(11) Bürger, H.; Cichon, J.; Goetze, U.; Wannagat, U.; Wismar, H. J. *J. Organomet. Chem.* **1971**, *33*, 1.
(12) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.
(13) Hursthouse, M. B.; Rodesiler, P. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2100.
(14) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669.
(15) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1166.
(16) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
(17) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
(18) Rossmanith, K.; Muckenhuber, E. *Monatsh. Chem.* **1961**, *92*, 600.
(19) Bernstein, E. R.; Chew, K. M. *Chem. Phys.* **1975**, *10*, 215.
(20) Marks, T. J.; Kennelly, W. J.; Kolb, J. R.; Shimp, L. A. *Inorg. Chem.* **1972**, *11*, 2540.
(21) Segal, B. G.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 844.
(22) Evans, D. F. *J. Chem. Soc.* **1958**, 2003.
(23) Räde, H. St. *J. Phys. Chem.* **1973**, *77*, 424.

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Fluoro-Containing Complexes of Chromium(III). 9. Resolution and Some Anation Reactions of the *cis*-Fluoroaquobis(ethylenediamine)chromium(III) Cation[1]

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The racemic cation *cis*-fluoroaquobis(ethylenediamine)chromium(III) was resolved into its chiral forms by the use of the $(+)_{5890}$-bromocamphor-π-sulfonate anion. The absolute configurations of the chiral forms were established by use of optical rotatory dispersion spectral studies. For the least soluble product, anation of the optical isomers with thiocyanate or fluoride ion in the solvent methyl alcohol takes place with retention of absolute configuration.

Introduction

The *cis*-fluoroaquobis(ethylenediamine)chromium(III) cation was first isolated as a solid salt in 1976.[2] The arrangement of the fluoro and aquo ligands in this complex was deduced from the method of synthesis and from electronic spectral studies. The purpose of this investigation was to provide unequivocal evidence for the cis geometry by resolving the complex into its optical forms. In addition, some anation reactions of the optical isomers were to be studied to determine if such reactions took place with retention of absolute configuration, isomerization, or racemization.

Experimental Section

***cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$.** This complex was prepared as described.[2] The entire sample, 8.5 g (17.5 mmol), was dissolved in 7 mL of water at room temperature. The resulting solution was filtered to remove a small amount of insoluble material, and the filtrate was cooled in an ice bath for 1 h. The cooled filtrate was stirred frequently during this time. At the end of 1 h the orange solid was collected, washed with acetone, and air-dried; yield 2.7 g, 32%. Anal. Calcd for *cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$: C, 9.99; H, 4.20; N, 11.65; Cr, 10.8. Found: C, 9.94; H, 4.22; N, 11.45; Cr, 11.2. The electronic absorption spectrum was in good agreement with the literature values.[2]

A rapidly stirred solution of 1.11 g (2.3 mmol) of recrystallized *cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$ in 10 mL of water was diluted in a dropwise fashion with a filtered solution of 1.62 g (4.75 mmol) of sodium tetraphenylborate in 5 mL of water. A pink precipitate formed at once when the tetraphenylborate solution was added. Another 20 mL of water was added to the reaction mixture, and the stirring was continued for an additional 10 min. The product was collected, washed with 10 mL of ice water, and air-dried for 2 h; yield 1.59 g, 79%. Anal. Calcd for *cis*-$[Cr(en)_2F(OH_2)][(C_6H_5)_4B]_2{\cdot}1.5H_2O$: C, 71.2; H, 6.95; N, 6.40; Cr, 5.95; F, 2.16. Found: C, 72.0; H, 7.20; N, 6.48; Cr, 5.85; F, 2.21. This synthesis has produced some erratic results in that the amount of hydrated water varies greatly depending on the drying conditions.

Resolution of *cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$. A 4.85 g (10 mmol) sample of recrystallized $(\pm)$-*cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$ in 5–6 mL of water was added with constant stirring to a filtered solution of 6.57 g (20 mmol) of ammonium *d*-α-bromocamphor-π-sulfonate in 30 mL of water. The reaction mixture was allowed to stand overnight at room temperature; the pink precipitate was collected, washed with acetone, and air-dried; yield 3.0 g, 71%. The entire sample of crude material was recrystallized from 35 mL of water at 60 °C; yield 1.08 g, 36%. Anal. Calcd for $[Cr(en)_2F(OH_2)][(+)\text{-}C_{10}H_{14}O_4BrS]_2{\cdot}H_2O$: C, 34.00; H, 5.67; N, 6.61; Cr, 6.13; F, 2.24. Found: C, 33.87; H, 5.60; N, 6.47; Cr, 6.20; F, 2.29. The optical rotatory dispersion spectrum of the complex was determined by using the following conditions: 0.2% aqueous solution of the complex, 0.100-dm cell, room temperature. The optical rotatory dispersion spectrum was characterized by α_x (α = specific rotation, x = wavelength in nm): α_{589} 57°; α_{553} 0°; α_{546} −38.0°; α_{520} −93°; α_{495} 0°. The entire sample was recrystallized from 9 mL of water at 60 °C. The optical rotations and elemental analysis did not change upon recrystallization. The electronic absorption spectrum of an aqueous solution of the complex was characterized by λ_{max} 503 nm (ϵ 72.5 M^{-1} cm^{-1}), λ_{min} 428 (ϵ 16.8), and λ_{max} 373 (ϵ 33.2).

A sample of recrystallized $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)\text{-}C_{10}H_{14}O_4BrS]_2{\cdot}H_2O$ lost no weight when dried over anhydrous magnesium perchlorate at room temperature and 0.05 torr for 18 h. In addition, the electronic spectra, molar absorptivities, and optical rotatory dispersion spectra of the undried and dried samples were identical within experimental error. However, the complex did lose 2 mol of water/formula weight of the complex when the material was dried at 120 °C for 18 h. Anal. Calcd for $[Cr(en)_2F(C_{10}H_{14}O_4BrS)](C_{10}H_{14}O_4BrS)$: C, 35.4; H, 5.45; N, 6.90; H_2O, 4.25. Found: C, 35.50; H, 5.50; N, 6.74; H_2O, 4.30. The optical rotatory dispersion spectrum of an aqueous solution of the heated material was nearly identical with that of an aqueous solution of pure ammonium *d*-α-bromocamphor-π-sulfonate of comparable concentration. The electronic spectrum of an aqueous solution of the dehydrated complex was characterized by λ_{max} 505 nm (ϵ 74.5), λ_{min} 430 (ϵ 20.7), and λ_{max} 373 (ϵ 38.6).

A 0.71-g (0.83-mmol) sample of recrystallized $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)\text{-}C_{10}H_{14}O_4BrS]_2{\cdot}H_2O$ was dissolved in 25 mL of water at room temperature. The solution was filtered, and the filtrate was treated with a filtered solution of 1.32 g (3.85 mmol) of sodium tetraphenylborate as described previously; yield 0.40 g, 55%. Anal. Calcd for $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(C_6H_5)_4B]_2{\cdot}1.5H_2O$: C, 71.2; H, 6.95; N, 6.40; Cr, 5.95; F, 2.16. Found: C, 72.0; H, 7.29; N, 6.22; Cr, 6.07; F, 1.75. The optical rotatory dispersion spectrum of a 0.3% solution of the complex in acetone was determined as described previously: α_{589} 0°; α_{546} −186°; α_{520} −162°; α_{500} 0°; α_{535} −200°; α_{460} 172°.

The resolution was repeated by using 1.0 g (2.06 mmol) of $(\pm)$-*cis*-$[Cr(en)_2F(OH_2)]I_2{\cdot}H_2O$ and 1.41 g (4.3 mmol) of the ammonium salt of *l*-α-bromocamphor-π-sulfonic acid as the resolving agent. The method was a scaled-down version of that described previously; yield 0.372 g, 43%. Anal. Calcd for $(+)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(-)\text{-}C_{10}H_{14}O_4BrS]_2{\cdot}H_2O$: C, 34.00; H, 5.67; N, 6.61; F, 2.24. Found: C, 34.10; H, 5.80; N, 7.08; F, 2.22. The entire sample was recrystallized from 3.5 mL of water at 60 °C; yield 0.103 g, 28%. The optical rotatory dispersion spectrum of 0.3% aqueous solution of the compound was characterized by α_{589} −49°, α_{556} 0°, α_{546} 39.0°, α_{520} 97°, and α_{494} 0°.

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Table I. Optical Rotatory Dispersion Data for Some Chromium(III) Amine Complexes

complex	λ,[a] M[b]	λ, M	λ, M	λ, M	λ, M	λ, M
$(-)_{546}$-$[Cr(en)_2F(OH_2)][Ph_4B]_2 \cdot 1.5H_2O$[c]	589, 0	546, −1625	535, −1748	520, −1415	500, 0	460, 1503
$(+)_{546}$-$[Cr(en)_2F(NCS)]ClO_4$	589, −47	546, 845	520, 1435	485, 0	449, −1130	
$(-)_{546}$-$[Cr(en)_2F(NCS)]SCN$[d]	589, 80	546, −859	520, −1396	486, 0	448, 1228	
$(-)_{546}$-$[Cr(en)_2F(NCS)]SCN$[e]	589, 80	546, −905	520, −1412	487, 0	450, 1135	
$(-)_{546}$-$[Cr(en)_2F_2]I$[f]	589, −64	546, −1449	530, −1641	495, 0	455, 1364	
$(+)_{546}$-$[Cr(en)_2F_2]I$[g]	589, 93	546, 1482				
Λ-$(+)_{589}$-$[Cr(en)_2Cl_2]^+$[h]	589, 600	550, 2100	505, 0	470, −800	440, −500	395, −1600

[a] Wavelength in nm. [b] Molar rotation, $M =$ (mol wt) (specific rotation/100). [c] Solvent was acetone. [d] Prepared from $(-)_{5461}$-$[Cr(en)_2F(OH_2)][C_{10}H_{14}O_4BrS]_2 \cdot H_2O$. [e] Prepared from $(-)_{5461}$-$[Cr(en)_2F(OH_2)][Ph_4B]_2 \cdot 1.5H_2O$. [f] Prepared from $(-)_{5461}$-$[Cr(en)_2F(OH_2)][C_{10}H_{14}O_4BrS]_2 \cdot H_2O$. [g] J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, 4, 1077 (1965). [h] I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem.*, 37, 1359 (1975).

Anation of $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)$-$C_{10}H_{14}O_4BrS]_2 \cdot H_2O$. A solution of 0.68 g (8.9 mmol) of ammonium thiocyanate in 7 mL of dry methyl alcohol was treated with 0.30 g (0.35 mmol) of solid $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)$-$C_{10}H_{14}O_4BrS]_2 \cdot H_2O$. The reaction mixture was stirred for 5–10 min at room temperature and filtered. The filtrate was allowed to stand in the dark for 3 h after which the orange precipitate was collected, washed with acetone, and air-dried; yield 0.052 g, 48%. A sample of the compound was dried at 125 °C prior to analysis. Anal. Calcd for $[Cr(en)_2F(NCS)]SCN$: C, 23.4; H, 5.35; N, 27.4. Found: C, 23.45; H, 5.30; N, 26.10. The electronic spectrum of an aqueous solution of the complex was characterized by λ_{max} 499 nm (ϵ 101.0) and λ_{max} 374 (ϵ 49.1) (lit.[2] λ_{max} 500 nm (ϵ 104), λ_{max} 373 (ϵ 50.0)). The optical rotatory dispersion spectrum of a 0.15% aqueous solution of the complex was characterized by α_{589} 26°, α_{580} 0°, α_{546} −276°, α_{520} −455°, α_{486} 0°, and α_{448} 400°.

A solution of 0.031 g (0.84 mmol) of anhydrous ammonium fluoride in 7.5 mL of dry methyl alcohol was treated with 0.32 g (0.38 mmol) of solid $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)$-$C_{10}H_{14}O_4BrS]_2 \cdot H_2O$. The solution was stirred for 5–10 min and then filtered, and the filtrate was allowed to stand for 2 h at room temperature. The red-purple solution was diluted with a solution of 0.10 g (0.69 mmol) of ammonium iodide in 1–2 mL of methyl alcohol. The precipitate was collected, washed three times with 5–10-mL portions of methyl alcohol, washed with acetone, and air-dried; yield 83 mg, 29%. Anal. Calcd for *cis*-$[Cr(en)_2F_2]I$: C, 14.2; H, 4.75; N, 16.6; F, 11.2. Found: C, 14.2; H, 4.64; N, 16.3; F, 10.9. The electronic spectrum was in good agreement with that reported previously.[3] The optical rotatory dispersion spectrum of 0.2% aqueous solution of the complex was characterized by α_{591} 0°, α_{589} −19.0°, α_{546} −445°, α_{530} −487°, α_{495} 0°, and α_{455} 405°.

A weighed sample of $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(C_6H_5)_4B]_2 \cdot 1.5H_2O$ (1.0 g, 1.14 mmol) was dissolved in 7 mL of dry methyl alcohol and treated with 4 times the theoretical amount of ammonium thiocyanate dissolved in 3 mL of dry methyl alcohol. The mixture was stirred for 2–3 min before the insoluble ammonium tetraphenylborate was removed by filtration and discarded. The filtrate was kept at room temperature for 18 h and the product which had been collected was washed with acetone and air-dried; yield 0.10 g, 28%. Anal. Calcd for *cis*-$[Cr(en)_2F(NCS)]SCN$: C, 23.4; H, 5.35; N, 27.4. Found: C, 23.0; H, 5.38; N, 27.1. The optical rotatory dispersion spectrum of a 0.1% aqueous solution of the complex was characterized by α_{589} 27°, α_{578} 0°, α_{546} −295°, α_{250} −460°, α_{487} 0°, and α_{450} 370°.

A second crop of crystals was collected from the original filtrate after 2 weeks. The product was washed and dried as described previously; yield 62 mg, 17.5%. Anal. Calcd for $[Cr(en)_2F(NCS)]SCN$: C, 23.4; H, 5.35; N, 27.4. Found: C, 23.2; H, 5.51; N, 27.6. The aqueous solution electronic absorption spectrum was characterized by λ_{max} 500 nm (ϵ 92), λ_{min} 423 (ϵ 21.1), λ_{max} 373 (ϵ 47.5). The optical rotatory dispersion spectrum for a 0.2% aqueous solution of the complex was characterized by α_{589} 10.0°, α_{578} 0°, α_{546} −88°, α_{520} −135°, α_{487} 0°, and α_{450} 114°.

Resolution of (±)-*cis*-$[Cr(en)_2F(NCS)]^+$. This cation was resolved by the published method.[2] Anal. Calcd for $(+)_{5461}$-$[Cr(en)_2F(NCS)][(+)$-$C_{10}H_{14}O_4BrS] \cdot H_2O$: C, 31.1; H, 5.55; N, 12.1. Found: C, 31.25; H, 5.64; N, 12.29. A 0.17% aqueous solution of the diastereomer was characterized by α_{589} 53°, α_{546} 198°, α_{520} 301°, α_{474} 0°, α_{456} −67°, and α_{428} 0°.

The complex was converted to the corresponding perchlorate, and the perchlorate salt was recrystallized three times to produce a sample of constant rotation. Anal. Calcd for $(+)_{5461}$-*cis*-$[Cr(en)_2F(NCS)]ClO_4$: C, 17.22; H, 4.58; N, 20.06. Found: C, 17.09; H, 4.58; N, 19.90. A 0.15% aqueous solution of the complex was characterized by α_{589} −13.4°, α_{585} 0°, α_{546} 242°, α_{522} 412°, α_{485} 0°, and α_{450} −326°. The circular dichroism spectrum was characterized by $\Delta\epsilon_{552}$ (M^{-1} cm^{-1}) −0.14, $\Delta\epsilon_{530}$ 0, and $\Delta\epsilon_{480}$ 0.63.

Separation of *cis*- and *trans*-$[Cr(en)_2F_2]^+$. A weighed sample, 100 mg, of *trans*-$[Cr(en)_2F_2]I$[4] in 50 mL of water was charged onto a column of Dowex 50W-X8 (50–100 mesh, H^+, column 15 cm × 1 cm) at 4 °C and eluted with 0.1 M sulfuric acid. The column was eluted at a rate of 0.7–0.8 mL/min and the eluate was collected in 7-mL fractions. The fractions were analyzed for chromium content, and an elution profile was established for this ion. The experiment was repeated under the same conditions using *cis*-$[Cr(en)_2F_2]I$. A 10% trans–90% cis mixture was prepared and qualitatively separated in this fashion.

A 100-mg sample of $[Cr(en)_2F_2]I$, prepared by the anation of *cis*-$[Cr(en)_2F(OH_2)]I_2 \cdot H_2O$ with ammonium fluoride in dry methyl alcohol, was dissolved in 30 mL of water and charged onto the column described above. Elution of the column with 0.1 M sulfuric acid and subsequent determination of the elution profile indicated less than 2% of the total chromium could be attributed to the presence of the trans isomer.

Analytical Methods and Instrumentation. The analytical methods and instrumentation were the same as those described previously.[5,6]

Results and Discussion

Resolution of the (±)-*cis*-fluoroaquobis(ethylenediamine)chromium(III) ion into its optical isomers absolutely confirms the cis arrangement of the monodentate ligands in the complex. Thus the earlier assignment of a cis geometry to this complex on the basis of electronic spectral data is correct. The least soluble diastereoisomer, $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)$-$C_{10}H_{14}O_4BrS]_2 \cdot H_2O$, formed when $(+)_{5890}$-$NH_4C_{10}H_{14}O_4BrS$ was used as the resolving agent. The $(+)_{5461}$ isomer of the complex was isolated by using $(-)_{5890}$-$NH_4C_{10}H_{14}O_4BrS$ as the resolving agent. The optical rotatory dispersion spectra and the specific rotations of the two isomers were reverse in shape and opposite in sign as expected. The absolute values of the specific rotations were in good agreement.

Thermal dehydration of $(-)_{5461}$-*cis*-$[Cr(en)_2F(OH_2)][(+)$-$C_{10}H_{14}O_4BrS]_2 \cdot H_2O$ resulted in the loss of 2 mol of water/formula weight of the complex. The analytical and weight loss data for the dehydrated product support the suggestion that the loss of the aquo ligand from the complex was accompanied by coordination of the bromocamphor-π-sulfonate anion. In addition, dehydration of the complex resulted in the complete loss of optical activity in the chiral cation.

The aqueous solution electronic spectrum of the dehydrated product matched the spectrum of pure *cis*-$[Cr(en)_2F(OH_2)]^{2+}$ very well in terms of the wavelengths of the absorption maxima and minimum, and the molar absorptivities at these points were in reasonable agreement with the values expected for *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. The presence of a large amount of trans isomer in the dehydration product would be expected to produce a general lowering of the molar absorptivities found for the heated material, and this did not occur. Thus the loss of optical activity from the chiral cation would appear to be largely, if not entirely, due to racemization which took place during the dehydration step.

The argument for the loss of optical activity via racemization rather than via isomerization is further supported by the observation that thermal dehydrations of trans isomers of the type [Cr(en)$_2$F(OH$_2$)]X$_2$ (X$^-$ = Cl$^-$, Br$^-$, SCN$^-$) produce cis FX isomers[4] whereas cis isomers of the type [Cr(en)$_2$Y(OH$_2$)]Z$_2$ (Y = Cl, Br, NH$_3$; Z = Cl, Br, I) appear to react with little or no isomerization.[7-11] However, the steric course of many of these reactions would appear to depend on the temperature as well as on the nature of the entering anion.

Removal of the optically active anion from (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O with sodium tetraphenylborate produced a compound whose optical rotatory dispersion spectrum was opposite in shape to that found for Λ(+)$_{5890}$-[Cr(en)$_2$Cl(OH$_2$)]$^{2+}$.[12] Thus the absolute configuration of (−)$_{5461}$-[Cr(en)$_2$F(OH$_2$)]$^{2+}$ would appear to be Δ. A previous study[2] assigned the Λ absolute configuration to (+)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]$^+$.

Additional support for the previous assignment of the Λ configuration to (+)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]$^+$ comes from the observation that the −, +, − sequence in the molar rotations at long wavelength is exactly the order found for (+)$_{5890}$-*cis*-[Cr(en)$_2$Cl$_2$]$^+$, an ion that has been assigned the Λ configuration by several investigators.[13-15] In addition, the signs and magnitudes of the $\Delta\epsilon$ values at long wavelengths for (+)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]$^+$ are consistent with an ion of Λ absolute configuration.

Anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O in dry methyl alcohol with potassium thiocyanate produces insoluble (−)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]SCN. Thus the anation of Δ(−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)]$^{2+}$ proceeds with retention of configuration as far the the optically active product is concerned to produce Δ-(−)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]$^+$.

In a similar fashion anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O with fluoride ion in dry methyl alcohol proceeds with retention of configuration as far as the optically active product is concerned. Isomerization of the cation would appear to be negligible.

The results of the ion-exchange experiments using (−)$_{5461}$-*cis*-[Cr(en)$_2$F$_2$]I obtained via anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O indicate that less than 2% of the chromium was present as the corresponding trans isomer. Thus 2% isomerization would appear to be an upper limit to the extent of the isomerization which accompanied the anation.

It was possible to isolate two fractions from the anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][(C$_6$H$_5$)$_4$B]$_2$·1.5H$_2$O with ammonium thiocyanate in dry methyl alcohol. The first fraction was (−)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]SCN. The second fraction (isolated after 2 weeks) exhibited lower molar absorptivities and greatly reduced specific rotations. It is not possible at this time to say if the loss of optical activity in the second fraction is due to racemization, isomerization, or the formation of a dithiocyanate complex.

The absolute values of the molar rotations of (+)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]ClO$_4$, obtained by direct resolution of the racemic cation, agree within 8% with values obtained for (−)$_{5461}$-[Cr(en)$_2$F(NCS)]SCN, prepared by anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·2H$_2$O with ammonium thiocyanate, except for the value at 589 nm. The appreciable difference at 589 nm is probably due to the difficulty of measuring small angles of rotation (Table I).

Similar behavior was noted when the absolute values of the molar rotations of the complex (+)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]ClO$_4$ were compared to the molar rotations of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(NCS)]SCN prepared from (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)][Ph$_4$B]$_2$·1.5H$_2$O. In this case the molar rotations differed by about 7%. These results would appear to support the conclusion that the anation of (−)$_{5461}$-*cis*-[Cr(en)$_2$F(OH$_2$)]$^{2+}$ with NCS$^-$ or F$^-$ in dry methyl alcohol proceeds with essentially 100% retention of absolute configuration as far as the least soluble product is concerned.

Registry No. Δ-(−)-*cis*-[Cr(en)$_2$F(OH$_2$)][(C$_6$H$_5$)$_4$B]$_2$, 69880-71-3; Λ-(+)-*cis*-[Cr(en)$_2$F(NCS)]ClO$_4$, 59796-03-1; Δ-(−)-*cis*-[Cr(en)$_2$F(NCS)](SCN), 69880-73-5; Δ-(−)-*cis*-[Cr(en)$_2$F$_2$]I, 69926-04-1; Δ-(−)-*cis*-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$, 69880-90-6; *cis*-[Cr(en)$_2$F(C$_{10}$H$_{14}$O$_4$BrS)][C$_{10}$H$_{14}$O$_4$BrS], 69880-74-6; Λ-(+)-*cis*-[Cr(en)$_2$F(OH$_2$)][(−)-C$_{10}$H$_{14}$O$_4$BrS]$_2$, 69880-76-8; Λ-(+)-*cis*-[Cr(en)$_2$F(NCS)][(+)-C$_{10}$H$_{14}$O$_4$BrS], 59796-02-0; *cis*-[Cr(en)$_2$F(OH$_2$)]I$_2$, 59765-91-2; *cis*-[Cr(en)$_2$F(OH$_2$)][(C$_6$H$_5$)$_4$B]$_2$, 69847-10-5.

References and Notes

(1) Part 8: J. W. Vaughn, G. J. Seiler, and D. J. Wierschke, *Inorg. Chem.*, **16**, 2423 (1977).

(2) J. W. Vaughn and A. M. Yeoman, *Inorg. Chem.*, **15**, 2320 (1976).

(3) J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, **4**, 1077 (1965).

(4) J. W. Vaughn, O. H. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

(5) J. W. Vaughn and G. J. Seiler, *Inorg. Chem.*, **13**, 598 (1974).

(6) J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, **8**, 1201 (1969).

(7) N. M. Hughes and W. R. McWhinnie, *J. Chem. Soc. A*, 592 (1967).

(8) P. Pfeiffer, *Ber. Dtsch. Chem. Ges.*, **40**, 3833 (1907).

(9) W. W. Fee, J. N. Mac. B. Harrowfield, and W. G. Jackson, *J. Chem. Soc. A*, 2612 (1970).

(10) C. F. Wong and A. D. Kirk, *Inorg. Chem.*, **17**, 1672 (1978).

(11) C. F. Wong and A. D. Kirk, *Can. J. Chem.*, **53**, 3388 (1976).

(12) I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem.*, **37**, 1359 (1975).

(13) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(14) E. Pederson, *Acta Chem. Scand.*, **24**, 3362 (1970).

(15) K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 802 (1966).