Structure and Polarized Spectra of *cis*-difluorotetraamminecobalt(III) Perchlorate, *cis*-$[CoF_2(NH_3)_4]ClO_4$

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The structure of *cis*-$[CoF_2(NH_3)_4]ClO_4$ has been determined by a single-crystal X-ray diffraction method. Crystals are tetragonal, space group $P4_1$ (or $P4_3$), a=7.2645(6), c=16.260(2) Å, V=858.1(2) Å^3, Z=4, T=297(1) K, final R=0.052 for 970 observed unique reflections. The coordinated F and N atoms could be distinguished unambiguously from each other based on the thermal parameters. The bond distances Co–F and Co–N are 1.828(6)—1.870(5) and 1.924(7)—1.944(7) Å, respectively. The absorption spectra of the single crystals have been examined in the visible and infrared regions with polarized radiation by the use of microspectrophotometers. The 584 nm band (B_1) was considered to borrow intensity from some A_1 bands through vibronic coupling with some B_1 vibrations, and the 504 nm band (A_2 & B_2) through some A_2 and B_2 vibrations. Two of the four ammine groups of this cobalt complex were found to give an NH_3 rocking frequency (860 cm^{-1}) higher by 50 cm^{-1} than the other two (at 810 cm^{-1}). This fact has been attributed to two inter-molecular hydrogen bonds (NH···F=2.85—2.68 Å) in which the former two ammine groups are involved.

In structural chemistry, the idea of combining an optical microscope and spectrophotometer emerged a long time ago, and its actual practice started some forty years ago. An extensive use of this combination, however, has become possible only recently, after a number of technological developments were made regarding both microscopes and spectrophotometers. We are now attempting to adopt this combination as a tool for elucidating the detailed electronic structures of some complex molecules in their single crystals, whose sizes cannot readily be greater than 50 μm (order of magnitude). The present paper deals with one part of our work along this line.

cis-Difluorotetraamminecobalt(III) perchlorate, *cis*-$[CoF_2(NH_3)_4]ClO_4$, is one of the new complexes which have recently been prepared.[1] It gives violet needle crystals. The crystal structure has now been determined, as detailed below. It has been found that all of the complex molecules are oriented with their C_2-axes approximately along the crystalline elongation direction, which is now established to be its tetragonal c-axis. Therefore, this crystal is extremely favorable for spectroscopic analyses of the complex molecule presently in question. By the use of polarized radiation, well characterized bands are expected to be newly resolved, and their transition moment directions determined. Some results of such analyses are reported below.

Experimental

Sample Preparation. Single crystals of *cis*-$[CoF_2(NH_3)_4]ClO_4$ were obtained by evaporating the solvent from an aqueous mixture of *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$ and NH_4F, as detailed in a previous paper.[1]

Structure Determination. Crystal data are as follows: $[CoF_2(NH_3)_4]ClO_4$, Formula weight 264.5, tetragonal $P4_1$ (or $P4_3$), a=7.2645 (6), c=16.260 (2) Å, V=858.1 (2) Å^3, Z=4, D_m (CCl_4/CH_3I)=2.04 (1), D_x=2.05 Mg m^{-3}, λ (Mo $K\alpha$)=0.71073 Å, μ=2.33 mm^{-1}, $F(000)$=536, T=297 (1) K. Crystals are purple needles elongated along c. A crystal of dimensions 0.08×0.08×0.5 mm was mounted on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The cell parameters were refined by least squares for 25 2θ values ($20<2\theta<30°$). The intensity measurements were performed using a 2θ=55° (h −9→9, k −9→9, l 0→21) by θ–2θ scan technique. Systematic absences were 0 0 l with $l\neq4n$. The variation of five standard reflections was $0.98<\Sigma(|F_o|/|F_o|_{initial})/5\leqq1.00$. 4015 reflections were measured and 2482 reflections were observed with $|F_o|<3\sigma(|F_o|)$. The number of unique reflections was 970, with R_{int}=0.022 after an absorption correction ($0.81<A<0.85$). The Laue group and systematic absences showed that the space group is $P4_1$ (or $P4_3$). The positions of the Co and Cl atoms were deduced from the Patterson function. All of the six coordinating atoms around the Co could be located by Fourier synthesis and tentatively refined using the nitrogen scattering factor. The isotropic thermal parameters of two atoms became smaller (1.2 Å^2) than those of the other four atoms, which ranged from 2.3 to 5.2 Å^2. Thus, these two atoms were assigned to be more electron-rich atoms, F. Then, all of the nonhydrogen atoms were refined anisotropically. Five out of twelve H atoms were located by a difference synthesis; the others were calculated. The coordinates of the H atoms were fixed according to the isotopic thermal parameter, B=4 Å^2. The function $\Sigma w||F_o|-|F_c||^2$ was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by a block-diagonal least-squares method. Final R=0.052, wR=0.053, S=2.04 for 970 unique reflections. The space group of the crystal specimen used for data collection appeared to be $P4_3$. The enantiomeric space group, $P4_1$, was rejected because of larger R factors, R=0.059, wR=0.064. The reflection/parameter ratio was 6.1 ($\Delta/\sigma<0.2$, $-0.8<\Delta\rho<1.2$ e Å^{-3}). Complex neutral-atom scattering factors were used.[2] The calculations were carried out on a FACOM M-380R computer at Keio university using the

UNICS-III computation program system.[3]

Visible Absorption Spectrum. The absorption spectra of a single crystal of the cis cobalt complex now in question were examined in the visible spectral region at two different orientations of the electric vector of the polarized radiation. The procedures for the microscopic spectral measurement and a curve-analysis method were both essentially the same as that described in a previous paper.[4]

Infrared Absorption Spectrum. A Jasco Micro FTIR-100 was used. A single crystal with the dimensions of 15×30 μm was placed under a microscope. Its transmittance spectra were recorded at two different polarizations of the radiation: one with $E//c$ and the other $E\perp c$, where E is the electric vector of the infrared radiation. For producing an infrared interferogram, 100 scans were accumulated with a resolution 4 cm^{-1} and with a cosine apodization function. A liquid-nitrogen-cooled mercury cadmium telluride detector was used.

Results and Discussion

Structure of $[CoF_2(NH_3)_4]ClO_4$. The final atomic parameters of non-hydrogen atoms and interatomic distances and bond angles are presented in Tables 1 and 2.[5] The Co atom is coordinated octahedrally by two F atoms and four NH_3 molecules, the former being in the cis positions. The average bond distance of the Co–F, 1.849 (6) Å, is 0.083 Å shorter than that of the Co–N, 1.932 (8) Å. This fact supports the distinction of F from NH_3 based on their thermal parameters in the refinement. The crystal structure is shown in Fig. 1. The bisector of the F–Co–F bond angle is approximately parallel to c. There exist intermolecular hydrogen bonds, N–H···F (or O), as shown in Table 3.

Group Theoretical Predictions. On the basis of the crystal structure just described, the number of optically active vibrations, in which the vibrations in all the

Table 1. Positional Parameters (×10⁴) and Equivalent Isotropic Temperature Factors

Atom	x	y	z	×10 B_{eq}/Å²
Co	2393(1)	2531(2)	0[a]	16
Cl	7448(3)	7402(3)	223(1)	29
F(1)	553(7)	2513(7)	−767(4)	38
F(2)	4216(7)	2516(7)	−812(3)	42
N(1)	532(10)	2575(11)	844(5)	33
N(2)	4296(9)	2555(9)	823(5)	31
N(3)	2383(9)	5205(9)	−47(5)	31
N(4)	2391(8)	−127(8)	−17(5)	24
O(1)	8798(13)	7491(14)	−441(7)	89
O(2)	7539(25)	5924(22)	693(12)	181
O(3)	7576(32)	9133(25)	511(13)	225
O(4)	5874(14)	7542(22)	−137(17)	233

a) This parameter was used to define the origin of the unit cell along z and is listed without e.s.d.

Table 2. Interatomic Distances (Å) and Angles (°)

Co–F(1)	1.828(6)	Co–N(4)	1.931(6)
Co–F(2)	1.870(5)	Cl–O(1)	1.460(11)
Co–N(1)	1.927(8)	Cl–O(2)	1.320(17)
Co–N(2)	1.924(7)	Cl–O(3)	1.345(19)
Co–N(3)	1.944(7)	Cl–O(4)	1.289(16)
F(1)–Co–F(2)	92.1(2)	N(1)–Co–N(4)	91.5(3)
F(1)–Co–N(1)	88.5(3)	N(2)–Co–N(3)	91.2(3)
F(1)–Co–N(2)	178.9(3)	N(2)–Co–N(4)	91.1(3)
F(1)–Co–N(3)	88.7(3)	N(3)–Co–N(4)	176.9(3)
F(1)–Co–N(4)	89.0(3)	O(1)–Cl–O(2)	115.5(9)
F(2)–Co–N(1)	179.2(3)	O(1)–Cl–O(3)	99.8(9)
F(2)–Co–N(2)	89.0(3)	O(1)–Cl–O(4)	104.9(8)
F(2)–Co–N(3)	88.9(3)	O(2)–Cl–O(3)	123.8(11)
F(2)–Co–N(4)	89.1(2)	O(2)–Cl–O(4)	111.8(10)
N(1)–Co–N(2)	90.5(3)	O(3)–Cl–O(4)	98.4(11)
N(1)–Co–N(3)	90.5(3)		

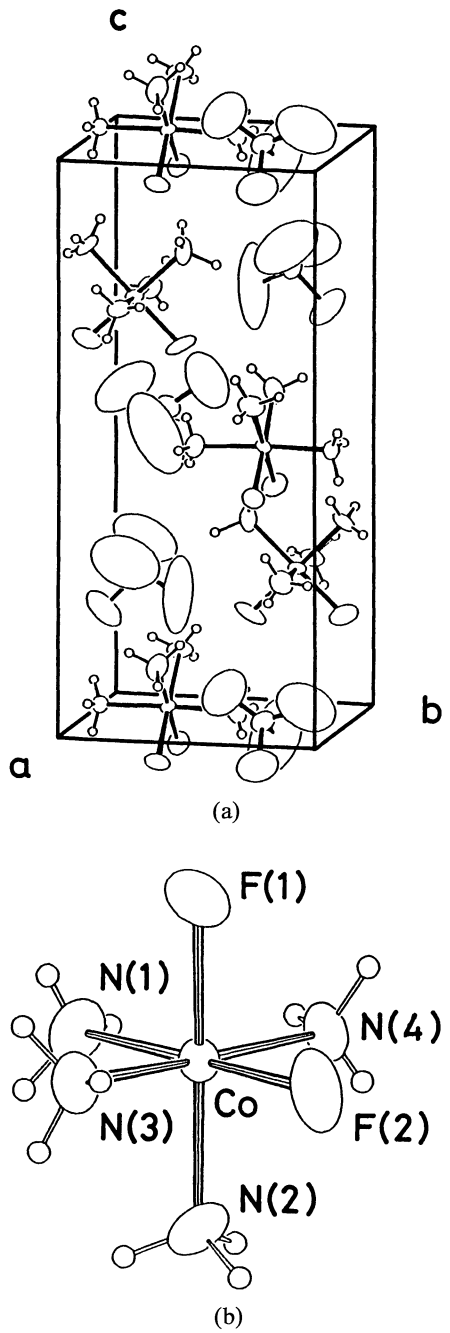

Fig. 1. (a) Crystal structure of *cis*-$[CoF_2(NH_3)_4]ClO_4$ and (b) molecular structure of the complex cation.

Bravais unit cells in the crystal take place in-phase, has been calculated for each type of vibration (Table 4). The $CoF_2(NH_3)_4^+$ ion has $3\times19-6=51$ intramolecular normal vibrations and the ClO_4^- ion has $3\times5-6=9$. Because four $CoF_2(NH_3)_4^+$ ions and four ClO_4^- ions are involved in the Bravais unit cell, $60\times4=240$ optically active intramolecular vibrations are expected for the crystal. Among them, 60 give their transition moments along the *c*-axis, 60 are infrared-inactive, and the remaining 120 are polarized along the perpendicular directions to the *c*-axis.

As long as the strict crystallographic symmetry is concerned, no further characterization is possible for these intramolecular vibrations. In a good approximation, however, every $CoF_2(NH_3)_4^+$ ion here has a pseudo-C_{2v} symmetry. As shown in Fig. 2, the C_2 symmetry axis is oriented along the crystallographic *c*-axis; We designate this the molecular *z*-axis. Two of the four Co–N bonds are in the plane which is formed by the two Co–F bonds; this plane is designated the molecular *xz*-plane, and the two NH_3 groups on the ends of these Co–N bonds are denoted by "NH_3-pair I." The two other Co–N bonds are both along the molecular *y*-axis, and are called "NH_3-pair II." The normal vibrations of the $CoF_2(NH_3)_4^+$ ion are now classified as given in Table 5.

The environment of the *d*-electrons of the Co atom is also considered to have nearly C_{2v} symmetry. The electron configuration of the ground state thus belongs to the A_1 species, and those corresponding to the T_{1g} species for the O_h symmetry turn out into three configu-

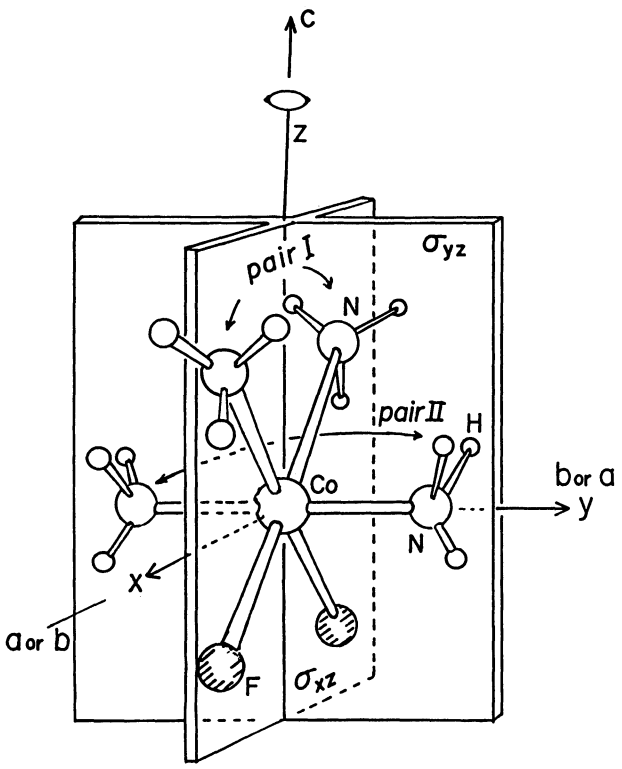

Fig. 2. An approximate symmetry (C_{2v}) of the $CoF_2(NH_3)_4$ ion in its crystal now in question. (*x*, *y*, *z*) are the molecular axes, (*abc*) are the crystallographic axes, and (*XYZ*) are the axes to express the molecular orbitals of the *d* electrons of the Co atom ($d_{X^2-Y^2}$, d_{YZ-ZX}, etc.) when its environment had the O_h symmetry.

Table 3. Intermolecular Hydrogen Bonds (Distances in Å)

A ··· H–B	(Symmetry code)[a]	A ··· B	A ··· H	H–B
F(1) ··· H(13)–N(1)	(i)	3.054(10)	2.424(5)	0.880(8)
F(1) ··· H(22)–N(2)	(i)	2.994(9)	2.276(5)	0.887(7)
F(1) ··· H(43)–N(4)	(i)	2.864(10)	2.358(6)	0.868(7)
F(2) ··· H(12)–N(1)	(ii)	3.065(9)	2.281(5)	0.877(8)
F(2) ··· H(23)–N(2)	(ii)	3.025(9)	2.211(5)	0.891(7)
F(2) ··· H(32)–N(3)	(ii)	2.854(9)	2.117(5)	0.886(8)
O(1) ··· H(33)–N(3)	(iii)	3.154(12)	2.347(10)	0.862(7)
O(4) ··· H(41)–N(4)	(iv)	3.051(14)	2.416(13)	0.689(6)

a) Symmetry code: (i) $-y, -x, -1/4+z$, (ii) $1-y, -x, -1/4+z$, (iii) $1+x, y, z$, (iv) $x, 1+y, z$.

Table 4. Number of In-Phase Normal Vibrations of Each Type in the *cis*-$[CoF_2(NH_3)_4]ClO_4$ Crystal

Space group					$P4_1$(or $P4_3$)	
Isomorphous point group					C_4(Factor group)	
Total number of molecules in the Bravais unit cell					8	
(Number of $CoF_2(NH_3)_4^+$ ions ..... 4)						
(Number of ClO_4^- ions ..... 4)						
Number of atoms in the Bravais unit cell					96	
	T	R	n	IR	Raman	
A	5	6	60	M_c	$\alpha_{a^2+b^2}$	α_{c^2}
B	6	6	60		$\alpha_{a^2-b^2}$	α_{ab}
E	10	12	120	M_a & M_b	α_{bc}	α_{ac}

T=Translational lattice vibrations. R=Rotatory lattice vibrations. n=Intramolecular vibrations.

Table 5. Number of Normal Vibrations of Each Type in the $CoF_2(NH_3)_4^+$ Ion

C_{2v}	IR	Raman	NH_3 sym. str.		NH_3 deg. str.		NH_3 sym. def.		NH_3 deg. def.		NH_3 rock.		NH_3 tors.		Co–N str.		Co–F str.	Skeletal def.	Total
			I	II	I	II	I	II	I	II	I	II	I	II	I	II			
A_1	M_z	α_{xx}, α_{yy}, α_{zz}	1	1	1	1	1	1	1	1	1	1			1	1	1	3	16
A_2		α_{xy}			1	1			1	1	1	1	1	1				2	10
B_1	M_x	α_{zx}	1		1	1	1		1	1	1	1	1		1		1	2	13
B_2	M_y	α_{yz}		1	1	1		1	1	1	1	1		1		1		2	12

sym.=symmetric, deg.=degenerate, str.=stretching, def.=deformation, rock.=rocking, tors.=torsional, I=$NH_3(1)$–$NH_3(2)$ pair, II=$NH_3(3)$–$NH_3(4)$ pair.

rations belonging to the B_1, A_2, and B_2 species. The electronic excited state T_{2g} in the O_h environment, however, splits into three states (A_1, B_2, and A_2) in the C_{2v} environment.

Visible Region Absorption Spectrum. The experimental results are shown in Fig. 3. As can be seen, two bands appear at about 20000 and 27000 cm^{-1}. The first band comprises two components. As was once pointed out by Yamatera,[6] two electronic transitions ($A_2 \leftarrow A_1$ and $B_2 \leftarrow A_1$) in the lower frequency region ($T_{1g} \leftarrow A_{1g}$ for O_h) are expected to have nearly equal frequencies, whereas $B_1 \leftarrow A_1$ should have an appreciably lower frequency than do the other two. Therefore, the lower-frequency component of the lower frequency group of bands is assignable to the $B_1 \leftarrow A_1$ transition ($d_{X^2-Y^2} \leftarrow d_{XY}$ for O_h, see Fig. 2 and its legend) and the other two to $A_2 \leftarrow A_1$ ($d_{X^2-Y^2} \leftarrow d_{YZ+ZX}$ for O_h) and $B_2 \leftarrow A_1$ ($d_{X^2-Y^2} \leftarrow d_{YZ-ZX}$ for O_h). The second group of bands ($T_{2g} \leftarrow A_{1g}$ for O_h) shows no explicit splitting, and is assigned to an overlapping of the following three transitions: $A_1 \leftarrow A_1$ ($d_{Z^2} \leftarrow d_{XY}$ for O_h), $B_2 \leftarrow A_1$ ($d_{Z^2} \leftarrow d_{YZ+ZX}$ for O_h), and $A_2 \leftarrow A_1$ ($d_{Z^2} \leftarrow d_{YZ-ZX}$ for O_h). (Note that the axis system XYZ for O_h is different from the system xyz for C_{2v}, see Fig. 2).

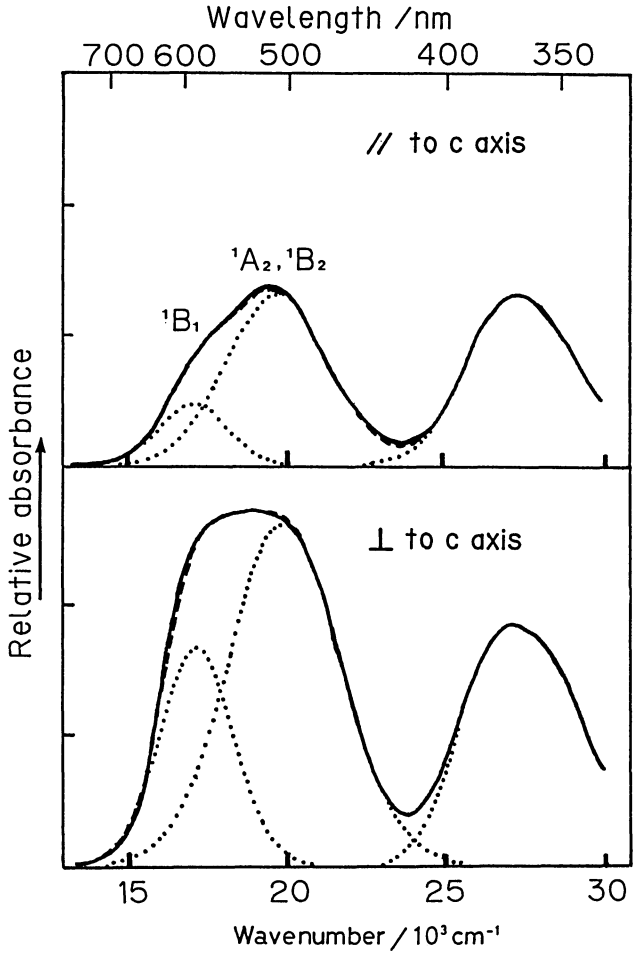

Fig. 3. Dichroic spectrum of a single crystal of *cis*-$[CoF_2(NH_3)_4]ClO_4$. Solid line, observed spectrum; dotted line, calculated Gaussian components; dashed line, sum of the Gaussian components.

We now examine the observed dichroism. Because all of the $CoF_2(NH_3)_4^+$ ions in the crystal are oriented with their C_2-axis along the crystallographic c-axis, only the A_1-type transition is expected to appear in the $E//c$ spectrum, as long as the selection rules of purely electronic transitions are taken into account. Actually, however, appreciable $E//c$ absorption intensities have been found (see Fig. 3) in the spectral regions assigned to the B_1 and A_2 & B_2 transitions. It is therefore quite certain that these intensities should be interpreted while taking vibronic coupling into consideration. The lowest-frequency (at 584 nm) electronic band, B_1, is considered to borrow some intensity from the A_1 band at 366 nm, or, more probably, from stronger A_1 bands somewhere in a higher frequency region through coupling with some of the B_1 vibrations. The higher-frequency components (at 504 nm) of the first band (A_2 and B_2) are considered to borrow some intensities from the A_1 bands through A_2 and B_2 vibrations. As can be seen in Fig. 3, the vibronic couplings are definitely greater for the latter (through A_2 and B_2 vibrations) than for the former (through B_1 vibrations). The number of B_1 normal vibrations is 13; this number is much smaller than the sum (22) of the numbers of the A_2 and B_2 normal vibrations (see the last column of Table 5). Therefore, one might assume that the number of the

vibrations active for intensity borrowing determines the transition intensity. To persue the consequence of this simple assumption, numbers were estimated for every electronic transition (Table 6). As can be seen in the last line of this table, the number of the possible cases of the vibronic couplings turns out to be nearly equal for the $//c$ component to that for the $\perp c$ component in every band now in question. It is therefore rather tempting to attribute the prominent perpendicular dichroisms actually observed for the 584 and 504 nm bands largely to their own electronic properties. It is probable, however, that the vibronic couplings do contribute not only to the $//c$ intensities, but also to the $\perp c$ intensities in these bands. It is also probable that, in every case, some of the possible vibrations and much greater contributions than do some of the other vibrations belonging to the same symmetry species; we must therefore study the nature of such vibronic couplings in more detail in the future.

Infrared Absorption Spectrum. The results of the measurements are given in Fig. 4. Six bands were observed at about 3250, 3180, 1620, 1265, 1090, and 850 cm^{-1}. On the basis of a previous study by Shimanouchi and Nakagawa[7] on $Co(NH_3)_6^{3+}$ and some other ammine complexes, these have been assigned, respectively, to NH_3 degenerate stretching, NH_3 symmetric stretching, NH_3 degenerate deformation, NH_3 symmetric deformation, ClO_4 T_2-type stretching, and NH_3 rocking vibrations (Table 7). Each band is found comprise approximately two components. Although each $CoF_2(NH_3)_4^+$ ion has four NH_3 groups, they are not equivalent to one another regarding the crystallographic symmetry. Practically, however, the two NH_3 groups of pair-I are similar to each other, and two of pair-II are similar (see Table 1 and 2). The two NH_3 groups of pair-I are equivalent if the molecular pseudo-C_{2v} symmetry is taken into account; likewise, the NH_3 groups of pair-II are equivalent. In addition, "inter-pair" vibrational interactions should be very small, based on their geometrical arrangements. For every NH_3 band, therefore, one of the two components is assigned to pair-I and the other to pair-II. These can be distinguished on the basis of the dichroic characters of the components.

An NH_3 symmetric deformation vibration, for example, has its transition moment (p) along the pseudo-C_3 axis. For each of the $NH_3(1)$ and $NH_3(2)$, the transition moment is directed at an angle of 45° to the c-axis. Therefore, the pair-I A_1 vibration causes an absorbance which is proportional to $(2p\cos 45°)^2=2p^2$. The B_1 absorbance should also be $(2p\cos 45°)^2=2p^2$, and no B_2

Table 6. Visible-Region Absorption Bands of *cis*-$[CoF_2(NH_3)_4]ClO_4$ Single Crystal

Frequency	17130 cm^{-1} (584 nm)	19840 cm^{-1} (504 nm)		27310 cm^{-1} (366 nm)		
Observed intensities[a] //|⊥	12/48	37/76		36/53		
Assignment	B_1	A_2	B_2	A_1	B_2	A_2
Intensities expected for purely electronic transitions[b] //|⊥	$0/b_1$	0/0	$0/b_2$	$a_1/0$	$0/b_2'$	0/0
Vibrations to reach A_1(//) Number	B_1 13	A_2 10	B_2 12	A_1 16	B_2 12	A_2 10
Vibrations to reach B_1(⊥) Number	A_1 16	B_2 12	A_2 10	B_1 13	A_2 10	B_2 12
Vibrations to reach B_2(⊥) Number	A_2 10	B_1 13	A_1 16	B_2 12	A_1 16	B_1 13
Average, ⊥	13	12.5	13	12.5	13	12.5
Relative numbers of possible cases of vibronic interaction //|⊥	13/13	22/25.5		38/38		

a) // refers to $E//c$, where E is the electric vector of the incident radiation, and ⊥ refers to $E\perp c$.
b) b_1=a proper intensity for the lowest electronic B_1 transition, b_2=a proper intensity for the lowest electronic B_2 transitions, b_2'=a proper intensity for the second lowest electronic B_2 transition.

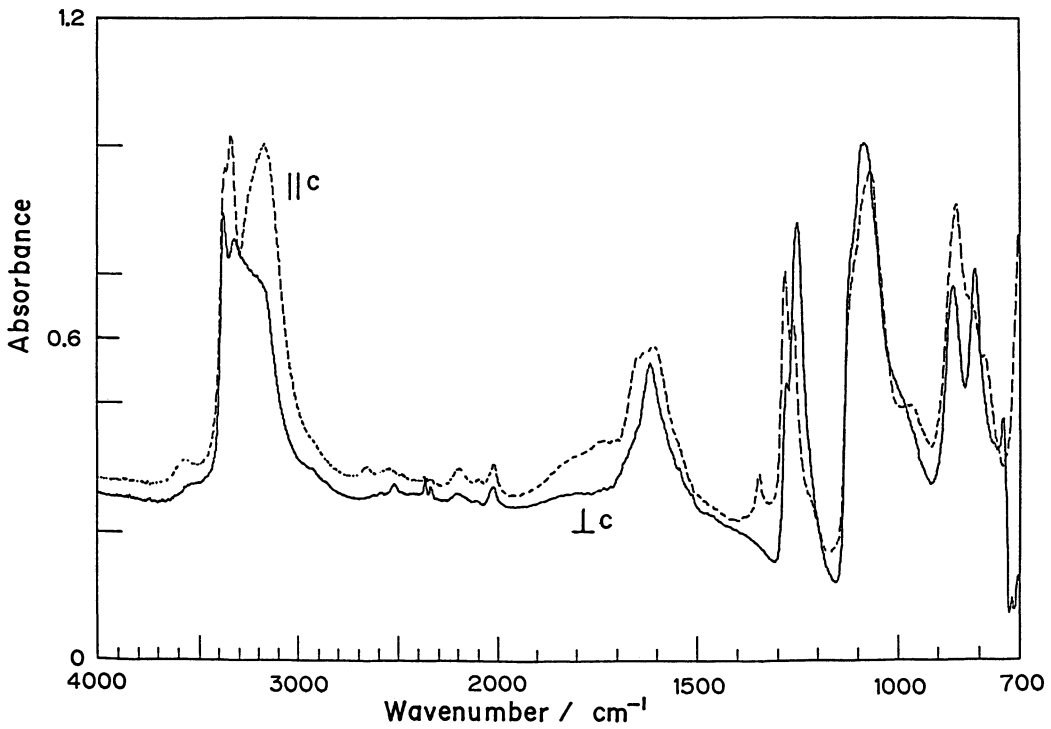

Fig. 4. Infrared dichroism spectrum of a single crystal of *cis*-$[CoF_2(NH_3)_4]ClO_4$. Solid line: the electric vector of the incident radiation is perpendicular to the *c*-axis. Dashed line: the electric vector is parallel to the *c*-axis.

Table 7. Infrared Absorption Bands and Their Dichroisms

Observed			Assignment[a]	Expected relative intensities
Frequency/cm	Dichroism			//⊥
3285	⊥	I	NH_3 deg. str.	2/3
3250	//	II		4/2
3180	//	I	NH_3 sym. str.	2/1
3170	⊥	II		0/2
1660	//	II	NH_3 deg. def.	4/2
1620	⊥	I		2/3
1280	//	I	NH_3 sym. def.	2/1
1250	⊥	II		0/2
1085	⊥		ClO_4 str. (T_2)	1/1
1070	//			
860	//	II	NH_3 rock.	4/2
810	⊥	I		2/3

a) str.=stretching, def.=deformation, rock.=rocking, sym.=symmetric, deg.=degenerate, I=NH_3-pair I (see Fig. 2), II=NH_3-pair II.

absorbance should result. From the average of the contributions of the four $CoF_2(NH_3)_4^+$ ions in the Bravais unit cell, the intensity ratio //⊥ of the pair-I NH_3 symmetric deformation band should be $2p^2/1p^2=2/1$. For each of the $NH_3(3)$ and $NH_3(4)$, on the other hand, the transition moment (p) now in question is directed perpendicularly to the *c*-axis. The pair-II A_1 vibration, therefore, causes no absorbance, whereas the pair-II B_2 vibration causes absorbance that is proportional to $(2p)^2$. Thus, the //⊥ intensities average out to $0/2p^2=0/2$. As can be seen in Fig. 4, the NH_3 symmetric deformation band comprises two components at 1280 and 1250 cm^{-1}. At 1280 cm^{-1} the dichroic ratio, //⊥, is found to be nearly 2/1. whereas at 1250 cm^{-1} it is almost 0/2. Therefore, the 1280 cm^{-1} component is assignable to pair-I and the 1250 cm^{-1} component to pair-II.

An NH_3 degenerate deformation vibration is considered to have two transition moments, which are directed perpendicularly to each other in the plane normal to the NH_3 pseudo-C_3 axis. By taking this into account, a similar analysis has revealed that the pair-I NH_3 degenerate deformation vibration causes the relative intensities $//\perp=2p^2/3p^2$ and that of pair-II $//\perp=4p^2/2p^2$.

Thus, the observed peak at 1660 cm^{-1}, which shows a strong parallel dichroism, is assignable to the pair-II NH_3 degenerate deformation vibration, and that at 1620 cm^{-1} to the pair-I NH_3 degenerate deformation vibration.

In a similar manner, assignments of the components of every band have been made, as shown in Table 7. As can be seen, the greatest frequency difference between the components was for the NH_3 rocking band. Here, the pair-II frequency is higher than that of pair-I by 50 cm^{-1}. This is explained by taking intermolecular hydrogen bonds into account. As shown in Table 3, two strong hydrogen bonds (N···F=2.85—2.86 Å) are found at F(1)···H(43)–N(4) and F(2)···H(32)–N(3). Therefore, some of the effective ∠H–N–Co and ∠H–N–H angle bending force constants should be appreciably greater for the pair-II NH_3 groups than the corresponding ones for the pair-I NH_3 groups. As can be seen in Fig. 4 and Table 7, the pair-II NH_3 degenerate deformation frequency (1660 cm^{-1}) is also higher than that of pair-I (1620 cm^{-1}). This fact may also be explained by the two strong intermolecular hydrogen bonds. A hydrogen bond generally causes a lowering of the stretching force constant of the N–H bond in question. The fact that the pair-II NH_3 degenerate stretching frequency (3250 cm^{-1}) is lower than that (3285 cm^{-1}) of pair-I may be interpreted as indicating such an effect of the hydrogen bonds. The fact, however, that the pair-I NH_3 symmetric deformation frequency (1280 cm^{-1}) is higher than that of pair-II (1250 cm^{-1}) is yet to be explained.

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References

1) Y. Mitsutsuka, E. Tursun, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **63**, 260 (1990).

2) "International Tables for X-ray Crystallography," Kynoch Press Birmingham, (1974), Vol. IV. (Present distributor Kluwer Academic Publishers, Dordrecht.)

3) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku,* **55**, 69 (1979).

4) Y. Mitsutsuka, I. Kondo, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **59**, 2767 (1986).

5) Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the nonhydrogen atoms, and the observed and calculated structure factors are deposited as Document No. 9112 at the Office of the Editor of Bull. Chem. Soc. Jpn.

6) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

7) T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, **3**, 1805 (1964).