approximate upper limit for the first hydrolysis constant, $^*K_1$, for the Co^{3+} ion: $^*K_1 \leq 0.01$ M. If ΔH for the hydrolysis reaction ($Co^{3+} + H_2O \rightleftarrows CoOH^{2+} + H^+$) is about 10 kcal mol^{-1}, as estimated by Sutcliffe and Weber,[10] then, at 25°, $^*K_1 \leq 0.05$ M.

In conclusion, the results presented in this note suggest that some kinetic mechanisms that have been proposed,[2] involving a large proportion of dimeric cobalt(III), may require reconsideration.

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Fluoro-Containing Complexes of Chromium(III). IV. The Reactions of *trans*-Fluoroaquobis(ethylenediamine)chromium(III) Perchlorate Monohydrate with Ammonium Chloride and Ammonium Bromide[1]

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Fluoro-containing complexes of chromium(III) of the type [Cr(AA)$_2$FX]Y (AA is a diamine) which involve a *trans* arrangement of the FX ligands are relatively rare and have not been investigated in detail. The confirmed *trans* complexes of this type with AA = ethylenediamine appear to be restricted to the F(H$_2$O),[3] F(ONO),[1] and F$_2$[1] complexes. When the bidentate ligand is changed from ethylenediamine to 1,3-propanediamine the *trans* FCl, FBr, F(NCS), and F(H$_2$O) complexes can be prepared.[4] *cis* complexes of the type [Cr(en)$_2$FX]Y are slightly more numerous than the corresponding *trans* materials. The series of *cis* complexes which have been isolated as solids include the FF,[5] FCl,[1] and F(NCS)[1] compounds.

The investigation described in this paper was undertaken to develop a suitable method for the preparation of a *trans* complex of the type [Cr(en)$_2$FX]Y which involved a halogen other than fluorine as the X ligand and to establish its structure.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive and care should be exercised when working with these materials.

***trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$.**—This complex was prepared by the method of Dahme.[3] *Anal.* Calcd for [Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$: C, 11.8; H, 4.4; N, 13.7; F, 4.7. Found: C, 11.9; H, 4.5; N, 13.7; F, 4.7.

***trans*-[Cr(en)$_2$FCl]ClO$_4$.**—A 3-g sample of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O was suspended in 200 ml of methanol and mechanically shaken for about 1 hr. At the end of this time, the undissolved material was removed by filtration and the orange-red solution treated with 1.5 g of solid ammonium chloride. The flask and contents were mechanically shaken for another 18 hr at room temperature. At the end of this time the pink crystals were collected, washed with methyl alcohol, and dried at 75°. *Anal.* Calcd for *trans*-[Cr(en)$_2$FCl]ClO$_4$: Cr, 15.9; H, 4.9; N, 17.1; C, 14.73; F, 5.8; Cl, 21.60. Found: Cr, 15.5; H, 5.0; N, 17.1; C, 15.0; F, 5.7; Cl, 21.45.

In aqueous solution at room temperature the complex exhibited absorption maxima at 553, 460, and 381 nm with molar absorptivities of 19.9, 21.5, and 27.4 M^{-1} cm^{-1}, respectively.

The solid-state absorption spectrum of the complex was determined in the 700–300-nm region by the potassium bromide pellet method. This spectrum exhibited two well-defined peaks and a shoulder in this region. The infrared spectrum in the 400–600-cm^{-1} region exhibited bands at 445, 492, 517, and 560 cm^{-1}. A 10^{-3} M aqueous solution of the complex exhibited a molar conductance of 142 ohms^{-1} at 25°.

Reaction of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$ with Ammonium Bromide.—A 3-g sample of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O was suspended in 200 ml of methanol and mechanically shaken for 1 hr. At the end of this time, the undissolved material was removed by filtration and the orange-red solution treated with 1.5 g of solid ammonium bromide. The flask and contents were mechanically shaken for 18 hr at room temperature. At the end of this time, no product had precipitated from solution. The reaction mixture was allowed to stand for 10 days at room temperature before the pink precipitate was collected by filtration, washed with methanol, and dried at 75° for 12 hr.

The infrared spectrum in the 400–600-cm^{-1} region was characterized by absorptions at 445, 495, 520, and 570 cm^{-1}, while the electronic spectrum in aqueous solution at room temperature exhibited absorptions at 525, 466, 400, and 350 nm. The molar absorptivities were 20.0, 23.2, 16.7, and 17.7 M^{-1} cm^{-1}, respectively. *Anal.* Calcd for *trans*-[Cr(en)$_2$F$_2$]Br: C, 16.6; H, 5.5; N, 19.3; F, 13.1; Br, 27.6. Found: C, 16.7; H, 5.5; N, 19.1; F, 13.1; Br, 27.5.

Synthesis of *trans*-[Cr(en)$_2$F(H$_2$O)]Br$_2$·DMF·H$_2$O.—Since it was not possible to prepare the bromofluoro complex in methyl alcohol, the solvent was changed to dimethylformamide and the reaction repeated. A 1.0-g (0.0025 mol) sample of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O was dissolved in 4–5 ml of Spectro grade dimethylformamide and 0.49 g (0.005 mol) of solid ammonium bromide was added. The solution was mechanically stirred for 10 min before a small amount of precipitate was removed by filtration and discarded. The filtrate was allowed to stand at room temperature for 5 hr before the dark red crystals were collected by filtration, washed with cold ethanol, followed by acetone, and air dried. This method produced *trans*-[Cr(en)$_2$F(H$_2$O)]Br$_2$·DMF·H$_2$O in 30% yield. *Anal.* Calcd for *trans*-[Cr(en)$_2$F(H$_2$O)]Br$_2$·DMF·H$_2$O: C, 18.3; H, 5.9; N, 15.3; F, 4.2; Br, 34.8. Found: C, 18.0; H, 6.0; N, 15.2; F, 4.2; Br, 34.9.

The electronic spectrum of the product obtained by this reaction in the 350–700-nm range was identical with that of the *trans*-Cr(en)$_2$F(H$_2$O)$^{2+}$ ion.

The electronic spectrum of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O was determined both in water and in dimethylformamide. The spectrum was markedly solvent dependent. In aqueous solution the complex exhibited absorption bands at 371 (31.2), 454 (25.6), and 519 nm (24.2 M^{-1} cm^{-1}) while in dimethylformamide the initial time spectrum was characterized by bands at 394 (34.0), 463 (28.7), and 524 nm (31.7 M^{-1} cm^{-1}). The spectrum of the dimethylformamide solution changed with time, and after 48 hr peaks were found at 506 (76.5) and 390 nm (31.2 M^{-1} cm^{-1})

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[1] For the previous publication in this series see J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

[2] National Science Foundation Undergraduate Research Participant, 1968–1969.

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[4] J. W. Vaughn, *Inorg. Nucl. Chem. Letters*, **4**, 183 (1968).

[5] K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, **82**, 6294 (1960).

and an ill-defined shoulder was found at 362 nm (~30 M^{-1} cm^{-1}). This aspect of the research is still under investigation.

The infrared spectrum of the product exhibited absorptions at 445, 482, 495, 530, and 570 cm^{-1} as well as a strong carbonyl band at 1665 cm^{-1}. The infrared spectra were determined with a Beckman IR-12 spectrophotometer. Cesium iodide plates and Nujol mulls were used in the 400–600-cm^{-1} region.

Discussion

The complex *trans*-[Cr(en)$_2$FCl]ClO$_4$ is apparently the first known example of a fluoro-containing complex of chromium(III) involving ethylenediamine as the bidentate ligand which contains fluorine and another different halogen in the *trans* positions. The assignment of the *trans* configuration is well supported by the following evidence.

(1) The corresponding *cis* isomer is known[1] and the electronic spectra of the two complexes are markedly different. The electronic spectrum of the *cis* complex exhibits absorption bands at 387 and 518 nm with molar absorptivities of 42.8 and 62.4 M^{-1} cm^{-1}, respectively, while the new product has absorption maxima at 381, 460, and 553 nm with molar absorptivities of 19.9, 21.5, and 27.4 M^{-1} cm^{-1}. The greater number of absorption bands in the new complex as well as the general lowering of the molar absorptivities is consistent with a *trans* structure for the product.

(2) The solid-state spectrum of this complex which consists of two well-defined bands and a shoulder is consistent with a *trans* structure; hence aquation is not responsible for the dominant features of the solution spectrum.

(3) The infrared spectrum in the 400–600-cm^{-1} region is also consistent with a *trans* structure.

Other workers[6,7] have utilized far-infrared spectral studies to distinguish the *cis* and *trans* forms of diacidobis(ethylenediamine) complexes of chromium(III). The results of these studies indicated that all *cis* complexes show a general pattern of more bands and more split bands in the 400–600 cm^{-1} region than the *trans* complexes.

In general the *trans* complexes exhibit three strong bands and one much weaker band in this region with the weaker absorption around 530–540 cm^{-1}. The data for the fluoro complexes studied in this investigation are given in Table I. Thus the data in Table I indicate that complexes **1–7** all involve a *trans* arrangement of the monodentate ligands and complexes **8–11** are *cis*. The bands at 548 cm^{-1} for complex **2** and 537 cm^{-1} for complex **5** are very weak. The band at 475 cm^{-1} has been tentatively assigned to a Cr–O frequency[7] and our data for complex **3** support this assignment. The bands in the 515–525-cm^{-1} range may be due to a Cr–F frequency since these bands were only found with complexes which contained the fluoro ligand.

The molar conductance of 142 ohms^{-1} is slightly higher than that usually found for 1–1 electrolyte but it is well below the value quoted for a 2–1 electrolyte.

The reaction of ammonium bromide with *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O in anhydrous methanol does not produce the corresponding bromofluoro complex as an insoluble product, but rather after prolonged standing the *trans*-difluoro complex is formed. The product of this reaction was determined to be *trans*-[Cr(en)$_2$F$_2$]Br and not *trans*-[Cr(en)$_2$FBr]F from an examination of the electronic spectral data and the molar absorptivities. The visible absorption spectrum of the product was identical within experimental error with that of an authentic sample of *trans*-[Cr(en)$_2$F$_2$]I prepared by another method. The final product in this reaction began to precipitate about 72 hr after the reactants were mixed whereas the similar reaction with ammonium chloride produced an insoluble product in about 18 hr. A slower reaction with ammonium bromide is in accord with the observation that the product formed requires that a fluoro ligand be released from one *trans*-Cr(en)$_2$F(H$_2$O)$^{2+}$ ion and picked up by another. The release of the fluoro ligand from a cation of charge +2 would be expected on the basis of electrostatics alone to be slow. The uptake of fluoride ion in the reaction is somewhat similar to what occurs during the late stages of the acid hydrolysis of *cis*-[Cr(en)$_2$F$_2$]I.[8]

TABLE I

INFRARED SPECTRA (600–400 CM^{-1}) OF SOME DIACIDOBIS(ETHYLENEDIAMINE) COMPLEXES OF CHROMIUM(III)

	Complex	Ir freq, cm^{-1}						
1	[Cr(en)$_2$F$_2$]I		443		492	523		565
2	[Cr(en)$_2$F(ONO)]ClO$_4$		448		490	515	548	560
3	[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$		445	475	500	526		565
4	[Cr(en)$_2$FCl](ClO$_4$)		445		492	517		560
5	[Cr(en)$_2$Cl$_2$](ClO$_4$)		450		493		537	559
6	[Cr(en)$_2$(ONO)$_2$](ClO$_4$)[6]		450		498		537	558
7	[Cr(en)$_2$F(H$_2$O)]Br$_2$·H$_2$O·DMF		455	482	495	530		570
8	[Cr(en)$_2$F$_2$]I		427	485	500	517, 525	537	562
9	[Cr(en)$_2$FCl]Cl	410	435	485		520		555
10	[Cr(en)$_2$Cl$_2$]I	409	426	480			542	555
11	[Cr(en)$_2$(ONO)$_2$](ClO$_4$)[6]	412	431	485			533	550

The reaction of *trans*-[Cr(en)$_2$F(H$_2$O)](ClO$_4$)$_2$·H$_2$O with ammonium bromide in dimethylformamide resulted in a smooth replacement of the perchlorate ion by bromide. The product formed was identified as perchlorate ion free by the absence of strong infrared bands near 1200 and 631 cm^{-1}. In no case was there any evidence for the replacement of the coordinated water molecule by the dimethylformamide. The carbonyl frequency in the free amide occurs at 1670 cm^{-1},[9] and is usually shifted by some 30–40 cm^{-1} on coordination. Since the carbonyl frequency did not shift significantly in the complex, the amide is not present as a coordinated group. Thus the dimethylformamide is present in the complex as a solvate along with the initial mole of water of hydration. That the complex isolated from the reaction has the *trans* structure is supported by the electronic and infrared spectral data (Table I).

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