Infrared Spectroscopic Studies of Hexammine- and Pentammine-chromium(III) Complexes

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Studies of the infrared spectra of the inorganic coordination compounds offer interesting information concerning the natures of the coordination bond and of the molecular structure. From this point of view, cobalt(III)-ammine complexes have been often investigated.[1-9] Chromium(III)-ammine complexes, on the other hand, have not been studied systematically. Indeed, Nakamoto et al.[9] reported on the effect of the outer ions on the infrared spectra of chromium(III)-ammine complexes. Their discussion, however, was mainly devoted to hexamminechromium(III) complexes.

In the present work, the infrared spectra of twenty-nine samples of hexammine and pentammine complexes of chromium(III) and cobalt(III) have been measured, and the shift of the observed bands with the change in the outer ions has been discussed.

Experimental

Preparation of Chromium(III)-Ammine Complexes. — Hexamminechromium(III) chloride and aquopentamminechromium(III) chloride were obtained, by the procedure given by King,[10] from the nitrates of the corresponding complexes, which had been prepared according to the method of Mori.[11] Bromides, iodides and perchlorates of hexammine- and aquopentamminechromium(III) complexes were prepared from the chlorides by the same method as reported by King.[10]

Halopentamminechromium(III) complexes were obtained by heating aquopentamminechromium(III) halide at 80~120°C for a few hours, and the outer ions of those complexes, if necessary, were converted by procedures similar to those used for hexamminechromium(III) complexes.

Some selected samples were deuterated by dissolving them in heavy water (D_2O). D_2O was subsequently removed by evaporation at reduced pressure, and the samples were dried in vacuo over P_2O_5.

Measurements of Infrared Spectra. — Infrared spectra were measured by using a Hitachi EPI-2G recording infrared spectrophotometer equipped with a potassium bromide foreprism and a grating double monochrometer. The potassium bromide disk method was employed for the measurement in the sodium chloride prism region, and both the potassium bromide disk and the Nujol mull methods, in the potassium bromide prism region. The values obtained by the Nujol mull method, however, were adopted for the determination of the wavelength of absorption peaks, because, in general, the spectra are clearer in the Nujol mull method than in the potassium bromide disk method.

The calibration of the frequencies was made with polystylene film, and with carbon dioxide and water vapor.

Results

Typical infrared spectra of hexammine- and pentamminechromium(III) complexes in the

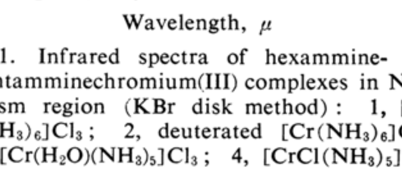

Fig. 1. Infrared spectra of hexammine- and pentamminechromium(III) complexes in NaCl prism region (KBr disk method): 1, $[Cr(NH_3)_6]Cl_3$; 2, deuterated $[Cr(NH_3)_6]Cl_3$; 3, $[Cr(H_2O)(NH_3)_5]Cl_3$; 4, $[CrCl(NH_3)_5]Cl_2$.

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sodium chloride prism region are shown in Fig. 1. They, and the spectra of other hexammine- and pentamminechromium(III) complexes, give four main absorption bands. Since these bands shifted to lower frequencies upon the deuteration of ammonia, they were assigned to be N–H stretching, degenerated deformation, symmetric deformation and rocking vibrations.[3] All spectra of $[CrX(NH_3)_5]Y_{2,3}$, where X is NH_3, H_2O and halide ions, and Y, ClO_4^-, NO_3^- and halide ions, shifted to higher frequencies in the N–H stretching vibration and to lower frequencies in the other three deformation vibrations when the outer ions were changed to the order of chloride, bromide and iodide, as Table I shows.

TABLE I. SHIFT OF ABSORPTION BANDS OF HEXAMMINE- AND PENTAMMINECHROMIUM-(III) COMPLEXES WITH VARIED OUTER IONS (SODIUM CHLORIDE PRISM REGION)

Complex	Wave number, cm^{-1}			
$[Cr(NH_3)_6](ClO_4)_3$	3311	1614	1339	743
$[Cr(NH_3)_6](NO_3)_3$	3268	1613	1304	747
$[Cr(NH_3)_6]Cl_3$	3185	1605	1307	748
$[Cr(NH_3)_6]Br_3$	3185	1603	1307	746
$[Cr(NH_3)_6]I_3$	3190	1600	1305	741
$[CrCl(NH_3)_5](ClO_4)_2$	3284	1600	1287	767
$[CrCl(NH_3)_5](NO_3)_2$	3279	1596	1285	765
$[CrCl(NH_3)_5]Cl_2$	3277	1600	1289	774
$[CrCl(NH_3)_5]Br_2$	3283	1595	1286	767
$[CrCl(NH_3)_5]I_2$	3280	1590	1284	755

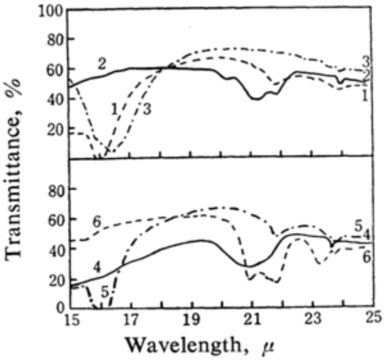

Fig. 2. Infrared spectra of hexammine- and pentamminechromium(III) complexes in KBr prism region (Nujol mull method): 1, $[Cr(NH_3)_6](ClO_4)_3$; 2, $[Cr(NH_3)_6]Cl_3$; 3, deuterated $[Cr(NH_3)_6]Cl_3$; 4, $[Cr(H_2O)(NH_3)_5]Cl_3$; 5, $[CrCl(NH_3)_5](ClO_4)_2$; 6, $[CrBr(NH_3)_5]Cl_2$.

Figure 2 shows the infrared spectra of several complexes in the potassium bromide prism region. From the assignment of the absorption bands of hexamminecobalt(III) ions,[8] the Cr–N stretching vibration is expected to be observed in this frequency region, but at somewhat lower frequencies than those of the corresponding cobalt(III) complex, because the coordination effect of chromium(III) is considered weaker than that of cobalt(III).[12] When the outer ions of hexamminechromium(III) are halide ions, three bands appear in the potassium bromide prism region. All these bands were assigned to be Cr–N stretching vibrations for the following two reasons. First, as the Cr–N stretching vibration of hexamminechromium(III) complex belongs to the F_{1u} species if the ammonia molecule is taken as a single group, this band splits into three components because of the lowering of symmetry which is caused by the formation of a hydrogen bond between ammonia and halide ion and by the deformation in the crystal state. Second, these bands shifted to lower frequencies upon the deuteration of the coordinating ammonia. The frequency ratio of the band of the undeuterated complex to that of the deuterated complex (ν_{NH_3}/ν_{ND_3}) is 1.09 (Table II), which is in good agreement with the theoretical value (1.06) calculated from a harmonic oscillator consisting of a chromium(III) atom and ammonia (or deuterated ammonia) group.

TABLE II. OBSERVED FREQUENCIES OF $[Cr(NH_3)_6]Cl_3$ AND $[Cr(ND_3)_6]Cl_3$

Frequencies of $[Cr(NH_3)_6]Cl_3$ ν_{NH_3}, cm^{-1}	Frequencies of $[Cr(ND_3)_6]Cl_3$ ν_{ND_3}, cm^{-1}	ν_{NH_3}/ν_{ND_3}
3257 sh	2415	
3185	2347 sh	
3130	2283	
1630	1171	
1307	1007	
748	603	
495 w	455 vw	1.09
473	435	1.09
456	424	1.08

In pentamminechromium(III) complexes, $[CrX(NH_3)_5]^{2,3+}$, similar phenomena were observed. A pentammine complex ion has C_{4v} symmetry, if the ammonia molecule is taken as a single group, and A_1- (Cr–X stretching, Cr–N symmetric stretching) and E-species (Cr–N asymmetric stretching) are infrared active. $[CrCl(NH_3)_5](ClO_4)_2$ gives two weak absorption bands, at 457 and 420 cm^{-1} (Fig. 2). When the outer ions were halide ions, three bands were observed in the potassium bromide prism region upon the split of E-species, as is shown in Table III. All these bands shifted to lower frequencies upon the deuteration of ammonia and when the outer ions were changed from

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TABLE III. OBSERVED FREQUENCIES $[Cr(NH_3)_6]Y_3$ AND $[CrX(NH_3)_5]Y_{2,3}$ IN KBr PRISM REGION (cm^{-1})

Complex ion	Outer ion				
	ClO_4^-	NO_3^-	Cl^-	Br^-	I^-
$[Cr(NH_3)_6]^{3+}$	458	467	495 473 456	488 468 453	475 462 449
$[Cr(H_2O)(NH_3)_5]^{3+}$	457	476	478	476	479
$[CrCl(NH_3)_5]^{2+}$	457 420	460	471 458 431	460 448 423	447 440 416
$[CrBr(NH_3)_5]^{2+}$		471^{sh}_{vw}	476	467	452
		462	459	451	440
		457^{sh}_{vw}	429	423	
$[CrI(NH_3)_5]^{2+}$		471^{sh}_{vw}	488 472		460
		463	462 426		453 440

chloride to iodide. When the outer ions were nitrate and perchlorate, which do not form a strong hydrogen bond, the splitting of the band was not observed. From this spectral evidence, it was concluded that the absorption bands of $[CrX(NH_3)_5]^{2,3+}$ appearing in the potassium bromide prism region were all due to the Cr–N stretching vibration, not to the Cr–X stretching vibration.

Discussion

Table I shows that the absorption bands of hexammine- and pentamminechromium(III) complexes shift with the change in outer ions. It is well known that the band shifts because of the formation of a hydrogen bond of the X···H–N type,[5] where X indicates halide ions or oxyacids. The strength of the hydrogen bond between the anions and ammonia increases in the order of ClO_4^-, NO_3^-, I^-, Br^- and Cl^-. Table I shows that the N–H stretching band shifts to lower frequencies, while the deformation band shifts to higher frequencies in the order of the strength of the hydrogen bonding. The relation between the rocking vibration frequencies and outer halide ions is shown in Table IV. The differences in frequencies (Δ) between the chloride and the iodide are 7 cm^{-1} in $[Cr(NH_3)_6]^{3+}$ and 13 cm^{-1} in $[Cr(H_2O)(NH_3)_5]^{3+}$, and 26 and 20 cm^{-1}, respectively, in the corresponding cobalt(III) complexes.

The effect of outer ions was remarkable in the potassium bromide prism region, also. As Table III shows, spectra shift to lower frequencies when the outer ions are changed from chloride to iodide. As explanation of this experimental data, it is considered that the M–N stretching vibrations shift to higer frequencies with an increasing strength of hydrogen bond formation because the M–N stretching vibration is apt to couple with the NH_3 rocking vibration.

The M–N stretching vibration band splits into three components when the outer ions are halide ions. The magnitudes of the split are 39, 35 and 26 cm^{-1} in the chloride, the bromide and the iodide of hexamminechro-

TABLE IV. EFFECT OF OUTER IONS ON THE FREQUENCIES OF THE ROCKING VIBRATION BAND OF NH_3 (cm^{-1})

Complex ion	Cuter ion			
	Cl^-	Br^-	I^-	Δ
$[Cr(NH_3)_6]^{3+}$	748	746	741	7
$[Co(NH_3)_6]^{3+}$	818	797	792	26
$[Cr(H_2O)(NH_3)_5]^{3+}$	756	752	743	13
$[Co(H_2O)(NH_3)_5]^{3+}$	837	832	817	20
$[CoF(NH_3)_5]^{2+}$	845	820	806	39
$[CrCl(NH_3)_5]^{2+}$	774	767	755	19
$[CrBr(NH_3)_5]^{2+}$	773	765	755	18
$[CrI(NH_3)_5]^{2+}$	768	—	752	16

TABLE V. OBSERVED FREQUENCIES OF SPLIT IN THE Cr–N STRETCHING VIBRATION BANDS OF HEXAMMINE- AND HALOPENTAMMINECHROMIUM-(III) HALIDES

Complex ion	Outer ion			
	Cl	Br^-	I^-	NO_3^-
$[Cr(NH_3)_6]^{3+}$	39	35	26	0
$[CrCl(NH_3)_5]^{2+}$	40	37	31	0
$[CrBr(NH_3)_5]^{2+}$	47	44	—	14
$[CrI(NH_3)_5]^{2+}$	26	—	20	13

mium(III) respectively. Table V summarizes the magnitude of the split in other complexes. In all cases, the magnitude of the split increases in the order of the iodide, the bromide and the chloride. From the facts that a stronger hydrogen bonding between an ammonia molecule and an outer ion results in a larger split of the M–N stretching vibration and that the M–N stretching vibration does not split in the perchlorate and the nitrate, it is expected that the main cause for the split and the shift of absorption band is the formation of the hydrogen bond.

Halopentamminechromium(III) complexes showed a tendency similar to that of hexamminechromium(III) complexes with regard to the split and the shift of absorption bands. These phenomena may be explained in the same way as were those of the hexamminechromium(III) complexes. Although the M–N stretching vibration did not split in $[Cr(NH_3)_6](NO_3)_3$, it did split to three components in $[CrX(NH_3)_5](NO_3)_2$, where X indicates halide ions. The magnitude of split, however, is smaller than that observed with the corresponding halides (Table V). This experimental result coincides with the view that a nitrate ion forms a weaker hydrogen bond with ammonia than a halide ion does. The differences in the M–N stretching frequencies between the chlorides and the iodides of $[CrX(NH_3)_5]^{2+}$ (X = halide ion) are almost equal; they are 18, 19 and 19 cm^{-1} when X is chloride, bromide and iodide ions respectively. It can be expected, from this fact, that coordinating halide ion has almost the same effect on the hydrogen bonding between the outer ion and the ammonia molecule. When coordinating halide ions were varied with the same outer ion, the M–N stretching bands shifted to slightly higher frequencies in the order of chloro-, bromo- and iodopentamminechromium-(III) complexes, that is, 460, 462 and 463 cm^{-1} in the nitrates. This fact that the magnitude of shift is not appreciable may indicate that the effects of coordinating halide ions on the adjacent M–N bond are almost the same.

The spectra of aquopentamminechromium-(III) complexes in the potassium bromide prism region were different from those of hexammine- and halopentamminechromium-(III) complexes, because only one absorption band was observed, even in the case of the halides. If the ammonia molecule is taken as a single group, an aquopentamminechromium(III) ion has C_{4v} symmetry and, consequently, should give at least two absorption bands.

This discrepancy may be explained as follows: $[Cr(H_2O)(NH_3)_5]^{3+}$ has a similar structure to that of the complex that has O_h symmetry because the mass of the ammonia molecule is almost equal to that of water molecule.[2] Moreover, since the electronegativity of the oxygen atom of water is larger than that of the nitrogen atom of ammonia, water can more easily form a hydrogen bond with an outer ion than ammonia does. The effect of the outer ion on the ammonia of $[Cr(H_2O)(NH_3)_5]^{3+}$ is small, and, consequently, no split of the M–N stretching band occurs. The M–N stretching frequencies of $[Cr(H_2O)(NH_3)_5]^{3+}$ were found to be 478, 476 and 479 cm^{-1} in the chloride, the bromide and the iodide respectively. These experimental results support the above consideration.

Summary

Twenty-nine samples of hexammine and pentammine complexes of chromium(III) and cobalt(III) have been prepared, and their infrared spectra have been measured in the region of $2\sim25\,\mu$. The absorption peaks of these complexes have been found to shift to higher frequencies in the N–H stretching vibrations, and to lower frequencies in the NH_3 deformation and the Cr–N stretching vibrations in the order of the chlorides, the bromides and the iodides. In a potassium bromide prism region, three absorption bands due to the Cr–N stretching vibrations have been observed in hexammine- and halopentamminechromium(III) halides, but only one in the aquopentamminechromium(III) complexes. The shifts of the absorption bands observed have been discussed from the standpoint of the hydrogen bond formation.

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