subsequent loss of hydrogen occurs on gentle heating. Reaction 4 is strongly reminiscent of reaction 3. A similar mechanism was proposed by Alper to interpret the desulfurization of thiobenzophenones by $[cpM(CO)_n]^-$ (M = Fe, *n* = 2; M = Mo or W, *n* = 3).[6] Such a reaction led to the cleavage of the cp–metal bond and to the formation of diarylfulvenes.

For clarification of the nature of V, the reaction of elemental sulfur with $[cpV(CO)_4]$[9] was carried out (eq 5). Compound

$$[cpV(CO)_4] + {}^1/_8S_8 \rightarrow (1/n)\underset{\mathrm{V}}{[cpVS]_n} + 4CO \qquad (5)$$

V was obtained as a microcrystalline solid from reaction 5. There is, however, a striking difference in composition, magnetic properties, and IR spectrum between complex V and $[(cp)_2V_2S_5]_n$ proposed to form in the reaction of $[cpV(CO)_4]$ with elemental sulfur in refluxing toluene for 16 h. Such a difference may be due to the significant difference in the experimental conditions.[23] The crucial point is, probably, the fact that the final solution was handled in the air. This might cause the transformation of a preliminary compound coming from reaction 5. We did not achieve a satisfactory knowledge of the nature of V because of its low solubility. Analytical data agree with the proposed formula, for which we found a magnetic moment of 1.36 μ_B at 292 K per vanadium atom. This cannot help in proposing a plausible structure for V in the absence of any information concerning its molecular complexity. We would draw attention to the close similarity between the desulfurization of thiobenzophenone and the deoxygenation of N_2O,[24] both promoted by vanadocene. The latter reaction produces a polynuclear monocyclopentadienylvanadium complex, $[(cp)_5V_5O_6]$ (IX). The resemblance between V and IX is not only restricted to their origin but can be extended, eventually, to their molecular complexity and to their magnetic properties.

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Registry No. I, 1277-47-0; II, 84332-78-5; V, 84332-80-9; I_2, 7553-56-2; CH_3I, 74-88-4; $Ph_2C{=}S$, 1450-31-3; $[CpV(CO)_4]$, 12108-04-2; sulfur, 7704-34-9.

Supplementary Material Available: Listings of structure factor amplitudes, thermal parameters (Table SI), and bond distances and angles (Table SII) (15 pages). Ordering information is given on any current masthead page.

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Fluoro-Containing Complexes of Chromium(III). 12. Preparation and Resolution of the *cis*-Fluoroamminebis(ethylenediamine)chromium(III) Cation[1]

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In 1975 Wong and Kirk[2] reported the first successful preparation of solid salts of the *cis*- and *trans*-$[Cr(en)_2FNH_3]^{2+}$ (en = ethylenediamine) cations via the ammonolysis of *trans*-$[Cr(en)_2FBr]Br$. The synthetic method, which involved Cr–Br bond rupture and Cr–NH_3 bond formation, produced both isomers with a cis/trans ratio of approximately 60/40. This preparative method, coupled with the rather high solubility of the cis isomer, resulted in a low overall yield of the cis isomer. Assignments of the cis and trans structures were made on the basis of the differences in molar absorptivities. This was necessary since both isomers have the same local site symmetry (C_{4v}), a situation which requires that the number of spin-allowed electronic transitions be the same for both isomers and that the wavelengths of maximum and minimum absorptions be essentially constant.

During the course of stereochemical investigations in this laboratory, it became necessary to develop a synthetic route that could be used to prepare the cis isomer in quantity and to establish unequivocally its structure; hence, the present study was undertaken.

Experimental Section

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

Preparation of Starting Materials. (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ was prepared as previously described.[3] (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ was converted to (±)-*cis*-$[Cr(en)_2F(OH_2)]I_2\cdot H_2O$ and then to (±)-*cis*-$[Cr(en)_2FCl]I$ via the published methods.[3,4] (±)-*cis*-$[Cr(en)_2FCl]I$ was utilized to obtain (±)-*cis*-$[Cr(en)_2FNH_3]ICl$ by the method used to prepare *trans*-$[Cr(tn)_2FNH_3]ICl$ (tn = 1,3-propanediamine) except that the ammonia was dried over sodium prior to use instead of being condensed directly from the cylinder.[5]

In a typical preparation of $[Cr(en)_2FNH_3]ICl$, a 6.2-g (17.5-mmol) sample of (±)-*cis*-$[Cr(en)_2FCl]I$ was reacted with 30–40 mL of dry liquid ammonia. The yield was 6.1 g (94%) of crude product. The electronic spectrum of the crude product in 0.1 M perchloric acid was characterized by λ_{max} 495 nm (ϵ 62.0 M^{-1} cm^{-1}), λ_{min} 416 (ϵ 17.7), and λ_{max} 359 (ϵ 38.6).

Isolation of (±)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$. A 1.0-g (2.7-mmol) sample of crude $[Cr(en)_2FNH_3]ICl$ was dissolved in 1.0 mL of 0.1 M perchloric acid, the orange solution was filtered, and the cold filtrate was diluted with perchloric acid as described by Wong and Kirk.[2] This method produced 0.30 g (27%) of the desired product. Anal. Calcd for (±)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$: C, 11.79; H, 4.66; N, 17.19. Found: C, 11.56; H, 4.42; N, 17.23. The electronic spectrum in 0.1 M perchloric acid was characterized by λ_{max} 496 nm (ϵ 64.9 M^{-1} cm^{-1}), λ_{min} 418 (ϵ 16.3), and λ_{max} 362 (ϵ 34.5) [lit.:[2] λ_{max} 494 (ϵ 64.9), λ_{min} 417 (ϵ 16.6), and λ_{max} 360 (ϵ 34.4)].

Isolation of (±)-*cis*-$[Cr(en)_2FNH_3]I_2$. A 5.5-g (14.8-mmol) sample of crude (±)-*cis*-$[Cr(en)_2FNH_3]ICl$ was dissolved in 10 mL of water at room temperature, and the solution was quickly filtered. The orange filtrate was diluted with 5 mL of 47% hydriodic acid and cooled in an ice bath for 15 min. The orange product was collected, washed with acetone, and air-dried. The yield was 5.2 g (76%).

An 11.6-g (25.1-mmol) sample of crude (±)-*cis*-$[Cr(en)_2FNH_3]I_2$ was dissolved with constant stirring in 50 mL of water at 25–30 °C. The orange solution was filtered, and the filtrate was cooled in an ice bath for 1 h. The orange solid was collected, washed with acetone, and air-dried. The yield was 6.0 g (52%). The electronic spectrum in 0.1 M perchloric acid was characterized by λ_{max} 495 nm (ϵ 65.9 M^{-1} cm^{-1}), λ_{min} 418 (ϵ 17.4), and λ_{max} 357 (ϵ 39.6). Anal. Calcd for (±)-*cis*-$[Cr(en)_2FNH_3]I_2$: C, 10.39; H, 4.11; N, 15.15; F, 4.11. Found: C, 10.48; H, 4.25; N, 15.08; F 3.98.

Resolution of (±)-*cis*-$[Cr(en)_2FNH_3]I_2$. A 5.0-g (10.8-mmol) sample of recrystallized (±)-*cis*-$[Cr(en)_2FNH_3]I_2$ in 40 mL of water at room temperature was added to a solution of 9.42 g (21.6 mmol) of $(+)_{589}$-silver bromocamphor-π-sulfonate[6] in 50 mL of water at 45–55

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°C. The reaction mixture was stirred at 50 °C for 10 min before being allowed to cool in the dark for 2 h. At the end of this time the precipitated AgI was removed by filtration, and the solid AgI was washed with water until the liquid was colorless. The orange filtrate was evaporated to dryness in the dark with a stream of air. At this point the solid was stirred with 75 mL of acetone for 45 min before the insoluble material was collected, washed with ether, and air-dried. The yield was 5.5 g (61%). The acetone extraction was repeated until the acetone was colorless (two more times). Evaporation of the acetone produced only intractable oils and tars. The final yield of acetone-insoluble material was 4.82 g (53%). Anal. Calcd for *cis*-$[Cr(en)_2FNH_3][(+)_{589}C_{10}H_{14}O_4BrS]_2{\cdot}0.5H_2O$: C, 34.40; H, 5.73; N, 8.36. Found: C, 34.34; H, 5.99; N, 8.35. The optical rotatory dispersion spectrum of a 0.2% aqueous solution of the complex at room temperature was characterized by $[\alpha]_x$ ($[\alpha]$ = specific rotation; x = wavelength in nm): $[\alpha]_{589}$ 52.8; $[\alpha]_{546}$ 52.8. A 4.50-g (5.4-mmol) sample of the compound was quickly dissolved in about 90 mL of methyl alcohol at room temperature. The product precipitated shortly after the crude material dissolved in the alcohol. The orange solid was collected, the filtrate was set aside, and the solid in the filter was washed with ether and air-dried. The yield was 2.7 g (60%). A 0.2% aqueous solution of the complex gave $[\alpha]_{589}$ 38.1 and $[\alpha]_{546}$ 34.3. The filtrate from above was cooled at 8 °C for 18 h before another 0.35 g of crystal was collected, washed, and air-dried as previously described. A 0.2% aqueous solution of the complex gave $[\alpha]_{589}$ 40.5 and $[\alpha]_{546}$ 34.5.

A 1.94-g (2.3-mmol) sample of the fraction with $[\alpha]_{589}$ 38.1 was dissolved in 92 mL of methyl alcohol at 50–52 °C, and the orange solution was quickly filtered. The filtrate was allowed to stand at room temperature in the dark for 2 h before the product was collected, washed with ether, and air-dried. The yield was 1.0 g (52%). Anal. Calcd for $(-)_{589}$-*cis*-$[Cr(en)_2FNH_3][(+)C_{10}H_{14}O_4BrS]_2$: C, 34.78; H, 5.67; N, 8.45. Found: C, 34.32; H, 5.82; N, 8.22. A 0.2% aqueous solution of the above fraction gave $[\alpha]_{589}$ 33.8 and $[\alpha]_{546}$ 25.4. The electronic spectrum of the complex in 0.1 M perchloric acid was characterized by λ_{max} 495 nm (ϵ 66.5 M^{-1} cm^{-1}), λ_{min} 416 (ϵ 17.1), and λ_{max} 360 (ϵ 36.4). One additional recrystallization did not change the specific rotations or the molar absorptivities.

Isolation of $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$. A weighed sample (0.500 g, 1.23 mmol) of $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3][(+)C_{10}H_{14}O_4BrS]_2$ ($[\alpha]_{546}$ 25.4) was dissolved in 2 mL of 1.0 M perchloric acid, and the solution was filtered. The stirred filtrate was diluted with 10 mL of absolute alcohol and then was cooled in an ice bath for 15–20 min. The precipitated orange solid was collected, washed quickly with four 10-mL portions of ether, and air-dried. The solid was dried in vacuo over magnesium perchlorate at room temperature for 48 h prior to analysis. Yield: 0.110 g (22%). Anal. Calcd for $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$: C, 11.79; H, 4.66; N, 17.19; Cr, 12.77; F, 4.66. Found: C, 11.85; H, 4.60; N, 17.00; Cr, 12.75; F, 4.63. The electronic spectrum in aqueous solution was characterized by λ_{max} 494 nm (ϵ 66.1 M^{-1} cm^{-1}), λ_{min} 417 (ϵ 17.6), and λ_{max} 360 (ϵ 35.6). A 0.2% aqueous solution of the complex gave $[\alpha]_{589}$ −53.4, $[\alpha]_{546}$ −106.8, $[\alpha]_{525}$ −119.1, $[\alpha]_{483}$ 0, $[\alpha]_{434}$ +271.1, and $[\alpha]_{356}$ +147.9.

High-Performance Liquid Chromatography Studies. High-performance liquid chromatography studies of aqueous solutions of the pure *cis*- and *trans*-$[Cr(en)_2FNH_3](ClO_4)_2$ as well as of the crude product obtained from the reaction of *cis*-$[Cr(en)_2FCl]I$ with anhydrous liquid ammonia were performed at ambient temperature with a Beckman Altex chromatograph. This instrument was equipped with Beckman 110A pumps, a Beckman 421 controller, a Micrometric variable-wavelength detector, a Beckman Ultrasil-CX column (4.6 mm × 25.0 cm), a Kepp Zonen recorder, and a Hewlett-Packard 3390A integrator. In all runs the column was protected by the appropriate guard columns. Prior to the elution studies the column was equilibrated with 20-column volumes of the eluant (0.3 M $(NH_4)_2SO_4$). In general the operating conditions were flow rate 1 mL/min, chart speed 1 cm/min, eluant 0.3 M $(NH_4)_2SO_4$, sample size 20.0 μL, and operating pressure <1000 psi.

A 0.016 M aqueous solution of authentic *cis*-$[Cr(en)_2FNH_3](ClO_4)_2$ was used to establish the cis ion's elution behavior. A calibration curve of area under the main peak vs. concentration was determined for six different dilutions of the 0.016 M aqueous solution of the cis complex. A similar calibration curve was determined for the pure *trans*-$[Cr(en)_2FNH_3](ClO_4)_2$. An aqueous solution of a weighed sample of the crude product from the reaction of *cis*-$[Cr(en)_2FCl]I$ with anhydrous ammonia was prepared; the pH was adjusted to that of the standard with dilute perchloric acid, and the solution was diluted to a known volume. An aliquot of this solution was injected into the high-performance liquid chromatograph, and the cis/trans ratio was determined from the working curves. The retention times were for pure *cis*-$[Cr(en)_2FNH_3](ClO_4)_2$ 4.74 ± 0.08 min and for pure *trans*-$[Cr(en)_2FNH_3](ClO_4)_2$ 5.19 ± 0.04 min. The crude product exhibited two major peaks with retention times of 4.80 ± 0.02 and 5.14 ± 0.03 min. The cis/trans ratio in the crude product was calculated to be slightly greater than 4.0/1.0.

Results and Discussion

The sealed-tube reaction of (±)-*cis*-$[Cr(en)_2FCl]I$ with dry liquid ammonia at room temperature results in the formation of unequal amounts of *cis*- and *trans*-$[Cr(en)_2FNH_3]ICl$. Product-isolation studies showed that the crude material contained greater than 70% of the cis isomer. Thus the preparative reaction represents an improved route for the synthesis of the *cis*-$[Cr(en)_2FNH_3]^{2+}$ cation.

The isomer of $[Cr(en)_2FNH_3]^{2+}$ characterized by λ_{max} 494 nm (ϵ 64.9 M^{-1} cm^{-1}), λ_{min} 417 (ϵ 16.6), and λ_{max} 362 (ϵ 34.4) has been shown by the isolation of one of its chiral forms to involve unequivocally a cis arrangement of the fluoro and ammine ligands. Thus the original assignment of the cis geometry to this complex on the basis of its molar absorptivity values by Wong and Kirk[2] is correct.

From considerations of the optical rotatory dispersion curves of $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3]^{2+}$, $(-)_{546}$-*cis*-$[Cr(en)_2F_2]^+$, $(-)_{546}$-*cis*-$[Cr(en)_2FNCS]^+$, and $(-)_{546}$-*cis*-$[Cr(en)_2F(OH_2)]^{2+}$, the absolute configuration of $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3]^{2+}$ was assigned as Δ.[3,7]

The results of the high-performance liquid chromatography studies confirm the product-isolation data and convincingly demonstrate the presence of the trans isomer in the crude product. The more accurate chromatography data indicate the cis/trans ratio to be 4/1 in the crude product obtained from the reaction of (±)-*cis*-$[Cr(en)_2FCl]I$ with dry liquid ammonia. The presence of the trans isomer indicates that the ammonolysis reaction must involve a contribution from a trigonal-bipyramidal intermediate since a reaction that involved only a tetragonal pyramid as an intermediate would require that the reaction occur with complete retention of the original cis geometry. Likewise, a displacement mechanism that involves cis attack can be eliminated since such a mechanism also requires that the geometry of the starting material be retained. A displacement mechanism that involves trans attack does lead to a cis–trans mixture, but the simple statistical ratio of 2/1 does not conform to the experimental data and can probably be eliminated for this reason. It is to be noted that the above discussion of the reaction mechanism is based on data from a very specific set of reaction conditions. Under other conditions the observed product ratios could well be different.

Acknowledgment. The author wishes to thank Professor A. D. Kirk for a sample of pure *trans*-$[Cr(en)_2FNH_3](ClO_4)_2$ for use in the HPLC studies.

Registry No. *cis*-$[Cr(en)_2FNH_3]ICl$, 84279-84-5; *trans*-$[Cr(en)_2FNH_3]ICl$, 84279-85-6; (±)-*cis*-$[Cr(en)_2FCl]I$, 62792-37-4; (±)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$, 58437-81-3; (±)-*cis*-$[Cr(en)_2FNH_3]I_2$, 84279-86-7; (−)-*cis*-$[Cr(en)_2FNH_3][(+)\text{-}C_{10}H_{14}O_4BrS]_2$, 84367-52-2; (−)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$, 84367-53-3.

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