[January, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 1—7 (1976)

Infrared Study of Aniline Adsorbed on Aluminum Halides and on Gallium Chloride

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(Received March 4, 1975)

Infrared study was made on aniline adsorbed on aluminum chloride, bromide and iodide. Aniline-d_0 (C_6H_5-NH_2), aniline-*N,N*-d_2, aniline-d_5 ($C_6D_5NH_2$) and aniline-d_7 were used. Aniline-d_0–gallium chloride system was studied for comparison. Only the bands associated with amino group showed large frequency shifts on complex formation. The structures of adsorbed molecules were discussed in terms of the frequency shift of bands, especially of those assigned to C–N stretching and ND_2 bending modes. The interaction of adsorbed aniline with aluminum chloride is rather weak and predominantly ionic. A strong chemisorption with the formation of an essentially covalent N···Al bond can be deduced for aniline adsorbed on aluminum bromide, iodide and gallium chloride. Such an ionic adsorption on aluminum chloride can be understood by considering the ionic structure of solid aluminum chloride. Some of the observed bands for aniline-d_5 are (cm^{-1}); 3424, 3350, 3312 (NH str.), 1620 (NH_2 bend.) and 1300 (CN str.).

Considering the importance of aluminum halides as catalysts for a large number of organic reactions, the spectroscopic study of organic molecules adsorbed on solid aluminum halides is of much interest. One of the authors (H. S.) studied the UV spectrum (300—150 nm) of aniline adsorbed on aluminum chloride, showing that it has an intermediate feature between free aniline molecule and toluene.$^{1)}$ This was interpreted by assuming the interaction of the lone pair on the nitrogen atom in aniline molecule with the vacant sp^3-type orbital on the aluminum atom in aluminum chloride.$^{2)}$ Thus, it is clear that some kind of adsorption complex is formed. Measurement of the IR spectrum is essential for a more detailed discussion on the structures of the adsorption complexes. Such a study, however, has not so far been made.$^{3)}$ We have measured IR spectra for aniline adsorbed on aluminum chloride, bromide and iodide. The study of aniline adsorbed on aluminum bromide in comparison with that on aluminum chloride is interesting if one considers the difference of these two halides as regards their crystal structures and the physical properties in the solid phase. It is known that the dimeric structure Al_2X_6 (X=Cl, Br) in the gas phase$^{4)}$ remains on transition to the liquid phase,$^{5-7)}$ but in the solid phase aluminum chloride has a crystal structure based on an ionic bonding scheme,$^{8)}$ while solid aluminum bromide retains the dimeric structure.$^{9)}$ The difference of structure in the solid phase is also reflected in their physical properties. Solid aluminum chloride has a significant electric conductivity; the conductivity increases as the melting point is approached but falls abruptly nearly to zero on melting; the volume increases sharply on melting.$^{10)}$ Pershina and Raskin$^{11)}$ showed that the Raman spectrum of solid aluminum chloride differs from that of liquid aluminum chloride, while the Raman spectra of these two phases coincide for aluminum bromide.$^{12)}$ In the present study, three deuterium-labelled compounds, *i.e.*, aniline-*N,N*-d_2 ($C_6H_5ND_2$), aniline-d_5 ($C_6D_5NH_2$) and aniline-d_7 ($C_6D_5ND_2$) were used together with aniline-d_0 ($C_6H_5NH_2$) to make the assignments of IR bands unambiguously by separating the bands related to the modes in amino group from those related to the modes in phenyl group. Aniline-d_0–gallium chloride system was studied for comparison.

Experimental

Materials. Aluminum chloride was prepared from aluminum and silver chloride *in vacuo*.$^{1)}$ Aluminum bromide or iodide was prepared in a similar way using the corresponding silver halide. Gallium chloride was prepared from gallium and silver chloride. All the compounds were stored in ampoules with break-off seals. Aniline-d_0 was distilled under reduced pressure, dried over potassium hydroxide and distilled again *in vacuo* before use. Aniline-*N,N*-d_2 was prepared by treating aniline with heavy water. Aniline-d_7 of minimum isotope purity of 99 atom% (J. T. Baker Chemical Co., Philipsburg, N. J., U. S. A.) was distilled under reduced pressure. Aniline-d_5 was prepared by treating aniline-d_7 with water. The three compounds were dried over anhydrous potassium carbonate and distilled *in vacuo* before use.

Procedure. The cell assembly used in IR measurement was similar to the one used previously,$^{1)}$ but was provided with NaCl or KBr windows. This was degassed thoroughly (more than two hours at 10^{-3} Torr) before use. After aluminum halide or gallium chloride was sublimed onto the NaCl or KBr window plate, aniline vapor was introduced into the cell. After evacuation, IR spectra were recorded on JASCO IRA-1 (for 4000—650 cm^{-1}) or IRA-2 (for 4000—400 cm^{-1}) recording spectrophotometers.$^{13)}$

Results

The following symbols are used: aniline-d_0 (**1**) aniline-*N,N*-d_2 (**2**), aniline-d_5 (**3**), aniline-d_7 (**4**), aluminum chloride (A), aluminum bromide (B), aluminum iodide (C), gallium chloride (D). The complexes are also shown by these symbols (*e.g.* **1**A for aniline-d_0–aluminum chloride complex).

Complexes of Aniline-d$_0$ *and Aniline*-N,N-d$_2$. IR spectra of **1**, **1**A, **1**B, **1**C and **1**D are shown in Fig. 1, and those of **2**, **2**A and **2**B in Fig. 2. The assignment of IR bands for **1** and **2** was well established by Tsuboi$^{14)}$ and Evans.$^{15)}$ The bands of **1** or **2** can be classified into two groups, those associated with (a) the phenyl group, and (b) the amino group (C–N stretching in-

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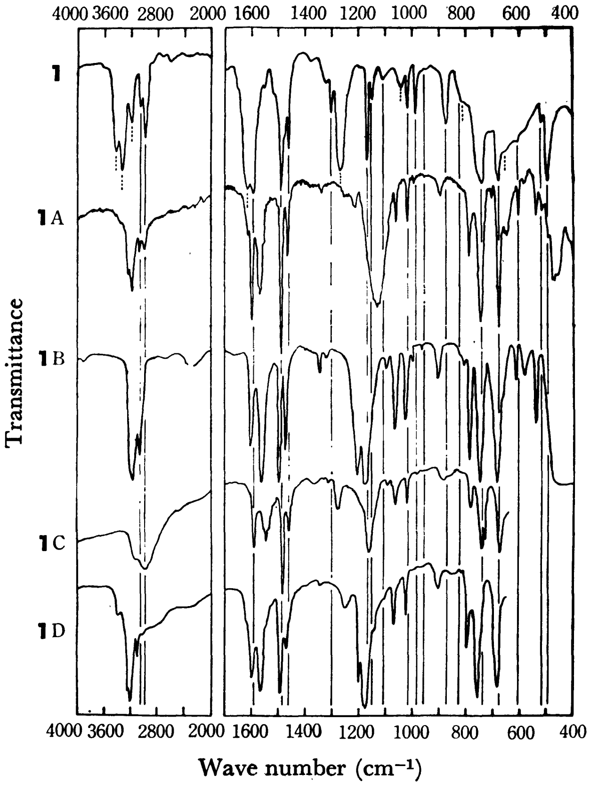

Fig. 1. IR spectra.
(**1**) aniline-d_0 (liq.).
(**1A**) aniline-d_0–aluminum chloride.
(**1B**) aniline-d_0–aluminum bromide.
(**1C**) aniline-d_0–aluminum iodide.
(**1D**) aniline-d_0–gallium chloride.

clusive). The full lines show the positions of bands belonging to group (a), dotted lines those of group (b). Some of the bands of complexes fell in the close vicinity of the bands belonging to group (a) of the free molecules, essentially retaining their relative intensities. These bands can be attributed to the modes within the phenyl group of the complex. The complex formation clearly gave little effect on the vibrations within the phenyl moiety. On the other hand, the bands of group (b) showed a large shift on complex formation. This shows that it is the amino group and C–N bond that are affected by complex formation and that the coordination of the amino group occurs on adsorption. The positions of bands thus attributed to amino group (C–N stretching inclusive) are listed in Table 1.

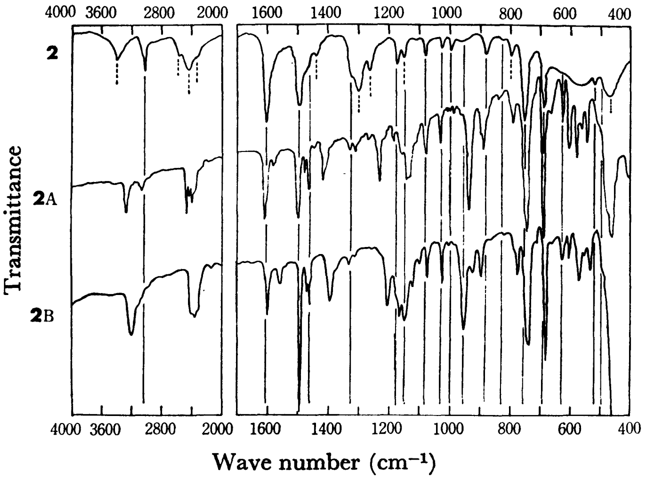

Fig. 2. IR spectra.
(**2**) aniline-N-N-d_2 (liq.).
(**2A**) aniline-N,N-d_2–aluminum chloride.
(**2B**) aniline-N,N-d_2–aluminum bromide.

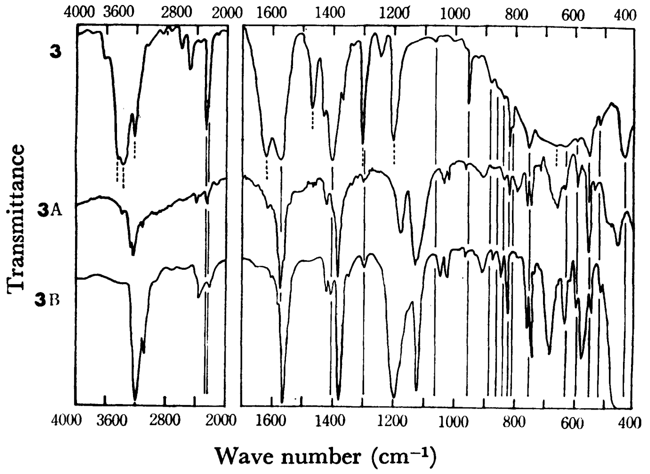

Fig. 3. IR spectra.
(**3**) aniline-d_5 (liq.).
(**3A**) aniline-d_5–aluminum chloride
(**3B**) aniline-d_5–aluminum bromide.

Complexes of Aniline-d$_5$ *and Aniline*-d$_7$. IR spectra of **3**, **3A** and **3B** are shown in Fig. 3, and those of **4**, **4A** and **4B** in Fig. 4. No IR spectrum of **3** seems to have been published. As to **4**, Ostrowska and Tramer$^{16)}$ published the wave numbers of IR bands in the region above 700 cm^{-1}. They gave assignments for some of the bands. Rai and Maheshwari$^{17)}$ gave the wave numbers of seven bands without assignments. The positions of bands in our spectrum are in line with theirs.$^{18)}$ Complete assignments of the bands for **3** and **4** were made. They are given in the Appendix. Since Ostrowska and Tramer$^{16)}$ did not give assignments

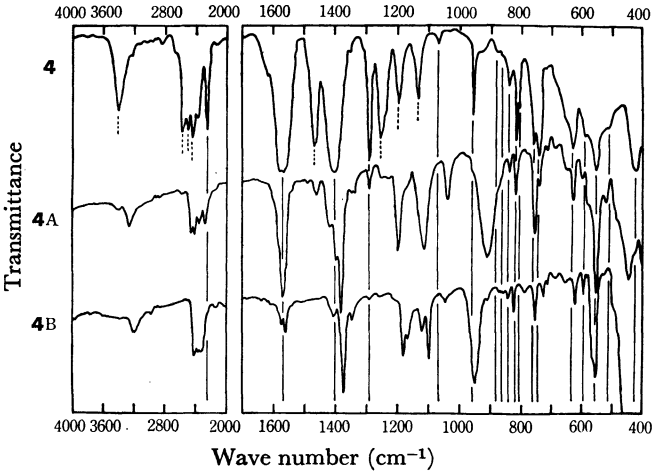

Fig. 4. IR spectra.
(**4**) aniline-d_7 (liq.).
(**4A**) aniline-d_7–aluminum chloride.
(**4B**) aniline-d_7–aluminum bromide.

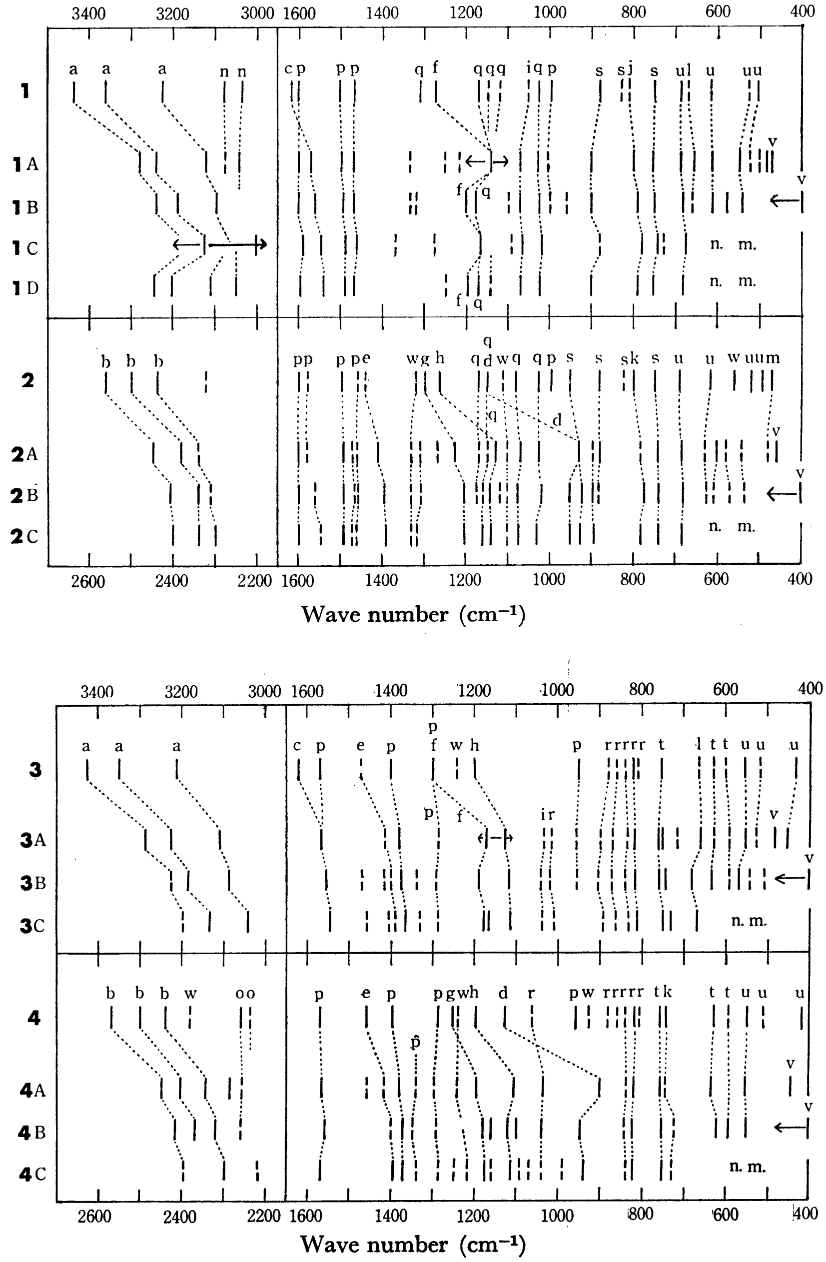

Fig. 5. IR spectra of aniline–aluminum halide and -gallium chloride complexes; positions of the bands. Solid lines show strong bands. Broken lines indicate weak bands (or a shoulder). Horizontal arrow shows the region covered by a very broad band. Corresponding bands are connected. **1.** aniline-d_0, **2.** aniline-N,N-d_2, **3.** aniline-d_5, **4.** aniline-d_7, A. aluminum chloride, B. aluminum bromide, C. aluminum iodide, D. gallium chloride, a. NH str., b. ND str., c. NH_2 bend., d. ND_2 bend., e. NHD bend., f. CN str. (NH_2), g. CN str. (ND_2), h. CN str. (NHD), i. NH_2 tw., j. NH_2 rock., k. ND_2 rock. (or tw.), l. NH_2 wag., m. ND_2 wag., n. CH str., o. CD str., p. ring str., q. CH in-plane bend., r. CD in-plane bend., s. CH out-of-plane bend., t. CD out-of-plane bend., u. ring def., v. AlX_3 skeletal vibration, w. combination band; n.m. region not measured.

for all the bands, those for **4** are given here for comparison with the assignments of bands in **3**. After these assignments were made, the IR bands of **3** and **4** were classified into groups (a) and (b) as for **1** and **2**. It was found that only the bands of group (b) showed a large shift on complex formation. The positions of bands thus attributed to the amino group (C–N stretching inclusive) are listed in Table 1.

The positions of observed bands for all the systems studied are shown in Fig. 5, with their assignments given by symbols.

TABLE 1. BANDS ASCRIBABLE TO THE AMINO-GROUP, POSITIONS OF BANDS IN cm^{-1}

Aniline-d_0 ($C_6H_5NH_2$)					Assignment	Aniline-d_5 ($C_6D_5NH_2$)			
free[a]	$AlCl_3$	$AlBr_3$	AlI_3	$GaCl_3$		free[a]	$AlCl_3$	$AlBr_3$	AlI_3
3436	3282	3238		3246	NH str.	3424	3290	3230sh	3200sh
3360	3238	3190	3124	3204		3350	3226	3184	3134
3222	3122	3094	3000			3212	3110	3084	3044
1617	1572	1559	1545	1562	NH_2 bend.	1620	1565[b]	1555[b]	1547[b]
					NHD bend.	1470	1415	1401	1389
1272	1140	1201	1164	1169	CN str.	1300	1165[c]	1191	1172
					CN str. (NHD)	1197	1125[c]	1119	1114
1051	1070	1071	1064	1067	NH_2 tw.		1033	1041	1035
810	799	789	781	791	NH_2 rock.				
670	655	660sh			NH_2 wag.	660	655	677	667
—	483 468	$\lesssim 400$[d]			AlX_3	—	480	$\lesssim 400$[d]	

Aniline-N,N-d_2 ($C_6H_5ND_2$)				Assignment	Aniline-d_7 ($C_6D_5ND_2$)			
free[a]	$AlCl_3$	$AlBr_3$	AlI_3		free[a]	$AlCl_3$	$AlBr_3$	AlI_3
3400	3258	3200	3165	NH str. (NHD)	3400	3244	3200	3178
2560	2446	2406	2400	ND str.	2570	2450	2414	2398
2500	2382	2340	2340		2500	2404	2360	2300
2438	2340sh	2310sh	2300		2442	2344	2320	2218
1440sh	1409	1393	1390	NHD bend.	1461	1415	1401	1398
1300	1227[e]	1203[e]	1203[e]	CN str.	1253	1196[e]	1178[e]	1173[e]
1260	1129	1145	1140	CN str. (NHD)	1197	1110	1120	1117
1150	931[e]	953[e]	950[e]	ND_2 bend.	1130	902[e]	948[e]	941[e]
798	784	775	780	ND_2 rock. (or tw.)	741	740	726	725
470	480			ND_2 wag.				
—	460	$\lesssim 400$[d]		AlX_3	—	446	$\lesssim 400$[d]	

a) Liq. film. b) The positions of bands ascribable to ring vibration. Bands related to NH_2 bending vibration seem to be superimposed on these bands. c) See Ref. 22. d) A strong band was present around or below 400 cm^{-1}. e) These two bands are attributed to the modes given by the coupling of CN stretching and ND_2 bending modes. (See Text.)

Discussion

Some characteristic bands of complexes are discussed below. Detailed information on the structures of adsorption complexes was obtained by examination of direction and magnitude of the frequency shifts. C–N stretching modes for NH_2 and ND_2 are shown as C–NH_2 and C–ND_2 stretching, respectively.

1) Aluminum Halide Complexes. *NH_2 (and ND_2) Stretching Vibration*: Substantial reduction was observed in the NH_2 stretching frequencies. The magnitude of the frequency shift for the complexes of **1** and **3** increased in the order: A<B<C. It amounted to about 160 cm^{-1} and more than 200 cm^{-1} for the complex of B and that of C, respectively. The relative order of the frequency shift was the same for ND_2 stretching frequencies (in the complexes of **2** and **4**).

NH_2 Bending Vibration: The band assigned to this mode shifted to lower frequencies in the complexes of **1**. The result is in line with that of aniline adsorbed on alumina.[3] The magnitude of the frequency shift was in the order: **1A**<**1B**<**1C**. In the complexes of **3**, this mode seems to be superimposed on the benzene ring stretching mode and the relative order of magnitude in the frequency shift was the same as above.

C–NH_2 Stretching Vibration: The 1272 cm^{-1} band of **1** has been assigned to the C–NH_2 stretching mode, which is lowered in frequency by the coupling with the NH_2 bending mode.[15] This band is higher in frequency than the corresponding band in aliphatic amines (*e.g.* 1044 cm^{-1} in methylamine[19]) due to the double bond character in the C–N bond.[15,20] The double bond character is given by the partial conjugation of the lone pair on the nitrogen atom with π-electrons in the phenyl group. The band in **1A**, **1B** or **1C** which is to be correlated with this band is at 1140 cm^{-1}, 1201 cm^{-1} or 1164 cm^{-1}, respectively. The relative order of magnitude of the shift was **1B**<**1C**<**1A**. An abnormally large shift for **1A** is to be noted. The 1140 cm^{-1} band in **1A** is peculiar as regards its very high intensity and broadness. The shifts to lower frequencies in the complexes **1B** and **1C** can be explained in terms of the decrease in the double bond character of C–N bond caused by the partial consumption of the lone pair on the nitrogen atom by the formation of N–Al coordination bond. However, the abnormally large shift in

1A can not be explained along this line, because the interaction of the lone pair with aluminum atom in **1A** is weaker than in **1B**, as revealed by their UV spectra.[21] For complexes **3A**, **3B** and **3C**, the band appearing in a position similar to that in the case of **1A**, **1B** and **1C**, respectively, can be assigned as due to this mode (Table 1), and the relative order of magnitude in the frequency shift was the same as above.[22,23]

C–ND$_2$ Stretching and ND$_2$ Bending Vibrations: A strong band near 1200 cm^{-1} in each of the complexes of **2** and **4** can be correlated to C–ND$_2$ stretching vibration.[23,24] The relative order of the magnitude in the frequency shift for the complexes of **2** and **4** is as follows; complex of A$<$ that of B$\lesssim$ that of C.

A strong band was found in the 900—950 cm^{-1} region in each of the complexes of **2** and **4**. This does not correspond to the bands of phenyl group. When the band around 1200 cm^{-1} was correlated to C–ND$_2$ stretching vibration, it remains as the only one to be correlated to ND$_2$ bending vibration. The frequency shift on complex formation is very large, the relative order of magnitude being as follows; complex of B$<$ that of C$<$ that of A. This order is exactly the same as that of the bands attributed to C–NH$_2$ stretching vibration. An extensive coupling should be assumed between C–ND$_2$ stretching and ND$_2$ bending modes in the complexes.

AlX$_3$ Skeletal Vibration: A strong band was found in the 450—480 cm^{-1} region or near (or lower than) 400 cm^{-1} for the complexes of A or those of B, respectively. The band can be attributed to AlX$_3$ skeletal vibration, since a band with a similar position and band shape was found in the NH$_3$–AlX$_3$ complex (X=Cl or Br).[25]

N···Al Stretching Vibration: No band with considerable intensity was found.

2*) Aniline-*d$_0$*-Gallium Chloride Complex*: IR spectrum was similar to that of **1B**.

The abnormally low frequency of the band attributed to C–NH$_2$ stretching vibration in aluminum chloride complexes (**1A** and **3A**) can be explained by assuming a large ionic character and the elongation of C–N bond in these complexes. The presence of such an ionic character in C–N bond can be understood if we consider the "ionic structure" of solid aluminum chloride. The aluminum atom in aluminum chloride carries some positive charge. On the other hand, aniline molecule is rather weakly adsorbed on the surface of aluminum chloride as revealed by its UV spectrum.[21] The IR spectrum shows that the coordination of the amino group occurs on adsorption. The positive charge on the aluminum atom polarizes the C–N bond giving large ionic character in this bond with the bond elongation. The abnormally high intensity of 1140 cm^{-1} band in **1A** would support the assumption of such an ionic C–N bond, since a large change in dipole moment is expected to accompany the C–N stretching vibration.

The abnormally large frequency shift of the bands associated with ND$_2$ bending vibration in **2A** and **4A** can be explained by considering the coupling of the modes. It is known that C–ND$_2$ stretching vibration and ND$_2$ bending vibration have little coupling with each other in the free molecule, though the two belong to the same symmetry species.[14] This situation changes, however, in the complexes we studied. If C–ND$_2$ stretching frequency is lowered by some ionic character brought into C–N bond and/or by a decrease in the double bond character of C–N bond, the separation between this and ND$_2$ bending frequencies becomes smaller, and the two modes will be brought into coupling. In the complexes of A, the pronounced reduction of C–ND$_2$ stretching frequency due to the ionic character of C–N bond brings this mode into an extensive coupling with ND$_2$ bending mode, the coupling causing two bands widely separated. It is probable that C–ND$_2$ stretching frequency falls down to nearly equal to or even lower than the ND$_2$ bending frequency in the free molecule, and these two modes are extensively mixed. As a result the higher wave number member of the coupled modes in the complex has apparently only a small shift toward a lower wave number as compared with the C–ND$_2$ stretching mode in the free molecule. The lower wave number member in the complex shows an abnormally large shift toward the lower wave number as compared with the ND$_2$ bending mode in the free molecule. This coupling is shown schematically in Fig. 6. It can be deduced that the adsorption of aniline on aluminum chloride is rather weak and predomiantly ionic, with a highly polarized C–N bond.

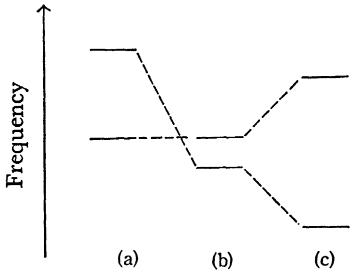

Fig. 6. Diagram showing the coupling of C–ND$_2$ stretching mode and ND$_2$ bending mode by complex formation.

(1) in free molecule (**2** or **4**).
(2) hypothetical case in which C–ND$_2$ stretching mode decreased in frequency and not coupled with ND$_2$ bending mode.
(3) (2)+coupling, the real case in the complex.

In the complexes of B and C, the interaction of the lone pair on the nitrogen atom in aniline molecule with aluminum halide is larger than in the case of complex of A, as revealed by their UV spectra.[21] The lone pair is partially consumed in the formation of the coordination bond to the aluminum atom, more or less covalent N···Al bond being formed. The hybridization of the nitrogen atom becomes closer to sp^3, and the double bond character of C–N bond decreases. In the complexes of B, the aluminum atom has no large positive charge and the polarization effect on C–N bond is small. If any polarization occurs, the effect will be compensated by the flow of electron from nitrogen atom to aluminum atom. The situation will be similar in the complex of C. In these complexes, the decrease in frequency of C–N stretching mode occurs by the reduction of double bond character of C–N bond.

TABLE 2. POSITIONS OF BANDS AND THEIR ASSIGNMENTS FOR ANILINE-d_5 AND ANILINE-d_7 (liq. film)

Aniline-d_5 ($C_6D_5NH_2$)	Aniline-d_7 ($C_6D_5ND_2$)	Assignment[a]	Corresponding band in	
			$C_6D_5CD_3$[b,d]	C_6D_6[c,d]
3424 s	—	NH str.		
—	3400 m	NH str. (NHD)		
3350 s	—	NH str.		
3212 m	—	NH str.		
2599 w	—	1300×2		
—	2570 m	ND str.		
—	2500 m	ND str.		
—	2442 m	ND str.		
	2382 sh	1197×2		
2260 m	2260 m	CD str.	2276 (ν_{20b})	2288 (ν_{20})
2240 sh	2240 sh	CD str.	2262 (ν_{20a})	
1620 s	—	NH_2 bend.		
1570 s	1570*s	ring str.	1583 (ν_{8a})	1558 (ν_8)
			1570 (ν_{8b})	
1470 w	1461 m	NHD bend.		
1400 s	1400*s	ring str.	1388 (ν_{19a})	1333 (ν_{19})
			1332 (ν_{19b})	
1300 s		CN str. (NH_2) +ring str.		
	1288 s	ring str.	1375 (ν_{14})	1282 (ν_{14})
	1253*m	CN str. (ND_2)		
1240 w	1240 sh	804+431?		
1197 m	1197 m	CN str. (NHD)		
	1130*m	ND_2 bend.		
	1066 w	CD bend. i.p.	972 (ν_3)	1059 (ν_3)
953 m	955 m	ring str.	961 (ν_{12})	970 (ν_{12})
	928 w	508+420		946 (ν_1)
880 vw	880*vw	CD bend. i.p.	880 (ν_{9a})	868 (ν_9)
860 vw	860*vw	CD bend. i.p.	869 (ν_{9b})	
				827 (ν_5)
				824 (ν_{15})
838 vw	838*w	CD bend. i.p.	840 (ν_{18a})	814 (ν_{18})
818 m	818*m	CD bend. i.p.	819 (ν_{18b})	
804 sh	804 sh	CD bend. i.p.	785 (ν_5)	
750 m	755 m	CD bend. o.p.	717 (ν_1, ν_{17b})	793 (ν_{17})
	741*m	ND_2 rock (or tw.)		
660 w		NH_2 wag.		
626 w	628 m	CD bend. o.p.	658 (ν_{10a})	664 (ν_{10})
594 w	593 vw	CD bend. o.p.	605 (ν_{11}, ν_{6b})	601 (ν_4)
552 s	553 s	ring def.	541 (ν_4)	579 (ν_6)
515 w	508 vw	ring def.	490 (ν_{6a})	496 (ν_{11})
431 s	420 s	ring def.		

a) i.p.=in plane, o.p.=out of plane. b) From Ref. 28. All the strong bands (with relative intensity greater than 8 in Table 2 in Ref. 28 except those assigned to CD_3 group vibrations) are listed. c) From Ref. 27. d) Numbering is after Refs. 27 and 28. * Ostrowska and Tramer (Ref. 16) gave assignments for these bands.

This will bring C–ND_2 mode into coupling with ND_2 bending mode to some extent, which will cause the low frequency shift of the bands associated with the ND_2 bending mode in these complexes. Since the reduction of C–ND_2 stretching frequency for these complexes is smaller than for the complex of A, the extent of this coupling should be smaller and hence the frequency shift in ND_2 bending mode also smaller. Thus, the adsorption of aniline on aluminum bromide and iodide can be shown to be a stronger chemisorption (with an essentially covalent N···Al bond) with C–N bond of less polarity than the adsorption on aluminum chloride. Judging from the magnitude of the frequency shifts of bands, the chemisorption on C is stronger than that on B.

In the complex **1D**, the IR spectrum was similar to that of **1B**, and the structure of the adsorbed complex would thus be similar to that of the complex **1B**.

A brief comment will be necessary as to the frequency shifts of NH stretching vibrations. The polarization of C–N bond in the complexes of A accompanies the polarization of N–H bond, reducing the frequencies of N–H stretching vibrations. The frequency shifts of N–H stretching vibrations in these complexes might be larger than in the complexes of B and C owing to this effect, as is the case for the C–N stretching vibrations. However, the observed magnitude of the shifts was in the order: A<B<C. This can be explained in the following way. There is another factor for reducing the frequencies of N–H stretching vibrations in the complexes of B and C, namely the substantial change in hybridization of the nitrogen atom toward sp^3.

Thus, detailed information on the structures of adsorbed molecules and also on the nature of adsorption (ionic or covalent) was obtained by analyses of the IR spectra.[26)]

Our thanks are due to Dr. Taruo Kurokawa, Kogaiboshi Kyokai, Kagoshima Pref., who allowed us the use of their JASCO IRA-2 infrared spectrophotometer.

Appendix

IR Bands of Aniline-d_5 *and Aniline-*d_7 *and Their Assignments.* Observed IR bands are listed in Table 2. For aniline-d_7, the positions of bands are in line with the data of Ostrowska and Tramer.[16,18)] The assignments of these bands were made as follows. The liquid film of aniline-d_7 was exposed to the air with repeated IR measurement at certain intervals. The content of aniline-d_7 decreased with an increase in aniline-d_5. The bands common to all the spectra were attributed to C_6D_5-group. The assignments were confirmed by comparison with IR bands of benzene-d_6[27)] and toluene-d_8.[28)] The bands found only in aniline-d_7 or in aniline-d_5 were associated to ND_2– or NH_2–group, respectively. The bands remaining in the intermediate state were assigned to NHD–group. The assignments were compared with those of the corresponding bands in aniline-*N*,*N*-d_2 and aniline-d_0.[14,15)] For aniline-d_7, Ostrowska and Tramer[16)] gave the assignments of nine bands (shown by asterisks in Table 2). Our assignments for these nine bands agree with theirs except for the band at 741 cm^{-1} which was assigned to CD out-of-plane bending mode.[16)] Although this assignment can not be ruled out completely, the band was assigned to ND_2 rocking (or twisting) mode in this paper, since no corresponding band was found in aniline-d_5.

References

1) H. Sato, K. Hirota, and S. Nagakura, This Bulletin, **38**, 962 (1965).

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21) The UV spectrum of **1B** was measured on a Shimadzu MPS-50L recording spectrophotometer. The shift of the bands toward shorter wavelength was larger than that in the case of **1A** (Ref. 1). The positions of observed UV bands for **1B** (253, 259, 265 nm, the highest peak being that of 259 nm.) were very close to those of anilinium ion $C_6H_5NH_3^+$ (248, 254, 260 nm in H_2SO_4 aq.; "DMS UV Atlas," Vol. IV, Butterworths, London, D6/4 (1968)). The species giving this UV spectrum, however, was not the anilinium ion, but the aluminum bromide complex, since the IR measurement on the same sample gave the characteristics of the complex. The UV spectrum of **1C** gave a broad band in the 246—274 nm region, with an absorption maximum at 258 nm. The location of this band is similar to that of **1B**.

22) For **3A**, two broad bands (1165 and 1125 cm^{-1}) were found in this region. The latter was assigned to C–NHD stretching mode. However, these two bands might result from two types of adsorbed molecules (adsorbed on two types of sites). If this is the case, the band associated to C–NHD stretching mode may be involved in the 1125 cm^{-1} band. It might be possible that the broad 1140 cm^{-1} band of **1A** is actually composed of two bands, one around 1165 cm^{-1} and the other around 1125 cm^{-1}.

23) The bands appearing in 1100—1120 cm^{-1} region seem to be attributable to NHD species, since they were found at the same positions (within experimental error) in the complexes of **3** and **4**, and at the positions close to these in the complex of **2**. (For the 1125 cm^{-1} band of **3A**, see footnote 22).

24) In the complexes of **2** and **4** with B and C, some of the bands assigned to CN stretching vibration were accompanied by another weak band, the nature of which is not clear. This may result from some chemical reaction occuring on these aluminum halides.

25) H. Sato, unpublished result.

26) The relative order of strength in chemisorption was revealed also in the difference of chemical stability of the complexes **1A** and **1B** when the cell systems were exposed to the air. The complex **1A** decomposed immediately to give the IR spectrum of anilinium ion salt, while the IR spectrum of **1B** did not change appreciably for hours.

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