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Fluorine Containing Coordination Compounds of Cr(III)

II. Crystal and Molecular Structure of *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ and *cis*-$[Cr(NH_3)_4F_2]ClO_4$

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Trans-$[Cr(NH_3)_4F_2]I \cdot H_2O$ (A) has monoclinic $P\,2_{1/m}$ (No. 11) space group with $a = 5.033\,(3)$, $b = 16.333\,(10)$, $c = 5.539\,(3)$ Å and $\beta = 98.47\,(3)°$, $Z = 2$. *Cis*-$[Cr(NH_3)_4F_2]ClO_4$ (B) has tetragonal space group $I\,4_{1md}$ (No. 109) with $a = 7.417\,(1)$, $c = 16.610\,(2)$ Å, $Z = 4$. Cr—F and Cr—N bonding distances are 1.894 (3); 2.087 and 2.083 (5) Å for A and 1.887 (6); 2.062 (5) and 2.051 (7) Å for B. Octahedral angles within the cations are close to 90° for both compounds. Cr—N bond *trans* to Cr—F bond in the *cis* compound is shorter. Structures were refined to R_2 values of 0.072 (A) and 0.058 (B). *Trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ has weak N—H—F hydrogen bonds between the cations. None such interactions were found in *cis*-$[Cr(NH_3)_4F_2]ClO_4$.

(Keywords: Crystal structure; Hydrogen-fluorine bond)

Fluorhältige Komplexe des Cr(III), *2. Mitt.: Kristall- und Molekülstruktur von* *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ *und* *cis*-$[Cr(NH_3)_4F_2]ClO_4$

Trans-$[Cr(NH_3)_4F_2]I \cdot H_2O$ (A) kristallisiert in der Raumgruppe $P\,2_{1/m}$ (No. 11) mit $Z = 2$ und $a = 5{,}033\,(3)$, $b = 16{,}333\,(10)$, $c = 5{,}539\,(3)$ Å und $\beta = 98{,}47\,(3)°$. *Cis*-$[Cr(NH_3)_4F_2]ClO_4$ (B) kristallisiert in der Raumgruppe $I\,4_{1md}$ (No. 109) mit $Z = 4$, $a = 7{,}417\,(1)$ und $c = 16{,}610\,(2)$ Å. Die Cr—F- und Cr—N-Abstände sind 1,894 (3); 2,087 (6), 2,083 (5) Å für A und 1,887 (6); 2,062 (5), 2,051 (7) Å für B. Die octaedrischen Bindungswinkel innerhalb der Kationen weichen nicht viel von 90° ab. Der Cr—N-Abstand in *trans*-Position der Cr—F-Bindung ist kürzer. Die Strukturen wurden bis zu Gütefaktoren R_2 0,072 (A) und 0,058 (B) verfeinert. Bei der Verbindung A wurden schwache N—H . . . F-Wasserstoff-Bindungen zwischen verschiedenen Kationen beobachtet, während bei der Verbindung B keine Wasserstoff-Bindungen vorhanden sind.

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Introduction

Structural studies of the $[\mathrm{Cr}L_4\mathrm{F}_2]X$ compounds are rare. The only two examples with the known crystal structure are $[\mathrm{Cr}(1,4,8,11\text{-tetraazaundecane})\mathrm{F}_2]\mathrm{ClO}_4$[1] and *trans*-$[\mathrm{Cr}(en)_2\mathrm{F}_2]\mathrm{ClO}_4$ (en = 1,2-diaminoethane)[2].

$[\mathrm{Cr}L_4\mathrm{F}_2]^+$ can exist in two geometric isomers—*trans* and *cis*. Rare examples where both isomers were isolated are $[\mathrm{Cr(NH_3)_4F_2}]^+$ (Ref. 3), $[\mathrm{Cr}(en)_2\mathrm{F}_2]^+$ and $[\mathrm{Cr}(pn)_2\mathrm{F}_2]^+$ (pn = 1,2-propandiamine)[4].

Although the *cis*-$[\mathrm{Cr(NH_3)_4F_2}]X$ is statistically the more probable product in the synthesis, the compound is difficult to isolate and transforms spontaneously to the *trans* form in solutions. For many compounds of the $[\mathrm{Cr}L_4\mathrm{F}_2]^+$ stoichiometry the *cis* isomer was never mentioned[5].

Infrared spectroscopy was often used as a simple qualitative method for identification of such isomeric pairs[6, 7]. The main argument in the interpretation of the infrared spectra is that lower symmetry of the *cis*-$[\mathrm{Cr(NH_3)_4F_2}]^+$ results in more sceletal vibrations compared to *trans*-$[\mathrm{Cr(NH_3)_4F_2}]^+$.

The structural analysis of the isomeric pairs gives the opportunity for the identification of the possible structural *trans* effect within the $[\mathrm{Cr(NH_3)_4F_2}]^+$ octahedron. Another objective of the work was to find out whether the differences in the ligand vibrations between *trans*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{I}\cdot\mathrm{H_2O}$ and *cis*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{ClO_4}$ have any ground in the shorter than *van der Waals* contacts between $\mathrm{NH_3}$ molecules and other electronegative atoms of the crystal lattice.

Experimental

Mixture of *trans* and *cis*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{I}$ was prepared reacting *trans*-$[\mathrm{Cr}py_4\mathrm{F}_2]\mathrm{I}$ and liquid ammonia at 100 °C[3]. The *cis* isomer is soluble in liquid ammonia. Recrystallization from water solution by the addition of the necessary anion gave single crystals of *trans*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{I}\cdot\mathrm{H_2O}$ and *cis*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{ClO_4}$.

Samples were analysed for chromium content and the results were close to the calculated values.

Infrared spectra were measured on mineral oil mulls between CsBr plates on a Perkin-Elmer model 521. Range was from 4000 to 300 $\mathrm{cm^{-1}}$.

Densities of the single crystals were determined by flotation.

The cell dimensions of both compounds were determined by the least squares method from the θ values of about 20 randomly chosen reflections. Angles were measured on the CAD-4, Enraf-Nonius, automatic diffractometer.

Data were collected on the same diffractometer coupled to a PDP-8 computer. The whole procedure was regulated with an internal set of computer programs.

Structure factors, on the relative scale, were calculated as usual[8]. 999 reflections up to $\theta = 27°$ were measured for *trans*-$[\mathrm{Cr(NH_3)_4F_2}]\mathrm{I}\cdot\mathrm{H_2O}$. MoK_α

radiation was used. 884 reflections satisfied the criteria $I > 4\sigma(I)$, where $\sigma(I)$ was based on the counting statistics. Applying the same condition, 354 reflections out of 383 measured for the *cis*-$[Cr(NH_3)_4F_2]ClO_4$ were considered observed. The sets of 884 and 354 reflections were treated further towards the solution and refinement of the structures.

Intensities were corrected for absorption effect. Scattering factors, including anomalous dispersion correction, were taken from standard literature[9, 10].

Patterson and *Fourier* functions helped to locate the atoms of *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$. *Cis*-$[Cr(NH_3)_4F_2]ClO_4$ had chromium atoms on the special position and the first step was *Fourier* synthesis. No attempt was made to locate the hydrogens in either structure.

The positional and anisotropic temperature factors were refined by full-matrix least squares refinement which converged at R_1, R_2 values of 0.065, 0.058 for *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ and 0.072, 0.058 values for *cis*-$[Cr(NH_3)_4F_2]ClO_4$. Both factors have the usual meaning[8].

Computer programs included in the Shelx 76 package were used in all calculations[11]. A table of observed and calculated structure factors can be requested from the authors.

Results and Discussion

Crystallographic data for both compounds are presented in Table 1. Positional, anisotropic temperature factors and bonding distances are in Tables 2, 3 and 4. Table 5 contains the infrared spectrum. Figures 1 and 2 illustrate the distribution of the ions and molecules in the unit cell.

Trans-$[Cr(NH_3)_4F_2]I$ can be prepared either from $[Cr\mathit{py}_4F_2]I$ and liquid NH_3[3] or by reacting $[Cr(NH_3)_4ClH_2O]Cl_2$ with NH_4F and

Table 1. *Crystal data for trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ *(A) and cis*-$[Cr(NH_3)_4F_2]ClO_4$ *(B)*

	A	B
Formula	$CrF_2H_{14}IN_4O$	$ClCrF_2H_{12}N_4O_4$
Formula weight	303.04	257.57
Space group	$P2_{1/m}$	$I4_{1md}$
a Å	5.033 (3)	7.417 (1)
b	16.333 (10)	7.417 (1)
c	5.539 (3)	16.610 (2)
α^0	90	90
β	98.47 (3)	90
γ	90	90
Volume Å^3	450.4	913.7
D_c gcm^{-3}	2.23	1.87
D_m	2.20 (4)	1.87 (2)
Z	2	4

Table 2. *Fractional atomic coordinates for trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ *(A) and cis*-$[Cr(NH_3)_4F_2]ClO_4$ *(B)*

Atom	x	y	z
A			
Cr	0.5	0	0.5
F	0.7391 (6)	0.0186 (2)	0.2716 (6)
N 1	0.2670 (10)	0.1005 (4)	0.3675 (9)
N 2	0.7384 (9)	0.0705 (3)	0.7606 (9)
I	0.2690 (2)	0.25	0.8640 (1)
O	0.7247 (62)	0.25	0.3857 (89)
B			
Cr	0	0	0.2000
F	0	0.1846 (10)	0.2781 (5)
N 1	0	0.2221 (7)	0.4521 (5)
N 2	0	0.1939 (12)	0.1120 (5)
Cl	0	0	0.6705 (2)
O 1	0	0.1495 (19)	0.7227 (12)
O 2	0	0.3380 (20)	0.8777 (14)

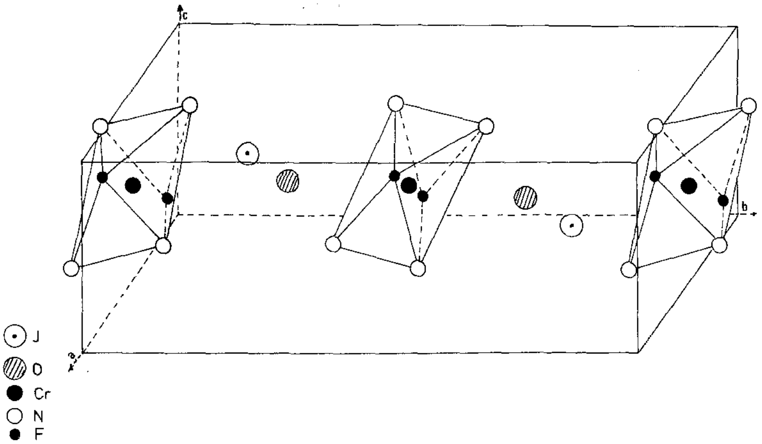

Fig. 1. Distribution of the $[Cr(NH_3)_4F_2]^+$, I^-, and O of the water molecule in the unit cell

$NaClO_4$[12]. The only way to obtain *cis*-$[Cr(NH_3)_4F_2]I$ was reaction between $[Crpy_4F_2]I$ and liquid NH_3 at 100 °C[3]. *Cis*-$[Cr(NH_3)_4F_2]ClO_4$ was prepared because salts of other anions did not give suitable single crystals.

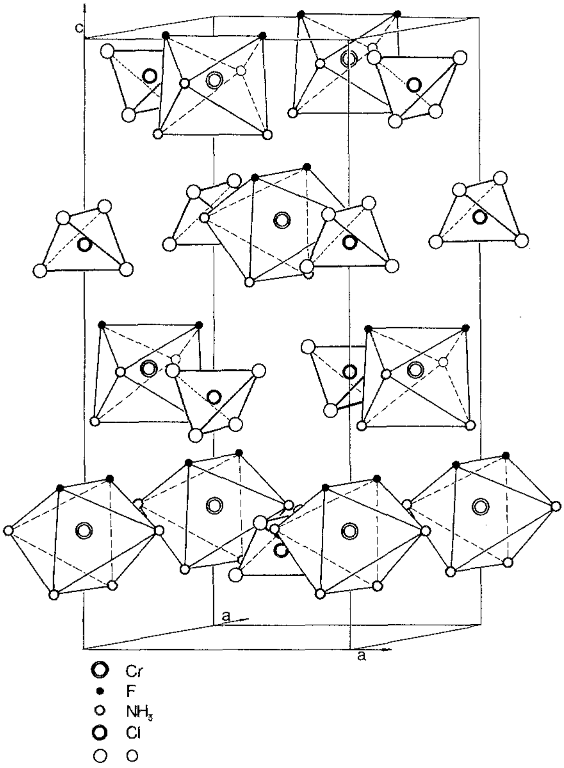

Fig. 2. Packing of the cations and anions in the unit cell of *cis*-$[Cr(NH_3)_4F_2]ClO_4$

Trans-$[Cr(NH_3)_4F_2]I \cdot H_2O$

The crystal structure of *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ contains cations $[Cr(NH_3)_4F_2]^+$, iodide ions and water molecules. Cations are located on the symmetry center with chromium on the special position 2d in the $P\,2_{1/m}$ (No. 11) space group. Water molecules and iodide ions are placed on the mirror planes at $y = 1/4$ or $3/4$. Two medium range contacts $O\,(x, y, z) — I\,(1 + x, y, z)$, 3.52 and $O\,(x, y, z) — I\,(x, y, —1 + z)$, 3.41 Å connect the iodide ions and water molecules into the . . . O—I—O—I . . . chain. Sum of the *van der Waals* radii of oxygen and iodine range from 3.45-3.62 Å[13].

Two independent Cr—N distances averaging 2.085 (6) Å are close to the ones found in $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 2\,H_2O$ with the values from 2.088 to 2.091 Å[14].

Table 3. *Anisotropic temperature parameters* (× *100*) *for trans*-$[Cr(NH_4)_4F_2]I \cdot H_2O$ (*A*) *and cis*-$[Cr(NH_3)_4F_2]ClO_4$ (*B*)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A						
Cr	2.65 (7)	2.10 (7)	1.26 (7)	0.16 (4)	0.58 (4)	—0.18 (4)
F	3.24 (15)	3.79 (19)	2.22 (15)	0.38 (13)	1.01 (12)	—0.24 (15)
N 1	4.41 (26)	2.99 (32)	3.12 (28)	—0.64 (18)	1.31 (21)	—0.50 (19)
N 2	3.90 (23)	3.28 (27)	2.15 (23)	—0.45 (19)	0.59 (18)	—0.37 (21)
I	9.93 (8)	2.30 (6)	4.19 (6)	0	2.18 (5)	0
O	10.66 (210)	20.84 (493)	28.93 (758)	0	3.76 (250)	0
B						
Cr	2.24 (5)	3.93 (7)	12.7 (6)	0	0	0
F	4.78 (23)	8.59 (34)	4.55 (28)	0	0	—3.79 (31)
N 1	2.47 (20)	6.19 (33)	4.20 (34)	0	—0.79 (28)	0
N 2	6.52 (38)	5.21 (35)	3.50 (37)	0	0	—2.12 (33)
Cl	5.95 (15)	3.34 (10)	2.74 (13)	0	0	0
O 1	17.30 (88)	9.84 (68)	21.61 (89)	0	0	—8.22 (69)
O 2	14.67 (85)	24.85 (96)	20.87 (96)	0	—7.80 (87)	0

[a] Temperature factors are of the form $[-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + \ldots]$.

Table 4. *Dimensions of trans*-$[Cr(NH_3)_4F_2]^+$ *(A)*, *cis*-$[Cr(NH_3)_4F_2]^+$ *(B), and* ClO_4^- *(B)*

Bond lengths, Å		Bond angles, deg	
A			
Cr—F	1.894 (3)	F—Cr—N 1	91.1 (2)
Cr—N 1	2.087 (6)	F—Cr—N 2	89.1 (2)
Cr—N 2	2.083 (5)	N 1—Cr—N 2	87.4 (2)
B			
Cr—F	1.887 (6)	F—Cr—N 2	88.9 (3)
Cr—N 1	2.062 (5)[a]	F—Cr—F	93.1 (3)
Cr—N 2	2.051 (7)	N 2—Cr—N 2	89.1 (2)
		F—Cr—N 2	178.0 (3)
		N 1—Cr—N 1	178.1 (2)
		N 1—Cr—F	89.3 (3)
		N 1—Cr—N 2	90.7 (2)
Cl—O 1	1.407 (10)	O 1—Cl—O 1	104.0 (1.8)
Cl—O 2	1.396 (10)[b]	O 2—Cl—O 1	108.3 (5)
		O 2—Cl—O 2	118.8 (2.1)

[a] N 1 (1/2 — y, 0, 3/4 + z).
[b] O 2 (1/2 — y, 0, 3/4 + z).

Cr—F distances found in [Cr(1,4,8,11-tetraazaundecane)F_2]ClO_4, 1.85 and 1.90 Å[5]; $NaMnCrF_6$, 1.91 Å[15]: $CsCrF_4$, 1.85 Å[16] and *trans*-[Cr(*en*)$_2F_2$]ClO_4, 1.887 (6) Å[2] are somewhat scattered but still close to 1.894 (3) Å found in *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$.

Shortest cation—cation contacts are between N 1 (x, y, z) — F $(1 + x, y, z)$, 2.95; N 2 (x, y, z) — F $(x, y, 1 + z)$, 2.95 and N 2 (x, y, z) — F $(1 - x, -y - z)$, 3.03 Å. Sum of the F + N *van der Waals* radii is from 3.05-3.15 Å[13] and we can assume that weak hydrogen bonds exist between cations.

Shortest cation—iodide and cation—water molecule contacts are: N 1 (x, y, z) — I (x, y, z), 3.68 and N 1 (x, y, z) — O (x, y, z), 3,35 Å. Both are outside the range of hydrogen bonding.

Cis-$[Cr(NH_3)_4F_2]ClO_4$

Cations and anions are distributed in layers. The first starts at z value 0.20 for chromium atom of the cation and $z = 0.17$ for the center of the anion. The distance between the layers is 1/4 of the z dimension.

Table 5. *Infrared spectra of trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ *(A) and cis*-$[Cr(NH_3)_4F_2]ClO_4$ *(B)*

λ [cm⁻¹]		Int.	λ [cm⁻¹]		Int.
A			B		
3555 3475	ν H_2O	w			
3270 3190 3135	ν NH_3	s	3380 3340 3275 3185	ν NH_3	m
1640 1625 1610 1600	δ d NH_3 δ H_2O	m	1625	δ d NH_3	m
1280	δ s NH_3	vs	1275 1260 1225	δ s NH_3	vs
			1075	ClO_4^-	s
755	ρ r NH_3	s	765 730	ρ r NH_3	s vs
			615	ClO_4^-	s
505	ν Cr—F	s	515 490	ν Cr—F	m m
445	ν Cr—N	m	460 405	ν Cr—N	w vw

s = strong, m = medium, w = weak, v = very.

Each cation or anion is tetrahedrally surrounded by four cations or anions. Both cation and anion lie on a twofold axis.

The Cr—F distance 1.887 (6) Å is not significantly different from the value found in *trans*-$[Cr(NH_3)_4F_2]^+$. Cr—N bonding distances are different. The one in the *trans* position to the fluorine is shorter 2.051 (7) vs. 2.062 (5) Å when nitrogens are *trans* to each other.

This difference is too small to be taken as the definite proof of the structural *trans* effect. We shall have to wait unitl more *cis*—*trans* pairs of this sort are structurally characterized.

The average value of the Cr—N bond lengths is significantly shorter for the *cis* compound; 2.055 (6) vs. 2.085 (6) Å.

All interionic contacts are long. Strongest cation—cation interaction is between F (x, y, z) — N 2 $(y, 1/2, 1/4 + z)$, 3.08 Å. Shortest cation—anion contact is between N 1 $(0, y, z)$ — O 1 $(1/2+y, 0, -1/4+z)$ 3.10 Å. Anion—anion distance between O 1 $(0, y, z)$ — O 2 $(0, y, z)$, 2.93 Å is the shortest. All nonbonded distances are outside the range of the hydrogen bonding.

Infrared Spectra

Infrared spectra of *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ and *cis*-$[Cr(NH_3)_4F_2]ClO_4$ reflect not only structural differences of the cations and different chemical composition, but also the presence of interionic interactions in the *trans*-compound.

Two absorptions at 3555 and 3475 cm^{-1} in the *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ have their origin in the symmetric and antisymmetric valence vibrations of the lattice water molecule. The positions and sharpness of the bands indicate that there are no hydrogen bonds of strongly directional character.

As expected, hydrogen bonding between NH_3 and electronegative counterpart shifts the N—H stretching bands to lower and the bending bands to higher frequencies[17]. Inspection of Table 5 clearly confirms that ν NH_3 in *trans*-$[Cr(NH_3)_4F_2]I \cdot H_2O$ absorb at lower and δ d, δ s, ρ r vibrations at higher frequencies compared to *cis*-$[Cr(NH_3)_4F_2]ClO_4$. As we stressed before, short enough N ... F non bonded distances definitely support the data obtained from the infrared spectra.

Infrared spectra of both isomers contain H_2O, NH_3, ClO_4^- and skeletal vibrations of the $[Cr(NH_3)_4F_2]^+$ cation. Bands at 445 cm^{-1} for *trans* and 460, 405 cm^{-1} in the *cis* isomer have their origin in the Cr—N stretching vibration. In $[Cr(NH_3)_6]Cl_3$ this band was found to be at 469 cm^{-1} (Ref. [18]).

The remaining absorptions at 505 and 515, 490 cm^{-1} are Cr—F stretching vibrations likely to be coupled with the vibrations including ammonia molecules. Splitting of the bands in the *cis* $[Cr(NH_3)_4F_2]^+$ is expected on the ground of lower molecular symmetry.

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