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Infrared Hole Burning and Conformational Change in a Borane−Ammonia Complex

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The N−D stretching region in the infrared spectrum of the ammonia complex of tris-(2-methoxymethyl-phenol)-borane containing one D atom has been examined. The N−D bands have been hole burned, and the resulting spectra reveal the reorientation kinetics of the ammonia. The ammonia is hydrogen bonded with the bond distances and reorientation barrier typical of other compounds. The N−D stretching frequencies are higher than those of comparison compounds.

I. Introduction

We have recently described a novel series of borane−ammonia complexes in which the ammonia is bonded to a substituted boron atom and the three hydrogen atoms are each hydrogen bonded to an oxygen atom of the substituants.[1] Among the most interesting of these compounds is the four-point binding complex of ammonia with tris-(2-methoxymethyl-phenol)-borane, $NH_3{\cdot}(C_8H_9O_2)_3B$ (MOM complex). A schematic version of the structure is shown in Figure 1, and an X-ray derived structure is shown in Figure 2. Each of the three ammonia hydrogens is hydrogen bonded to one of the phenolic oxygens. The MOM complex has a unique structure, and to investigate the nature of the hydrogen bonding, we carried out infrared hole burning on the N−D bands of a MOM complex in which the NH_3 had been monosubstituted with a deuterium. Infrared hole burning of the N−D stretching bands has previously been shown[2] to identify the absorption bands arising from the hydrogen-bonded hydrogens (deuteriums). The holes arise by the internal rotation of the nitrogen moiety, thus identifying the bands that belong to a specific nitrogen and providing information on the dynamics of the reorientation of the nitrogen-containing group. This in turn yields estimates of the barrier to the rotation. The compounds we have investigated previously include numerous ammonium salts as well as compounds containing the NH_3^+ moiety such as amino acid salts.[3] The MOM complex is the first compound we have hole burned that contains a NH_3 (NH_2D) group that is formally neutral.

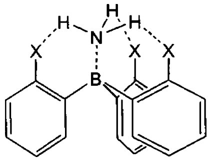

Figure 1. The general binding scheme between the amino group and the borane. The dashed lines indicate the binding interactions between ammonia and a simple MOM complex. Here, the X group is $-O-CH_2-O-CH_3$ with each ammonia hydrogen bonding to one of the phenolic oxygens.

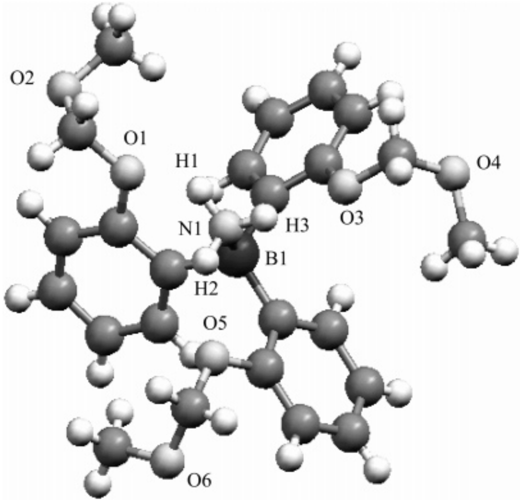

Figure 2. A representation of the MOM complex crystal structure. The space group is *C*2/*c*. There are hydrogen bonds between N1 and O1, O3, and O5. H2 is also involved in a bifurcated hydrogen bond to O2′ on an adjacent MOM complex, which is not shown.

II. Experimental Section

The synthesis of the ammonia adduct of tris-(2-methoxy-methyl-phenol)-borane, $NH_3{\cdot}(C_8H_9O_2)_3B$, was carried out as described by Hughes et al.[1] One of the last steps in the synthesis was addition of the reactants to a saturated aqueous solution of NH_3. The desired concentration of deuterium (2%) was added to the aqueous solution of NH_3 during this step for the preparation of the partially deuterated complexes. The product was then purified. Single crystals of the tris-(2-methoxymethyl-phenol)-borane complex were crushed, mulled in mineral oil, and placed between CaF_2 windows. Infrared spectra were taken on a Nicolet 8500 FTIR Spectrometer in the range of 2000−4000 cm^{-1} with 1 cm^{-1} resolution using an InSb detector. The samples were verified to be at thermal equilibrium before each of the hole-burning experiments by waiting until no spectral changes could be observed over spans of a half hour.[4] To follow the kinetics of the decay of the bands after hole burning, the spectra were taken at fixed intervals. Between observations, the infrared light from the spectrometer source was blocked from the sample by means of the beam shuttle of the spectrometer.

III. Results and Discussion

The structure of the MOM complex at room temperature as determined by X-ray crystallography is shown in Figure 2. The crystal is monoclinic with space group *C*2/*c* (#15), and each

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TABLE 1: Hydrogen Bonding Data for the MOM Complex $NH_3\ (C_8H_9O_2)_3B$

N−H···O	N···O (Å)^{a}	−N−H···O (deg)^{a}	assignment (cm^{-1})^{b}
N1−H1···O1	2.778(3)	127.460	2472
N1−H2···O5	2.727(4)	126.914	2453
N1−H3···O3^{c}	2.724(5)	129.078	2447
N1−H3···O2′^{c,d}	2.978(4)	119.690	

[a] These numbers are from the room-temperature X-ray data from ref 1. The numbers in parentheses are error estimates. The N−H distance was fixed at 0.95 Å. [b] N−D infrared stretching band, from this work. [c] H3 participates in a bifurcated hydrogen bond. [d] O2′ is located in an adjacent MOM complex.

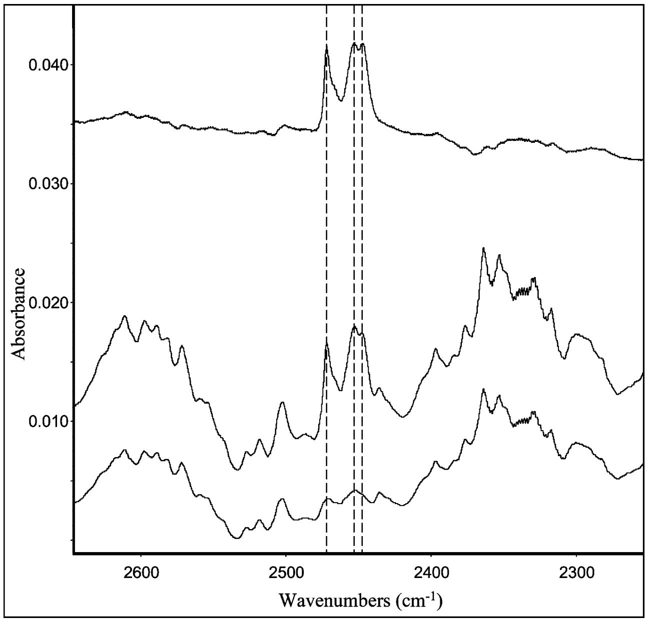

Figure 3. Infrared spectra for the MOM complex at 20 K. The middle spectrum is of the complex with 2% deuterium and the lower spectrum is of the nondeuterated complex. The upper spectrum is the difference spectrum after the nondeuterated spectrum has been subtracted from the 2% deuterated spectrum.

unit cell contains eight identical molecules in C_1 sites. The boron atom is bonded to three ortho-methoxymethyl-phenol groups such that the rings form a propeller pattern and the oxygens are all on the same side of the molecule. The ammonia nitrogen binds with the center boron atom, allowing each of the three ammonia hydrogens to hydrogen bond to the separate oxygens on the methoxymethyl-phenol groups. The symmetry of the overall complex is nearly C_3. However, there are three different [N−H···O] distances and angles between the ammonia and the host molecule (Table 1). One of these hydrogen bonds is bifurcated with an additional putative hydrogen bond to an oxygen of an adjacent MOM complex. The infrared spectra of the nondeuterated and 2% deuterated complexes at 20 K and their difference are shown in Figure 3. The difference spectrum shows three bands at 2447, 2453, and 2472 cm^{-1}. These N−D stretching bands occur at considerably higher frequencies than the N−D bands seen in the other ammonium ion systems we have investigated.[2−4]

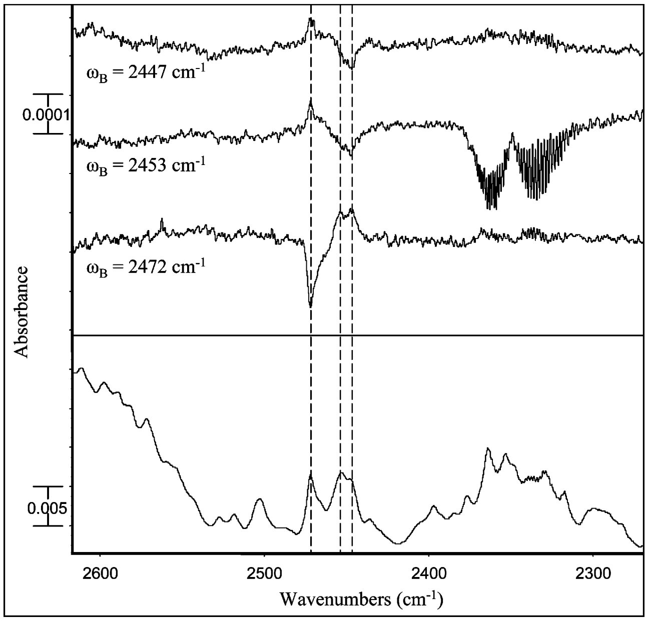

Figure 4. Infrared hole-burning results for the MOM complex at 35 K. The upper three spectra are the differences of spectra taken immediately before and after 30-min irradiations at 2447, 2453, and 2472 cm^{-1}. The lower spectrum is the original spectrum before irradiation. The large feature around 2350 cm^{-1} is background carbon dioxide.

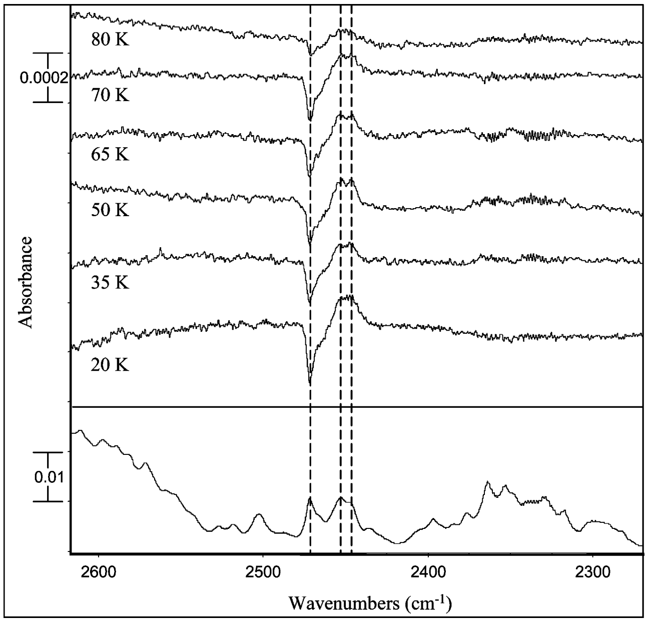

Figure 5. Infrared spectra of the MOM complex showing the hole-burning results for the irradiation at 2472 cm^{-1} at six different temperatures. The upper spectra are the difference of spectra taken immediately before and after 30-min irradiations at each temperature. The lower spectrum is the original before hole burning.

The peak at 2472 cm^{-1} was initially chosen for hole burning since it is clearly separated from the other two peaks. At 20 K, irradiation at this wavenumber produced a hole at 2472 cm^{-1} and a broad antihole at 2450 cm^{-1}. However, 16 h after the initial irradiation, the hole had decayed to only about 75% of its original depth. When the hole-burning experiment was repeated at 35 K, the decay time decreased appreciably. Figure 4 shows the hole-burning results at 35 K for each of the three N−D stretching frequencies. Hole burning at 2472 cm^{-1} produced a hole and antihole pattern similar to that before, although this time the antihole had two closely separated maxima at 2447 and 2453 cm^{-1}. Irradiation of the N−D bands at 2447 and 2453 cm^{-1} resulted in nearly identical hole-burning patterns. Each produced a broad hole centered at about 2447 cm^{-1} and a small, but sharp, antihole at 2472 cm^{-1} (Figure 4). The two N−D stretching bands at 2447 and 2453 cm^{-1} probably

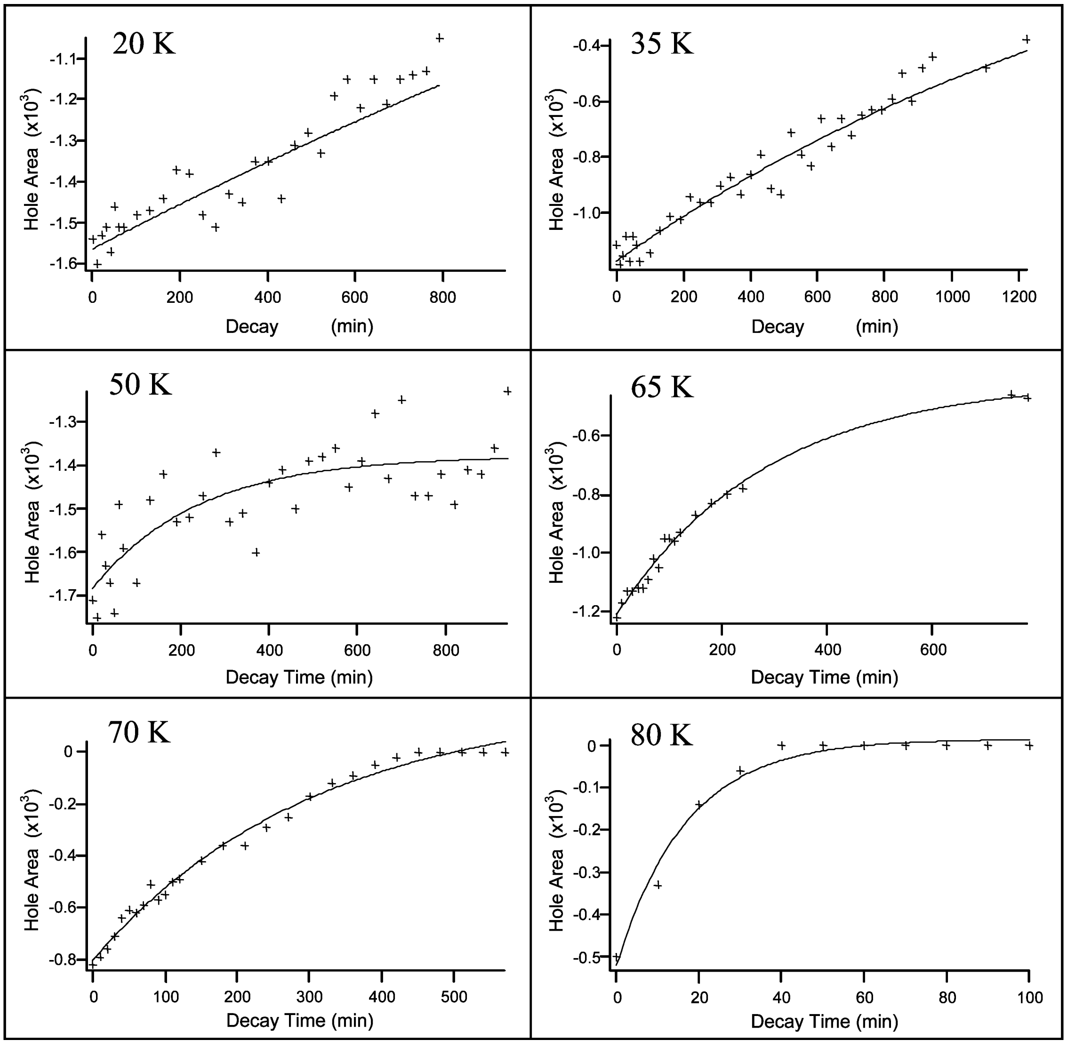

Figure 6. Plots of the hole area vs time during the decay of the hole at 2472 cm^{-1} after 30-min irradiations of the MOM complex at six different temperatures. The initial size of the hole is at 0 min. The rate of decay increases with temperature. The individual rate constants from simple exponential curve fits are listed in Table 2. (The data at 50 K is considerably noisier than that at the other temperatures.)

are too overlapped to be separately hole burned under these conditions: the overlap leads to the broad hole instead.

The difference spectrum (Figure 3) and the hole-burning data (Figure 4) show that the MOM complex has three different N−D hydrogen-bonding bands, and a reasonable assignment of these bands can be made by comparison with the X-ray data, which is shown in Table 1. For analysis of the X-ray data, the N−H distance was fixed at 0.95 Å. An attempt was made to resolve the differences among the N−H bonds, but the results showed differences smaller than the estimated errors, and so the numbers reported here are for fixed N−H distances. The assignment uses the well-established correlation of the stretching frequencies with the other properties of the hydrogen bonds.[2,5] Table 1 shows that the two hydrogen-bonding distances between N1 and O3 and O5 are very similar, while the third hydrogen bond to O1 is definitely longer. This is consistent with the positions of the N−D infrared bands with two of the N−D bands close together and one at a higher wavenumber (Figure 3). The N−D bands can be assigned to the hydrogen bonds as H3 at 2447 cm^{-1}, H2 at 2453 cm^{-1}, and H1 at 2472 cm^{-1}.

TABLE 2: Hole Filling for the MOM Complex: Observed Rates, *k*, and High Temperature Limiting Rates,[a] k_{ht}

T (K)	*k* (min)	1/*T*	ln(*k*)	ln(k_{ht})[a]
20	0.000384	0.05	−7.86	−40.77
35	0.000663	0.028571	−7.32	−19.17
50	0.00416	0.02	−5.48	−10.53
65	0.0035	0.015385	−5.65	−5.88
70	0.00585	0.014286	−5.14	−4.77
80	0.0592	0.0125	−2.83	−2.97

[a] Rates calculated from a fit to the highest temperature points.

To investigate the size of the rotational barrier, the hole-burning experiment was performed at six different temperatures over the range of 20−80 K. The N−D band at 2472 cm^{-1} was irradiated at each temperature for 30 min, and the subsequent decay was monitored. Figure 5 shows the series of the initial difference spectra after irradiation of the 2472 cm^{-1} band for each of the six temperatures. It was found that 80 K was the highest temperature that produced an observable hole, and this disappeared into the noise at less than 40 min. The kinetic plots of the hole area decay versus time for each temperature are shown in Figure 6, and Table 2 lists the rate constants derived from simple exponential curve fits of the data.

The rate constants do not fit a standard straight-line Arrhenius plot of the logarithm of the rate versus the reciprocal of the temperature (Figure 7) but instead are indicative of the simultaneous occurrence of multiple rate processes.[2] At high temperature, we expect the equilibration of the NH_2D moiety to occur by rotation over the top of an activation barrier. The apparent activation energy can change with temperature, and at high enough temperatures, the activation energy should match

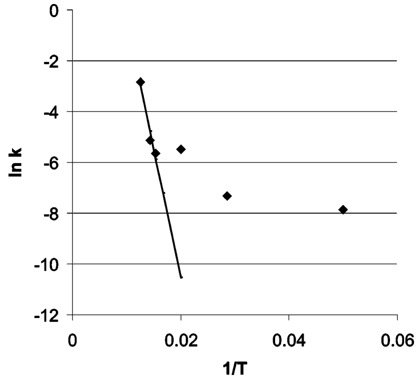

Figure 7. Plot, ◆, of the natural logarithm of the rate for decay of holes burned in the MOM complex at 2472 cm^{-1} vs the reciprocal of the temperature. The straight line is fit to the first three data points and has an apparent activation energy of 8.4 kJ/mol. See also Table 2.

the energy of the top of the potential-energy barrier. At low temperatures, equilibration can occur by tunneling through the barrier with an apparent activation energy an order of magnitude lower. At intermediate temperatures, an Arrhenius plot of the rates will not be linear. To determine the high-temperature activation energy, the three highest temperature points are fit by a straight line, which yields an apparent activation energy of 8.4 kJ/mol. This value is a lower limit to the height of the potential energy barrier. At low temperatures, the plot flattens out as expected. The errors are larger for the lower temperature determinations of the rate (Figure 6, 20, 35, 50 K). However, if we were to assume only one rate process and extrapolate the high-temperature rates to lower temperatures (Table 2), the rates at the lower temperatures would be too slow to see any change at all.

We have seen a plot with the form of Figure 7 for other molecules. An example is one of the ammonium ions in ammonium sulfate[2,6] for which the barrier height is 12 kJ/mol and the apparent high-temperature activation energy from the plot is 6.8 kJ/mol. The highest temperature at which we could follow the relaxation was 60 K. The molecule with the largest apparent barrier we have been able to hole burn is ammonium tartrate. We were able to follow the kinetics to 90 K and found an apparent barrier of 18 kJ/mol.[7] However, this molecule relaxes in a more complicated manner involving a multidimensional pathway.

IV. Summary and Conclusion

The barrier to reorientation of groups such as NH_3 (NH_2D), just like internal rotation of an ordinary rotor, depends on the symmetry of the rotating group. Since the NH_3 we are considering has close to threefold symmetry, the barrier may be expected to be in the same range as that for other groups such as NH_4^+ that can reorient by rotation about a threefold axis, and indeed this turns out to be the case.[8] However, the barrier to reorientation does not correlate in a simple way to the strength of the constituent hydrogen bonds. The hydrogen bond distances are typical of NHO hydrogen bonds, but as we have mentioned, the frequencies are relatively high and do not fit on the known correlation curves which relate such distances to frequencies.[5] This is perhaps explained by the unique geometry of the MOM complex, which has NHO bond angles of about 125°. High hydrogen bond frequencies usually indicate weak hydrogen bonds, but there is no indication that this is the case for our system.

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