348				

[a] The asterisks denote symmetrically equivalent atoms. [b] At 118 K (from this work).

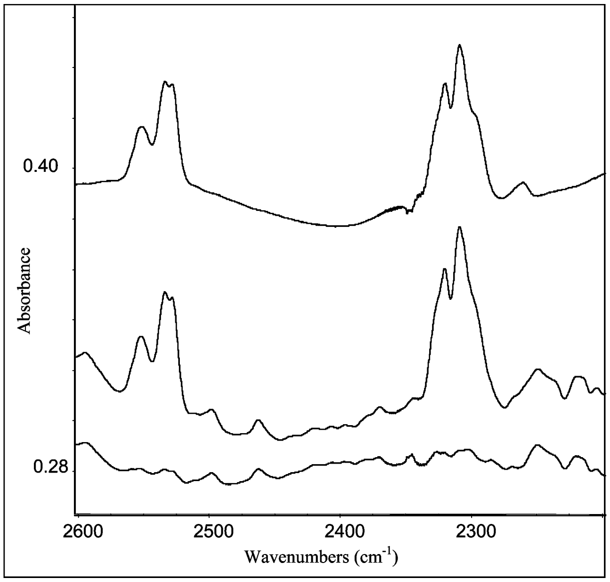

Figure 2. Infrared spectra for the 18-c-6 ammonium bromide complex at 13 K. The middle spectrum is for the complex with 2% deuterium, and the bottom spectrum is for the nondeuterated complex. The top spectrum is the difference spectrum between the deuterated and nondeuterated spectra. The N−D stretching bands are near 2300 cm^{-1}, and the O−D bands are near 2550 cm^{-1}.

the nondeuterated and 2% deuterated 18-c-6 ammonium bromide complexes at 13 K are shown in Figure 2. Two groups of new broad peaks appear in the ranges of 2260−2340 and 2515−2565 cm^{-1} in the spectrum of the deuterated sample. The lower frequency group corresponds to N−D stretching bands, while the higher frequency group is due to O−D stretching bands of the partially deuterated water molecules.

The hole-burning experiment was performed on the 2% deuterated 18-c-6·NH_4Br sample and identified two separate groups of interrelated bands. Group I contains the bands at 2260, 2308, and 2326 cm^{-1}, while group II consists of the bands at 2295, 2320, and 2343 cm^{-1}. These hole-burning results are shown in Figures 3 and 4, respectively.

The fact that there are two separate sets of bands shows that there are two nonequivalent ammonium ions in this crystal structure at low temperature. The broad and obviously composite bands centered near 2300 cm^{-1} are made up of components whose centers are difficult to define. The most obvious strategy to deconvolute these composite bands is to take the peaks of the holes and antiholes that appear upon hole burning at other wavenumbers. For example, irradiating the sample at 2330 cm^{-1} for 10 min produces a hole with a minimum at 2326 cm^{-1}, which we then take as the center of one component band. Additionally, during the sample's relaxation, most of the burns, including one at 2266 cm^{-1}, produced antiholes at 2260 cm^{-1}, so we take 2260 cm^{-1} as the center of another band. The positions of the bands arrived at are listed in Table 1. There is some indication that the decay of the holes and antiholes after irradiation is nonmonotonic. We will discuss this phenomenon for the clearer example of iodide complex **I**.

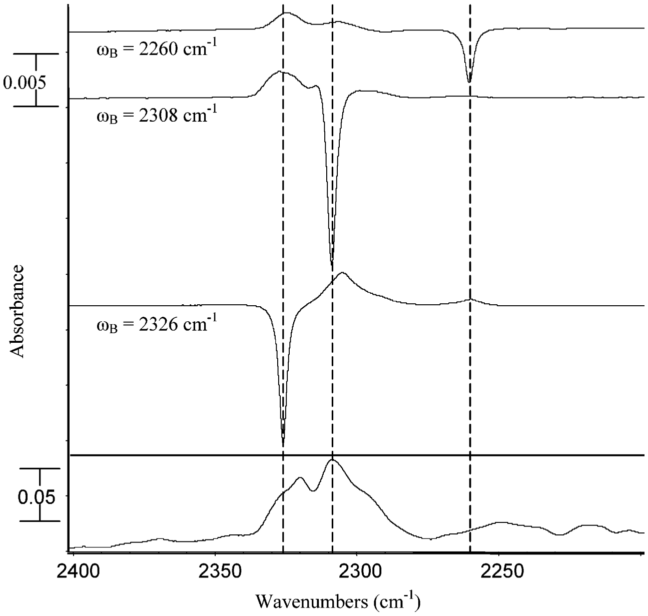

Figure 3. Group I infrared hole-burning results for the 18-c-6 ammonium bromide complex with 2% deuterium at 13 K. The top three spectra are the difference spectra taken immediately before and after 10 min irradiations at 2260, 2308, and 2326 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation.

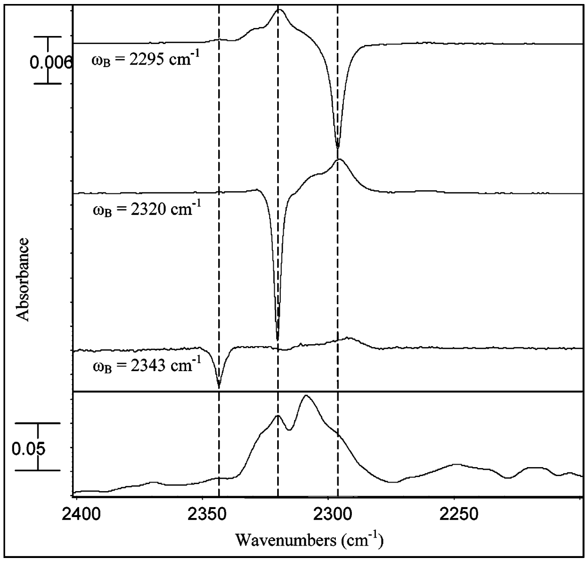

Figure 4. Group II infrared hole-burning results for the 18-c-6 ammonium bromide complex with 2% deuterium at 13 K. The top three spectra are the difference spectra taken immediately before and after 10 min irradiations at 2295, 2320, and 2343 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation. The vertical scale of the spectrum for the 2343 cm^{-1} irradiation has been expanded by a factor of 3 compared to those of the other two irradiations.

The two sets of hole-burning bands show that there are two inequivalent ammonium sites, while the X-ray studies at both room temperature and 118 K show only one. We took infrared spectra at a series of temperatures to look for possible phase transitions, but did not find any sharp breaks in the spectra. However, the difference spectra obtained from spectra taken at

TABLE 2: Hydrogen-Bonding Data for the 18-c-6 Ammonium Chloride Complex

A−H···X[a]	A···X[b] (Å)	N−H[b] (Å)	N−H···X[b] (deg)
N1−H25···O1	2.888	0.81	175.32
N1−H26···Cl1	3.209	0.76	156.71
N1−H27···O3	2.888	0.84	172.60
N1−H27*···O3*	2.888	0.84	172.60
N2−H28···O5	2.888	0.73	179.94
N2−H29···Cl2	3.271	0.98	171.72
N2−H30···O7	2.906	0.77	168.48
N2−H30*···O7*	2.906	0.77	168.48
O9−H···Cl1[c]	3.221		
O9−H···Cl2[c]	3.273		
O10−H···Cl1	3.232		
O10−H···Cl2	3.213		

[a] Asterisks denote symmetrically equivalent groups. [b] At 146 K. [c] O9 has 0.6 occupancy.

different temperatures showed peaks at the frequencies of the holes and are in agreement with the assignment to two discrete ammonium sites.

3.1. 18-c-6 Ammonium Chloride Complex. The crystal structure for the 18-c-6 ammonium chloride complex, $C_{12}H_{24}O_6 \cdot NH_4Cl \cdot 2H_2O$, is of P_{nam} symmetry and is structurally isomorphic with the bromide complex.[12] However, our putative crystal of this complex examined by X-ray analysis at 146 K turned out to have a space group of $P2_1/m$ (No. 11) with $Z = 4$ containing two nonidentical $C_{12}H_{24}O_6 \cdot NH_4Cl \cdot 2H_2O$ units. One of the water molecule sites refined to only 60% occupancy in the final model. Each of these units still contains a crystallographic mirror plane that places each ammonium ion in a C_s symmetry site. The ammonium ions also retain their hydrogen-bonding geometry, forming three hydrogen bonds to the three closest oxygens in the crown ether rings and another hydrogen bond to their respective chlorine anion. These hydrogen-bonding data are shown in Table 2. The hydrogen atoms on the ammonium ions and water molecules were located in a difference Fourier map, and it can be seen that each water molecule forms hydrogen bonds to both chlorine anions, creating a network of hydrogen bonds as in the P_{nam} room-temperature structure.[12] The X-ray data at 146 K are given in Appendix S2 in the Supporting Information.

The infrared spectra of the nondeuterated and 2% deuterated 18-c-6 ammonium chloride samples at 14 K are shown in Figure 5. The spectra do not show obvious N−D and O−D stretching bands. However, the best candidates for the N−D bands are the small group of peaks between 2295 and 2335 cm^{-1} since they appear in the same N−D stretching band region as in the 18-c-6 ammonium bromide complex. Hole burning of the 2% deuterated 18-c-6 ammonium chloride produced the results shown in Figure 6, which are described briefly in the caption. We did not assign the 18-c-6 ammonium chloride hole-burning results due to the low intensities of the holes and antiholes. However, the number of holes is consistent with the presence of two crystallographically distinct ammonium groups. Since only five of the expected six holes appeared during the hole-burning experiment, either two of the holes were overlapped or one of the holes was too weak to detect.

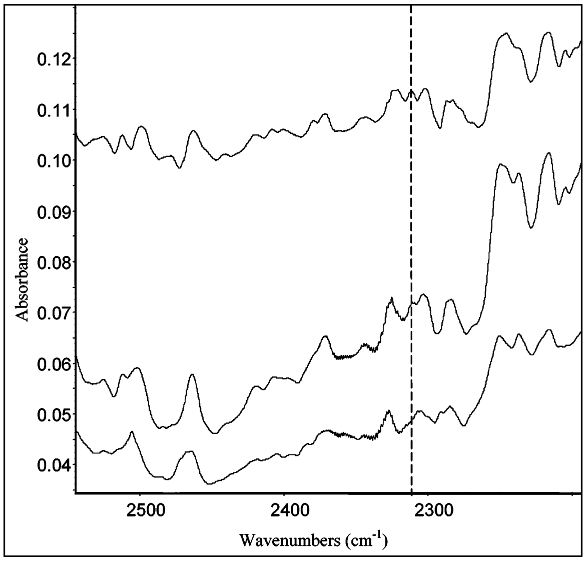

Figure 5. Infrared spectra for the 18-c-6 ammonium chloride complex at 14 K. The middle spectrum is for the complex with 2% deuterium, and the bottom spectrum is for the nondeuterated complex. The difference spectrum is at the top. The dashed line at 2311 cm^{-1} marks the clearest difference between the deuterated and nondeuterated spectra in the N−D stretching band region.

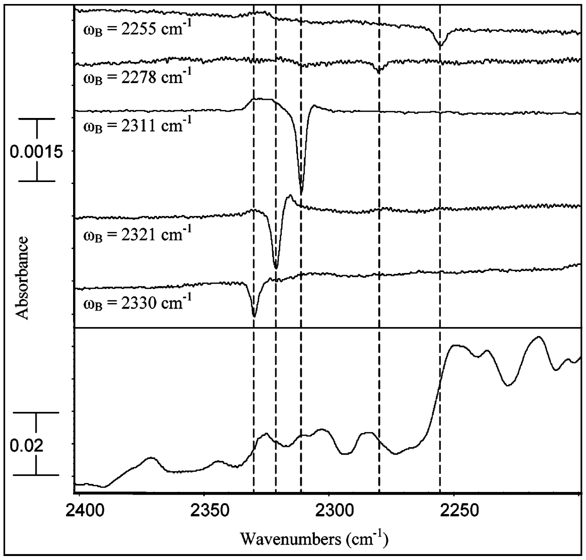

Figure 6. Infrared hole-burning results for the 18-c-6 ammonium chloride complex at 14 K. The top five spectra are the difference spectra taken immediately before and after 10 min irradiations at 2255, 2311, and 2330 cm^{-1} and 20 min irradiations at 2278 and 2321 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation.

3.2. 18-c-6 Ammonium Iodide Complex I. The 18-c-6 ammonium iodide complex, $C_{12}H_{24}O_6 \cdot NH_4I \cdot H_2O$, has not been reported before. At 103 K, we found an orthorhombic crystal with a space group of $P2_12_12_1$ (No. 19) and $Z = 4$. This crystal had one water molecule per crown ether ammonium ion group, as opposed to the chloride and bromide complexes that each had two. The X-ray data for the iodide complex are in Appendix S3 in the Supporting Information. The hydrogen atoms were not located, although hydrogen atoms on the carbon atoms were included in the structure determination at their usual positions. The X-ray data show that the ammonium ion, which is in a C_1 symmetry site, still has the standard hydrogen-bonding arrangement. The hydrogen-bonding data for the ammonium ion are shown in Table 3. The water molecule appears to hydrogen bond with the iodine anion.

The spectrum of the 2% deuterated 18-c-6 ammonium iodide complex at 13 K shows several broad overlapped peaks in the N−D stretching band region from 2293 to 2340 cm^{-1} and another peak at 2253 cm^{-1} (Figure 7). There are also several possible O−D stretching bands from the water molecule at 2464, 2504, and 2520 cm^{-1} (not shown). The hole-burning results are shown in Figure 7 and reveal five distinct N−D bands at 2253,

TABLE 3: Hydrogen-Bonding Data for 18-c-6 Ammonium Iodide Complex I

A−H···X[a]	A···X[b] (Å)	infrared band (cm^{-1})	A−H···X[a]	A···X[b] (Å)	infrared bands (cm^{-1})
N1−H···O1	2.91	2321	N1−H···I1	3.43	2253
N1−H···O3	2.90	2316	O7−H···I1	3.76	2462, 2504, 2520
N1−H···O5	2.89	2304			

[a] The hydrogens were not located. [b] At 103 K.

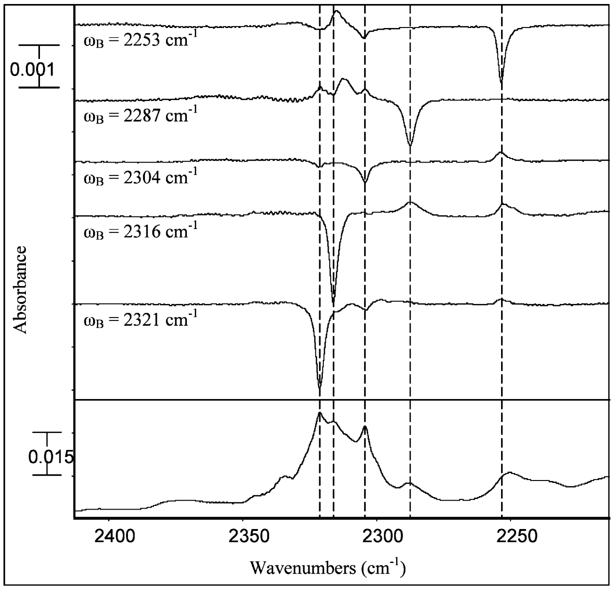

Figure 7. Infrared hole-burning results for the partially deuterated 18-c-6 ammonium iodide complex **I** at 13 K. The top five spectra are the difference spectra taken immediately before and after 10 min irradiations at 2253, 2287, 2304, 2316, and 2321 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation.

2287, 2304, 2316, and 2321 cm^{-1}. However, the hole/antihole at 2287 cm^{-1} is anomalous. The spectral changes in the 2287 cm^{-1} band disappear in about 10 min after irradiation, while each of the holes and antiholes in the other four locations persist for more than 10 h. Furthermore, the irradiation at 2287 cm^{-1} did not initially create an antihole at 2253 cm^{-1}, but an antihole at 2253 cm^{-1} begins to appear and grow after 10 min. Therefore, the four N−D bands at 2253, 2304, 2316, and 2321 cm^{-1} appear to be the four dominant hydrogen bond frequencies, and the feature at 2287 cm^{-1} is assigned as a sum or difference band or as a band due to some disorder in the crystal. We have observed nonmonotonic growth and decay and transfer of intensity among holes/antiholes before in a number of ammonium-containing crystals such as ammonium triflate.[13]

The hydrogen atoms were assumed to be between the appropriate A and B atoms and were not explicitly located in the X-ray analysis, but this is sufficient to assign the N−D band frequencies to their most probable hydrogen bond. With the N−D band at 2253 cm^{-1} assumed to be due to the hydrogen bond from the ammonium ion to the iodide anion, the rest of the hydrogen-bonding distances in Table 3 can be correlated with the infrared frequencies.

TABLE 4: Hydrogen-Bonding Data for 18-c-6 Ammonium Iodide Complex II

A−H···X	A···X[a] (Å)	N−H[a] (Å)	N−H···X[a] (deg)	infrared bands (cm^{-1})
N1−H51···O13	2.794	0.848	167.98	2290
N1−H52···O7	2.871	0.842	170.24	2308
N1−H53···O11	2.834	0.848	152.76	2278
N1−H54···O9	2.922	0.862	165.85	2330
N2−H55···O1	2.914	0.849	158.98	2324
N2−H56···O5	2.842	0.852	173.17	2278
N2−H57···I1	3.552	0.850	154.15	2256
N2−H58···O3	2.889	0.849	167.88	2315
O13−H···O14	2.770			
O13−H···O15	3.880			
O14−H···O15	2.717			
O13−H···I2	3.617			2441, 2478, 2526, 2528, 2534, 2566
O14−H···I2	3.668			
O15 − H···I2	3.567			
O15−H···I1	3.531			

[a] At 151 K.

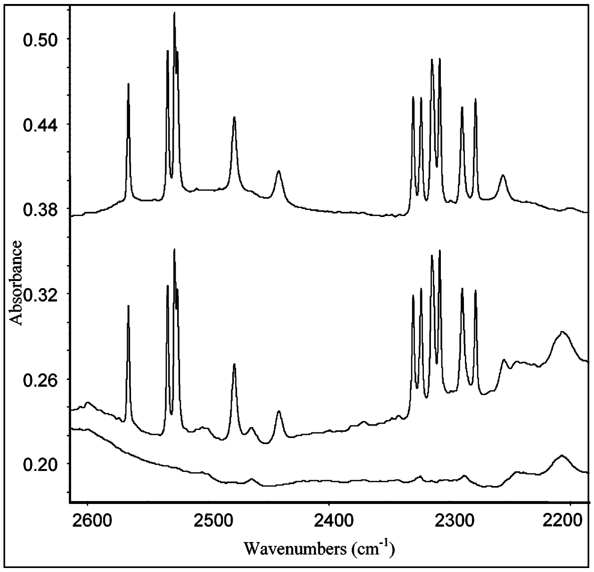

Figure 8. Infrared spectra for 18-c-6 ammonium iodide complex **II** at 10 K. The middle spectrum is for the complex with 2% deuterium, and the bottom spectrum is for the nondeuterated complex. The top spectrum is the difference spectrum.

3.3. 18-c-6 Ammonium Iodide Complex II. A new 18-c-6 ammonium iodide complex (**II**), which turned out to be $2(C_{12}H_{24}O_6)\cdot 2(NH_4I)\cdot 3H_2O$, was made serendipitously and showed a very different infrared spectrum. It was found that the new iodide complex is monoclinic with a space group of $P2_1/c$ (No. 14) and $Z = 8$ at 151 K. The asymmetrical unit now contains two crown ether rings, two ammonium ions, two iodine anions, and three water molecules, shown in Figure S1 in the Supporting Information. Each ammonium ion hydrogen bonds to one of the crown ether rings with the same three-point binding geometry as in the other 18-c-6 ammonium halide complexes, and each of the ammonium ions sits in a C_1 symmetry site. The fourth hydrogen bond is different for each ammonium ion though, since one of the ammonium ions hydrogen bonds to an iodine anion while the other hydrogen bonds to a water molecule. The hydrogen-bonding data are shown in Table 4. The three water molecules hydrogen bond to each other and to the iodine anions. The X-ray data are given in Appendix S4 in the Supporting Information.

Figure 8 shows the infrared spectra of the nondeuterated and 2% deuterated iodide complexes at 10 K. The 2% deuterated spectrum shows a series of sharp resolved peaks in the N−D and O−D stretching band regions that are listed in Table 4. The six O−D bands match the expected number from the X-ray data, but the seven N−D bands appear to be one short of the eight different hydrogen bonds expected from the two inequivalent C_1-symmetry ammonium ions. Hole burning (Figures 9 and 10) revealed two different sets of holes/antiholes, each set

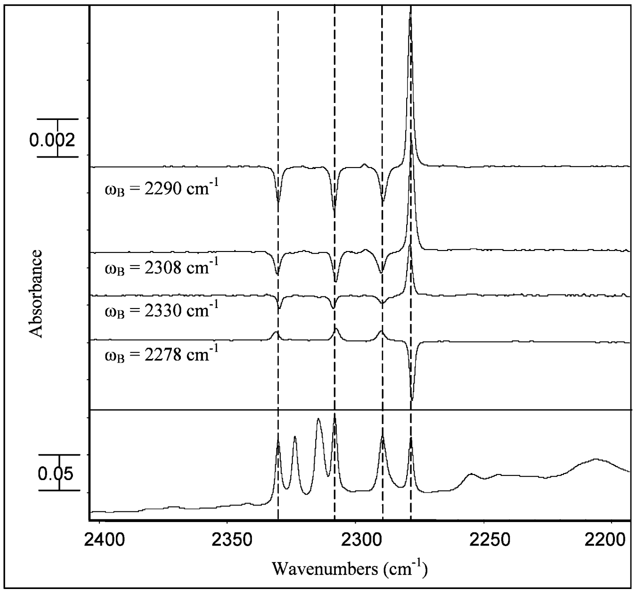

Figure 9. Infrared hole-burning results for 18-c-6 ammonium iodide complex **II** at 20 K. The top four spectra are the difference spectra taken immediately before and after 10 min irradiations at 2278, 2290, 2308, and 2330 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation. The spectrum of the sample irradiated at 2290 cm^{-1} has been compressed by a factor of 2 compared to those of the other samples.

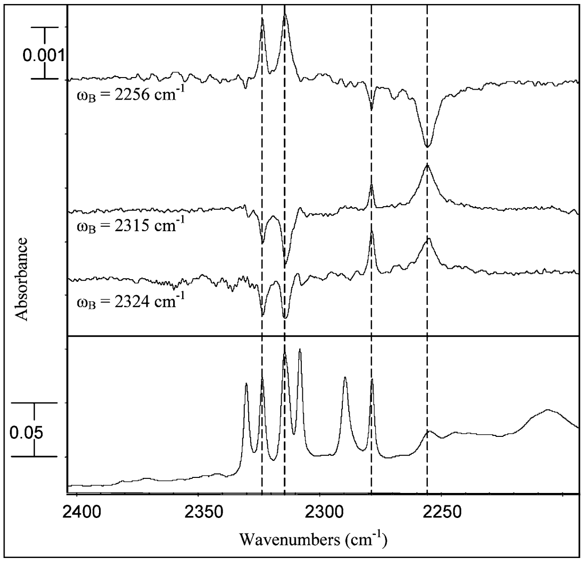

Figure 10. Infrared hole-burning results for 18-c-6 ammonium iodide complex **II** at 20 K. The top three spectra are the difference spectra taken immediately before and after 10 min irradiations at 2256, 2315, and 2324 cm^{-1}. The bottom spectrum is the original spectrum before irradiation. The dashed lines are at 2324, 2315, 2278, and 2256 cm^{-1}.

corresponding to one of the ammonium ions. Note the feature at 2278 cm^{-1} that appears in both sets, which we suggest arises from a hydrogen bond on each of the two ammonium groups. The tentative assignment of the infrared N−D bands of iodide complex **II** can be seen in Table 4. In this complex, there is only one hydrogen bond between an ammonium ion and an iodine anion. This arrangement is analogous to that of the other 18-c-6 ammonium halide complexes, and we assign the ammonium iodide hydrogen bond in the same way to the N−D band at 2256 cm^{-1}. Then the rest of the ammonium oxygen hydrogen bonds simply follow the usual correlations with the exception of the band at 2278 cm^{-1}, which has been assigned to the two most similar hydrogen bond distances.

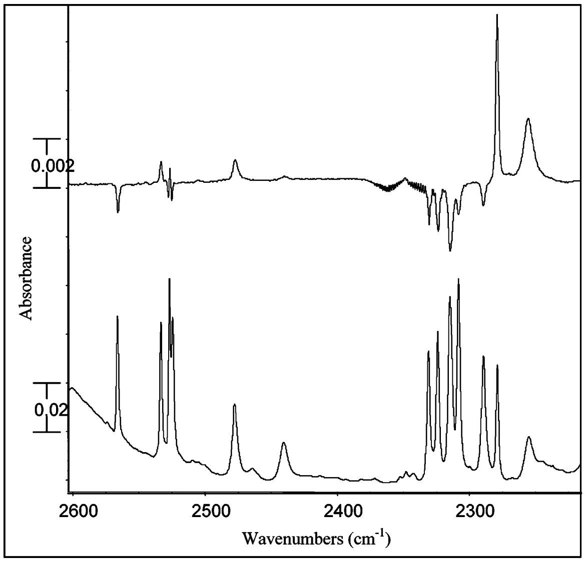

Figure 11. Infrared spectra for the broad-band irradiation of 18-c-6 ammonium iodide complex **II** at 10 K. The bottom spectrum is for the complex with 2% deuterium, and the top spectrum is the difference spectrum taken before and after a 10 h broad-band irradiation. All seven of the N−D bands and all six of the O−D bands show spectral changes.

It is not clear why all of the irradiations for 18-c-6 ammonium iodide complex **II** produced more than one hole upon hole burning. Apparently, one of the N−D orientations for each ammonium ion at 2256 and 2278 cm^{-1} is "favored" over the others. This is illustrated further by the broad-band irradiation results for this complex, shown in Figure 11. In the broad-band experiment, the broad infrared source from the FTIR spectrometer irradiated the sample for 10 h. Since the exciting infrared light simultaneously contains the frequencies of all of the N−D bands, the most favored N−D orientations should end up with the largest increase in their populations. The broad-band irradiation of iodide complex **II** results in strong antiholes at 2256 and 2278 cm^{-1} and holes at the other five N−D band positions, as expected. The broad-band irradiation in Figure 11 also excited the O−D bands, producing spectral changes in all six positions, which suggests that the O−D bands in this complex may be hole burnable.

The decays of the ammonium ion holes/antiholes are monotonic and persist for more than 10 h. The temperature dependence of the 18-c-6 ammonium iodide complex **II** spectra shows no evidence of a phase transition.

3.4. 18-c-6 Ammonium Nitrate Complex.

The 18-c-6 ammonium nitrate complex, $C_{12}H_{24}O_6{\cdot}NH_4NO_3$, can be crystallized as a monohydrate or without any water molecules in the crystal structure depending upon the solvent used during preparation.[9] The room-temperature X-ray structure of the monohydrated 18-c-6 ammonium nitrate complex shows that it crystallizes in the $P2_1/c$ (No. 14) space group with $Z = 4$.[9] The ammonium ion is in a C_1 site and adopts the same hydrogen-bonding geometry to the crown ether ring as in the previous 18-c-6 ammonium ion complexes (Table 5). The ammonium ion also has a hydrogen bond to one of the oxygens of the nitrate anion, which in turn hydrogen bonds to the water molecule.

The infrared spectrum for each type of nondeuterated 18-c-6 ammonium nitrate complex at 15 K is shown in Figure 12. The figure also shows the spectrum of the deuterated monohydrate in which there are clearly three sharp bands in the N−D stretching region at 2311, 2323, and 2328 cm^{-1}, as well as two sharp bands in the O−D stretching region at 2561 and 2600 cm^{-1}. The infrared hole-burning data are very clear for the 18-

TABLE 5: Hydrogen-Bonding Data for the 18-c-6 Ammonium Nitrate Complex

A−H···X	A···X[a] (Å)	N−H···X[a] (deg)	infrared bands (cm^{-1})
N1−H1···O1	2.883	171.9	2323
N1−H2···O8[b]	2.908	172.9	2328
N1−H3···O5	2.895	163.4	2323
N1−H4···O3	2.855	158.2	2311
O9−H···O10[b]	2.931		2561, 2600

[a] Room-temperature X-ray data from ref 9. [b] Oxygen atoms 7−9 are from the nitrate ion, and oxygen atom 10 is from a water molecule.

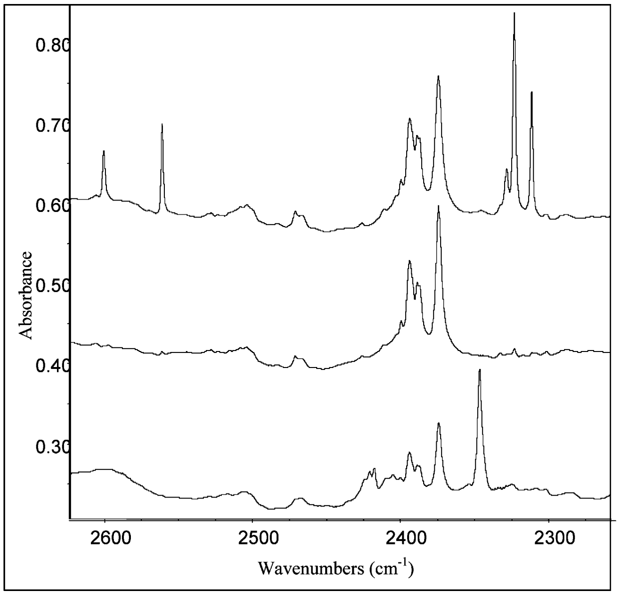

Figure 12. Infrared spectra for the 18-c-6 ammonium nitrate complexes at 15 K. The middle and bottom spectra are for nondeuterated complexes after using diethyl ether and benzene as solvents, respectively. The top spectrum is for the deuterated monohydrate complex from diethyl ether, which shows three N−D bands at 2311, 2323, and 2328 cm^{-1} and two O−D bands at 2561 and 2600 cm^{-1}.

c-6 ammonium nitrate complex. The hole-burning results for the three irradiations at 2311, 2323, and 2328 cm^{-1} are shown in Figure 13. Each of these irradiations produced a clear hole at the location of the irradiation frequency and an antihole at the other two positions. There were no other spectral changes produced during the hole-burning experiment. Although the assignment of these N−D bands appears to be straightforward, there are only three N−D bands instead of the four N−D stretching bands implied by the C_1 symmetry. Therefore, the most likely possibility is that two of the N−D bands are at the same frequency. The decay process of the holes and antiholes is a little more complicated than the initial hole-burning results, although there is still no sign of a fourth N−D position. The pair of holes and antiholes that appear at 2311 and 2323 cm^{-1} from the irradiations at these same two frequencies both decay on about the same 3 h time scale, but then they switch (the hole becomes an antihole and vice versa) and continue to grow for several more hours. The band at 2328 cm^{-1} does not participate in this behavior and simply decays after about 5 h. We assign the most intense N−D band as arising from the two bonds of similar intermediate length (Table 5) and the 2328 cm^{-1} band as due to the bond with the unique ammonium bond to the nitrate ion.

3.5. 18-c-6 Amminetrifluoroboron Complex. There have been several studies which have shown that a substituted or coordinated ammonium group, R−NH_3, such as amminetrifluoroboron, can also form a stable complex with an 18-c-6 crown ether ring.[10] The hydrogen-bonding geometry between the host ring and the amino group follows the same basic pattern as in the 18-c-6 ammonium halide complexes. Previous room-temperature X-ray data have shown that the 18-c-6 amminetrifluoroboron complex, $C_{12}H_{24}O_6{\cdot}BF_3NH_3{\cdot}CH_2Cl_2$, is an orthorhombic crystal with space group $P2_12_12_1$ (No. 19) and $Z = 4$.[10] The X-ray crystal structure shows that the amino group of the BF_3NH_3 molecule hydrogen bonds to the three oxygens on one side of the crown ether ring and the BF_3 group points away from the ring. The BF_3 group adopts a *gauche* orientation with respect to the amino group. The hydrogen-bonding data are given in Table 6. Spectra were taken with low concentrations of deuterium, and since the spectra of the 2% and 5% samples were very similar overall, the 5% sample was used for the hole-burning experiments due to the stronger absorption of the N−D stretching bands.

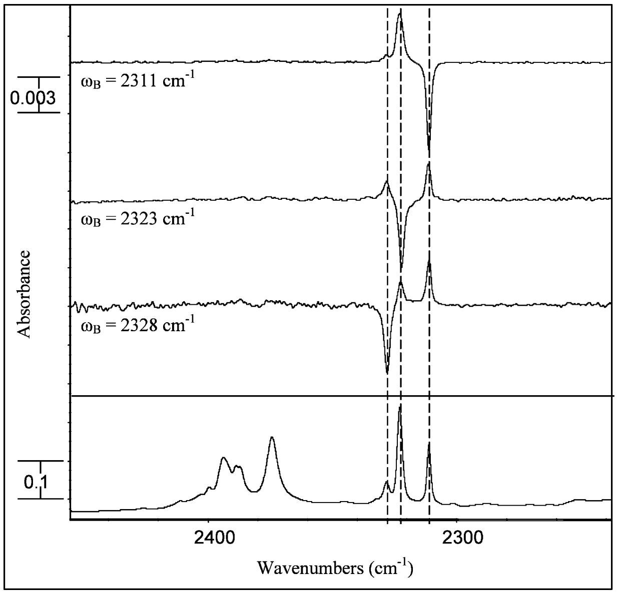

Figure 13. Infrared hole-burning results for the 18-c-6 ammonium nitrate complex at 15 K. The top three spectra are the difference spectra taken immediately before and after 10 min irradiations at 2311, 2323, and 2328 cm^{-1} (dashed lines). The bottom spectrum is the original spectrum before irradiation. Note that the scale of the top irradiation has been reduced by a factor of 5 compared to those of the other irradiations.

TABLE 6: Hydrogen-Bonding Data for the 18-c-6 Amminetrifluoroboron Complex

A−H···X	A···X[a] (Å)	N−H[a] (Å)	N−H···X[a] (deg)	infrared band (cm^{-1})
N1−H^a···O13	2.93	0.960	170	2373
N1−H^b···O7	2.92	0.960	177	2369.5
N1−H^c···O1	2.95	0.960	166	2380

[a] Room-temperature X-ray data from ref 10.

The infrared spectra of the nondeuterated and 5% deuterated 18-c-6 amminetrifluoroboron complexes are shown in Figure 14. The contribution due to the addition of deuterium to the system is the broad absorbance increase over the range of 2364−2392 cm^{-1}. Even though the spectra are complicated by the proximity of the peak at 2364 cm^{-1}, the difference spectrum shows three N−D stretching peaks: two relatively sharp, but overlapped, bands with maxima at 2370 and 2372.5 cm^{-1} and one weaker broad band appearing around 2380 cm^{-1}. The close proximity of these N−D bands is in agreement with the X-ray

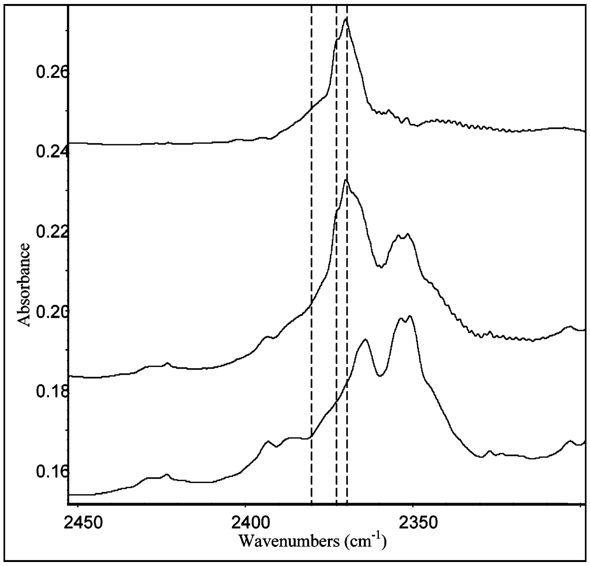

Figure 14. Infrared spectra for the 18-c-6 amminetrifluoroboron complex at 12 K. The middle spectrum is for the complex with 5% deuterium, and the bottom spectrum is for the nondeuterated complex. The top spectrum is the difference spectrum after the nondeuterated spectrum has been subtracted from the 5% deuterated spectrum. The dashed lines are at 2380, 2373, and 2369.5 cm^{-1}.

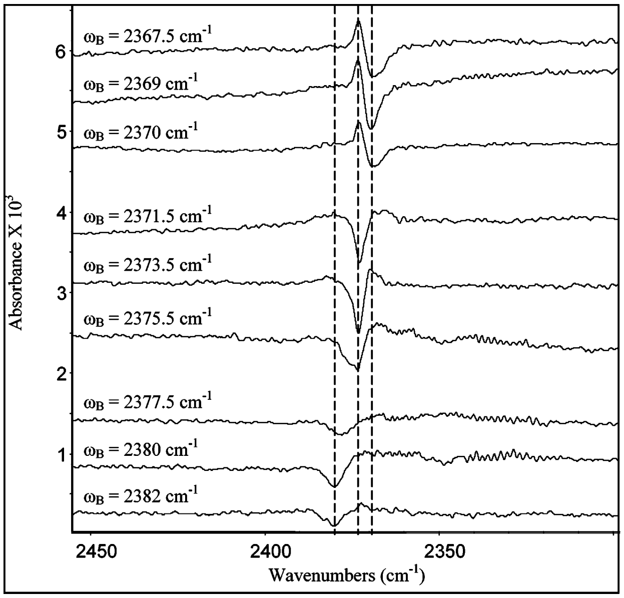

Figure 15. Infrared hole-burning results for the 18-c-6 amminetrifluoroboron complex at 12 K. These spectra are the difference spectra taken immediately before and after 10 min irradiations. Each group of three spectra are the closest irradiations to the hydrogen-bonding frequencies. The dashed lines are at 2380, 2373, and 2369.5 cm^{-1}.

data since there are in fact three different hydrogen bonds with very similar bond distances.

The 18-c-6 amminetrifluoroboron complex was hole burned with a series of 10 min irradiations at 12 K. The difference spectra from the irradiations are shown in Figure 15. The hydrogen-bonding bands appear close together and were identified from the location of the holes and antiholes, which tend to appear at specific positions even when the irradiation frequency was set to a different location. This is most evident for the three irradiations at 2371.5, 2373.5, and 2375.5 cm^{-1}, which all produced holes at 2373 cm^{-1}, as well as the three irradiations at 2367.5, 2369, and 2370 cm^{-1}, each of which produced a hole at 2369.5 cm^{-1} and an antihole at 2373 cm^{-1}. The irradiation at 2373.5 cm^{-1} also created an antihole at 2369.5 cm^{-1}, but there were no other significant spectral changes in any of these irradiations. Irradiations at frequencies above 2377 cm^{-1} only produced small broad holes and did not show any clear antiholes. Our assignment is listed in Table 6.

4. Summary and Conclusions

We have synthesized a number of 18-c-6 complexes and found some new ones, although all of the complexes are the same as or very similar to ones known previously. We have been able to hole burn the N−D stretching bands in each of the six 18-c-6 complexes we have tried. These complexes seem quite different from most of the simpler ammonium compounds that we have studied previously. We have found some examples of more complicated ammine compounds such as the complex with a substituted borane.[6] This latter complex is similar to those of the amino acid salts, which we have also been able to burn,[5] since the nitrogen is bonded to only three hydrogen atoms rather than four. Not all ammonium compounds will hole burn under the conditions of our experiments; the barriers to rotation of the nitrogen moiety must be in the range of 8−24 kJ/mol. We conclude that barriers of the 18-c-6 complexes must fall in this range.

Although the complexes all have similar ammonium crown ether geometries, the details cover much of the range of phenomena that have been observed in other ammonium compounds. The N−D bands are either bunched together (ammonium bromide) or distinctly separated in frequency (ammonium iodide **II**). The holes may show simple monotonic decay or involve transfer of the holes/antiholes among the hydrogen bonds of more than one ammonium ion (ammonium iodide **I**).

Calculation of the frequencies and the anharmonic couplings of these complicated systems (i.e., the complexes in their solid-state environments) should eventually reveal the basis for these phenomena.

Acknowledgment. We are indebted to Dr. Fred Hollander and Dr. Allen Oliver for the X-ray analyses. We gratefully acknowledge the support of the U.S. Department of Energy through Grant No. DE-FG02-01ER45912.

Supporting Information Available: Figure S1, a diagram of the crystal structure of 18-c-6 ammonium iodide **II**, and Appendices S1, S2, S3, and S4, the X-ray structure reports for the low-temperature structure of the ammonium bromide, chloride, iodide **I** and iodide **II** complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Vötgle, F.; Weber, E. *The Chemistry of Ethers, crown ethers, hydroxyl groups and their sulphur analogues*; Patai, S., Ed.; Wiley, New York, 1980; Part 1.

(2) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

(3) Inoue, Y.; Gokel, G. W. *Cation binding by Marcocycles*; Dekker: New York, 1990.

(4) Strauss, H. L. *Acc. Chem. Res.* **1997**, *30*, 37−42.

(5) Li, H. W.; Strauss, H. L. *J. Phys. Chem. B* **2001**, *105*, 2250−2255.

(6) Endicott, C. A.; Strauss, H. L.; Hughes, C. C.; Trauner, D. *J. Phys. Chem. A* **2005**, *109*, 7714−7717.

(7) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.

(8) Nagano, O.; Kobayashi, A.; Y. Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 790.

(9) Doxsee, K. M.; Francis, P. E.; Weakley, T. J. R. *Tetrahedron* **2000**, *56*, 6683.

(10) Colquhoun, H. M.; Jones, G.; Maud, J. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 63.

(11) Kung, A. H.; Fei, Suli; Strauss, H. L. *Appl. Spectrosc.* **1996**, *50*, 790−794.

(12) Pears, D. A.; Stoddart, J. F.; Fakley, M. E.; Allwood, B. E.; Williams, D. J. *Acta. Crystallogr., C* **1988**, *44*, 1426.

(13) Chen, Z.; Fei, S.; Strauss, H. L. *J. Phys. Chem. A* **1997**, *101*, 1640−1645.