solvents or are in the presence of good donor molecules. Conversely, β-diketone complexes show marked infrared shifts under similar conditions.[32] Steric interaction of the base molecule with the ethylene bridge might, of course, prevent close approach of the donor atom to the vanadium atom in the β-ketimine complexes. It must be pointed out that lack of spectral variation with solvent cannot be construed as evidence for nonexistent or even weak interaction of the donor atoms with the vanadium. Thermodynamic measurements are needed to settle this point.

In the β-diketone oxovanadium(IV) complexes, the axial oxygen atom dominates the ligand field about the metal. Implicit in this is the substantial $p\pi \rightarrow d\pi$ bonding between the axial oxygen and vanadium atoms. It is reasonable to expect that addition of a donor molecule to the vanadium atom opposite to the axial oxygen would effect the $p\pi \rightarrow d\pi$ interaction. This should lead to a change in the d-orbital energy levels, and, consequently, the spectral properties would change with solvent. An important consideration here is the extent of ligand–metal $p\pi \rightarrow d\pi$ interaction with the in-plane donor atoms. To the extent that this is important, axial π interaction should be lessened. If this occurs, one would expect that axial coordination to the vanadium atom of a donor molecule might not effect the energy of the d levels to a large extent. As a result the spectral properties would not be markedly dependent on the donor properties of the solvent. It has been suggested[21,29] that with porphyrin ligands there is a greatly increased π bonding of the metal with the in-plane donor atoms (nitrogen) over that for the β-diketones. The esr parameters reported here can be interpreted from the point of view that π bonding of the in-plane ligands is greater for the β-ketimines than for the β-diketones (but less than for the porphyrins). The decreased solvent dependence of the spectra noted here for the β-ketimines might then be a consequence of this. The fact that the vanadium axial oxygen stretching frequency for the β-ketimine complexes is ~20 cm^{-1} lower than that for the β-diketone compounds might also be evidence for a weakened vanadium–axial oxygen bond.

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[32] J. Selbin, L. H. Holmes, and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

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Fluoro-Containing Complexes of Chromium(III). III. The Synthesis and Characterization of Some Fluoroacidobis(ethylenediamine)chromium(III) Complexes[1]

By Joe W. Vaughn, Otto J. Stvan, Jr.,[2] and Virgil E. Magnuson[3]

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A series of five new monofluoro complexes of chromium(III) of the type $[Cr(en)_2FX]^{n+}$ (en is ethylenediamine) has been prepared and characterized. The complexes which contain Cl^-, Br^-, I^-, or NCS^- as the X^- group all appear to involve a *cis* arrangement of the FX ligands. However, those complexes which contain ONO^- or F^- as the X^- groups appear to have the FX ligands *trans* to each other. Structures were established *via* ultraviolet–visible spectral studies, by ion-exchange techniques, and in one case by the resolution of a complex into its optical antipodes. In addition, new synthetic methods are presented for some known complexes of chromium(III).

Introduction

Complexes of the general type $[Cr(en)_2FX]^{n+}$ have not been investigated to any great extent for those cases where X is a uninegative monodentate ligand. In 1957 Dahme[4] reported the syntheses of fluorohydroxobis(ethylenediamine)chromium(III) chloride, fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate, and difluorobis(ethylenediamine)chromium(III) chloride. This work was followed by the synthesis of *cis*-difluorobis(ethylenediamine)chromium(III) iodide by Fehrmann and Garner[5] in 1960. In addition, these workers presented evidence for the *cis*-fluoroaquobis(ethylenediamine)chromium(III) ion in solution.

The present investigation was initiated to develop suitable synthetic methods for the preparation of unknown fluoro complexes of the type $[Cr(en)_2FX]^{n+}$ and if possible to determine the spatial relationship of the F and X ligands.

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[1] For the previous publication in this series see J. W. Vaughn, L. N. Coward, and B. K. Winter, *Inorg. Chem.*, **5**, 2061 (1966).

[2] Taken in part from a thesis submitted by O. J. S. to the Graduate School of Northern Illinois University in partial fulfillment for the M.S. degree.

[3] National Science Foundation Research Participant.

[4] W. Dahme, Dissertation, Clausthal Bergakad, Germany, 1957, p 36; A. Katowski, Ed., "Gmelins Handbuch der Anorganischen Chemie, VIII Auflage, Chrom," Vol. 52 Part C, Verlag Chemie, Weinheim/Bergstrasse, 1965, p 190.

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

Experimental Section

Synthesis of *trans*-Difluorobis(ethylenediamine)chromium(III) Chloride.—This complex was prepared by the following method which was based on the earlier work of Dahme[4] for the synthesis of fluorohydroxobis(ethylenediamine)chromium(III) chloride.

A solution of 30 g (0.11 mole) of chromium(III) chloride hexahydrate in 100 ml of water was placed in a 400-ml polyethylene beaker and diluted with 24 g (0.60 mole) of a 48% solution of hydrofluoric acid. The beaker was packed in ice and 100 g (1.58 moles) of aqueous 95% ethylenediamine was added dropwise over a period of 1 hr. After the addition of the ethylenediamine was completed, the dark red-purple solution was heated for 2 hr on a steam bath to complete the reaction. The solution which had darkened in color during the heating was transferred to an evaporating dish and the excess water was removed by heating for an additional 2 hr at 90–95°. During this time a crust formed on the surface of the liquid and this was broken up frequently during the late stages of the evaporation. At the end of the 2 hr the reaction mixture was cooled to 10° in an ice bath and filtered. The crystals which had precipitated were collected, washed with 100 ml of alcohol followed by 100 ml of acetone, and air dried. The above procedure yielded 15.5 g or 56% of reddish orange crystals. *Anal.* Calcd for $[Cr(en)_2F_2]Cl$: Cr, 21.2; Cl, 14.5. Found: Cr, 21.0; Cl, 14.3. A 10^{-3} M aqueous solution of the complex had a molar conductance of 106 ohm^{-1} at 25°. This indicated the complex to be a 1–1 electrolyte.

A 1.0-g (0.0041-mole) sample of crude difluorobis(ethylenediamine)chromium(III) chloride was dissolved in 6 ml of water at room temperature and filtered. The filtrate was treated with 2 ml of a saturated aqueous solution of sodium iodide at room temperature. The orange-pink precipitate which formed at once was collected by filtration, washed with acetone, and air dried. A yield of 1.0 g (0.0030 mole) or 73% based on $[Cr(en)_2F_2]Cl$ was obtained. A sample was recrystallized from water and analyzed. *Anal.* Calcd for $[Cr(en)_2F_2]I$: Cr, 15.4; I, 37.7; F, 11.2; C, 14.2; H, 4.8; N, 16.6. Found: Cr, 15.6; I, 37.5; F, 11.3; C, 14.2; H, 4.8; N, 16.6.

The final product was shown by ion-exchange methods to be contaminated with another material. A weighed sample of the doubly recrystallized material was dissolved in a minimum amount of water at room temperature and charged onto a column of Dowex 50W-X4 (100–200 mesh, H^+ form, column 8 cm × 1 cm). The column was washed free of iodide with water and eluted with *ca.* 60 ml of 0.3 N perchloric acid. A red fraction was quickly and completely eluted from the column at a flow rate of 1–2 ml/min. This fraction had a visible absorption spectrum nearly identical with that of the material which had not been ion exchanged. Further, this fraction accounted for 85–90% of the material placed on the column.

The small dark red band which was not eluted from the column with 0.3 N acid was slowly eluted with *ca.* 150 ml of 0.6 N acid or more rapidly with *ca.* 100 ml of 0.9 N acid. In both cases the band was eluted as a light purple solution. The visible absorption spectrum consisted of two bands and the wavelengths of maximum absorption were 518 and 362 mμ. This fraction accounted for about 5% of the material placed on the column.

The corresponding bromide was prepared in a slightly different fashion. A 2.45-g (0.01-mole) sample of crude $[Cr(en)_2F_2]Cl$ was dissolved in 6 ml of water at room temperature. The solution was filtered and the filtrate was cooled in an ice bath to 10°. A solution of 2 g (0.019 mole) of sodium bromide in 2 ml of water was added and the reaction mixture was kept on ice. The product precipitated on stirring and scratching the beaker after about 5 min. The final product was collected by filtration, washed with acetone, and air dried.

A 10^{-3} M aqueous solution of the complex had a molar conductance of 111 at 25°, and its visible absorption spectrum was identical with that of recrystallized difluorobis(ethylenediamine)chromium(III) iodide. *Anal.* Calcd for $[Cr(en)_2F_2]Br$: Cr, 17.9; Br, 27.6. Found: Cr, 18.2; Br, 27.9. Concentrated aqueous solutions of difluorobis(ethylenediamine)chromium(III) chloride produced precipitates when treated with saturated aqueous solutions of potassium thiocyanate, potassium nitrate, and sodium perchlorate.

The assignment of the *trans* configuration was on the basis of the visible absorption spectrum which was markedly different from that of the *cis* isomer.[6] Also, the behavior of the complex on the ion-exchange column was taken as added evidence for a *trans* structure. The spectrum of a 0.03 M aqueous solution of the *trans* complex prepared from twice recrystallized material had well-defined peaks at 466 and 350 mμ, a broad shoulder near 525 mμ, and an ill-defined peak at 400 mμ. The molar absorptivities were 24, 18, 19, and 16 l. $mole^{-1}$ cm^{-1}, respectively. The molar absorptivities may well be slightly in error since we were not able to obtain a sample of the *trans* complex which, when eluted from a column of Dowex 50W-X4, did so without a faint red fraction being retained on the column.

For comparison purposes the *cis* isomer exhibited absorption maxima at 378 and 516 mμ with molar absorptivities of 39.5 and 75.5 l. $mole^{-1}$ cm^{-1}, respectively.

Fluoroaquobis(ethylenediamine)chromium(III) Perchlorate Monohydrate.—The method described by Dahme[4] was utilized with some minor modifications.

A solution of 10 g (0.041 mole) of *trans*-difluorobis(ethylenediamine)chromium(III) chloride in 50 ml of 72% perchloric acid was prepared and filtered to remove any undissolved solids. The solution was allowed to stand for 1 hr at room temperature and then diluted by the dropwise addition of 15 ml of water. The bright orange crystals which had precipitated were collected by filtration, washed with 50 ml of alcohol followed by 50 ml of acetone, and air dried; yield, 10 g (58%). *Anal.* Calcd for $[Cr(en)_2(H_2O)F](ClO_4)_2 \cdot H_2O$: Cr, 12.2. Found: Cr, 12.0.

An aqueous solution of this complex had absorption maxima at 371, 454, and 519 mμ; the molar absorptivities were 31.2, 25.6, and 24.2 l. $mole^{-1}$ cm^{-1}, respectively.

A 10^{-3} M aqueous solution of this complex had a molar conductance of 264 at 25° which is within the range for a 2–1 electrolyte. The water of hydration was removed by drying the complex *in vacuo* over phosphorus pentoxide for 12 hr at room temperature. *Anal.* Calcd for $[Cr(en)_2(H_2O)F](ClO_4)_2$: 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.

This compound was dissolved in concentrated hydrochloric or hydrobromic acid and the resulting solution was allowed to stand for 12–18 hr at room temperature. The gray-green or dark green crystals which had precipitated were collected, washed with acetone, and air dried for an extended period of time before being dried *in vacuo* at 100°. *Anal.* Calcd for *trans*-$[Cr(en)_2Cl_2]ClO_4$: C, 14.0; H, 4.7; N, 16.4; Cl, 20.7. Found: C, 14.0; H, 4.8; N, 16.4; Cl, 20.3. Calcd for *trans*-$[Cr(en)_2Br_2]ClO_4$: C, 11.1; H, 3.7; N, 13.0. Found: C, 11.2; H, 3.9; N, 12.9.

A 1.0-g (0.0023-mole) sample of fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate was dissolved in 5 ml of 72% perchloric acid and the solution was filtered. The solution was allowed to stand for 12–14 hr at room temperature before being cooled in an ice bath and filtered. The orange crystals which had precipitated were collected, washed with acetone, and air dried. Conductance measurements on a 10^{-3} M aqueous solution at 25° indicated the product to be a 2–1 electrolyte. *Anal.* Calcd for $[Cr(en)_2F(H_2O)](ClO_4)_2 \cdot H_2O$: Cr, 12.2. Found: Cr, 11.8.

The absorption spectrum of the recovered material in aqueous solution was identical with that of the starting complex.

In an attempt to replace the aquo ligand in fluoroaquobis(ethylenediamine)chromium(III) perchlorate under less stringent conditions than treatment with concentrated hydrochloric acid and still keep the fluoro group intact, the solid complex was shaken with a solution of dry hydrogen chloride in absolute alcohol for several hours. This resulted in the production of *trans*-dichlorobis(ethylenediamine)chromium(III) perchlorate.

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

A 1.0-g (0.0023-mole) sample of $[Cr(en)_2F(H_2O)](ClO_4)_2 \cdot H_2O$ was dissolved in 10 ml of 48% hydrofluoric acid and 2.0 g (0.035 mole) of ammonium bifluoride was added. This solution was evaporated to dryness on a steam bath and the green precipitate was washed with water and acetone and air dried. This solid was identified as $(NH_4)_3CrF_6$ by its infrared spectrum and X-ray powder pattern [d (Å), I/I_0] given as follows for $(NH_4)_3CrF_6$. Lit. values (ASTM X-Ray Powder Data File 2-1137 (1960)): 5.22, 40; 4.52, 40; 3.20, 70; 2.26, 100; 2.02, 50; 1.84, 40; 1.73, 100. Found: 5.21, 30; 4.60, 50; 3.20, 70; 2.27, 100; 2.03, 40; 1.85, 50; 1.74, 100.

Two methods were ultimately found to replace the aquo ligand in the complex under mild conditions and to keep the fluoro group intact.

A 2.0-g (0.0047-mole) sample of fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate was dissolved in the minimum amount of 48% hydrofluoric acid at room temperature and 1 ml of water was added. The solution was filtered to remove any undissolved solids and the solution was allowed to stand for 2–3 hr at room temperature. At the end of this time the orange precipitate was collected by filtration, washed with acetone, and air dried; yield, 0.35 g (24%). *Anal.* Calcd for $[Cr(en)_2F_2]ClO_4$: C, 15.5; H, 5.2; N, 18.1; F, 12.3; Cr, 16.8. Found: C, 15.9; H, 5.4; N, 18.1; F, 12.6; Cr, 16.6.

A 10^{-3} M aqueous solution of this complex had a molar conductance of 111 at 25° which indicated the complex to be a 1–1 electrolyte. The absorption spectrum of a 0.01 M aqueous solution was identical with that previously described for the *trans* complex.

A 1.0-g (0.0023-mole) sample of $[Cr(en)_2F(H_2O)](ClO_4)_2 \cdot H_2O$ was dissolved in *ca.* 3–4 ml of H_2O at room temperature, 4 drops of glacial acetic acid was added, and the solution was cooled in an ice bath to 5°. The starting complex precipitated as the solution was cooled. Solid sodium nitrite, 1.2 g (0.017 mole), was added to the solution and the precipitated starting material. The reaction mixture was kept in ice and stirred until everything dissolved. About 5 min after everything had dissolved, 1.2 g (0.01 mole) of solid anhydrous sodium perchlorate was added and the solution was stirred until dissolution was complete. The beaker and its contents were kept in ice for 2 hr after the addition of the sodium perchlorate. The orange crystals which had precipitated were collected by filtration, washed with acetone, and air dried. *Anal.* Calcd for $[Cr(en)_2ONOF]ClO_4 \cdot H_2O$: Cr, 14.7; C, 13.5; H, 5.1; N, 19.8; F, 5.4. Found: Cr, 14.2; C, 13.7; H, 5.1; N, 19.8; F, 5.4. A 10^{-3} M aqueous solution of this complex had a molar conductance of 124 at 25°. The hydrated complex was dried *in vacuo* over phosphorus pentoxide for 12 hr at room temperature. *Anal.* Calcd for $[Cr(en)_2ONOF]ClO_4$: C, 14.3; H, 4.8; N, 20.8; F, 5.7. Found: C, 14.1; H, 4.8; N, 20.7; F, 5.6. The ultraviolet–visible spectrum of this complex was determined in Eastman Spectro Grade dimethylformamide at room temperature.

Anion Replacement on Fluoroaquobis(ethylenediamine)chromium(III) Perchlorate Monohydrate.—An aqueous solution of fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate was treated with excess colorless, concentrated hydriodic acid and allowed to stand at room temperature. In a very short time orange crystals of $[Cr(en)_2(H_2O)F]I_2 \cdot 0.5H_2O$ precipitated. *Anal.* Calcd for $[Cr(en)_2(H_2O)F]I_2 \cdot 0.5H_2O$: C, 10.1; H, 4.0; N, 11.8; F, 4.0; I, 53.9; H_2O, 5.7. Found: C, 9.8; H, 4.0; N, 11.5; F, 4.2; I, 53.4; H_2O, 5.4.

A 10^{-3} M aqueous solution of this complex had a molar conductance of 259 at 25° which indicated the complex to be a 2–1 electrolyte. This complex did not lose its coordinated water when heated for several days at 110°, and there was essentially no loss of water of hydration after 16 hr at this temperature. Absorption spectra of the heated and unheated (110°) samples were virtually identical. However, the complex dehydrated to deep purple crystals when heated at 160–170° for 12 hr. This color change was accompanied by a 5.4% loss in weight.

Owing to the high solubilities of the corresponding chlorides and bromides in water, a slightly different method was used to replace the perchlorate ion. A solution of 2 g (0.0046 mole) of fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate in 15 ml of water was slowly (*ca.* 1 ml/min) passed through an anion-exchange column of Dowex 2-X8 (50–100 mesh, Cl^- form). The column was eluted with enough water to remove most of the red fraction. The effluent and its eluate were added to 500 ml of acetone; the fluffy pink precipitate was collected by filtration, washed with acetone followed by ether, and air dried. A final yield of 1.2 g or 87% of fluoroaquobis(ethylenediamine)chromium(III) chloride monohydrate was obtained. *Anal.* Calcd for $[Cr(en)_2F(H_2O)]Cl_2 \cdot H_2O$: Cl, 23.8; H_2O, 12.1. Found: Cl, 23.5; H_2O, 11.8.

The above anion replacement was repeated in exactly the same way except that the resin was in the bromide form. This procedure produced 1.5 g or 84% of fluoroaquobis(ethylenediamine)chromium(III) bromide monohydrate as a pink solid. *Anal.* Calcd for $[Cr(en)_2F(H_2O)]Br_2 \cdot H_2O$: Br, 41.3; H_2O, 9.30. Found: Br, 41.2; H_2O, 9.1.

The absorption spectrum of an aqueous solution of this complex was virtually identical with that of the initial perchlorate complex.

A somewhat more rapid method was used for the synthesis of $[Cr(en)_2F(H_2O)](SCN)_2$. A solution of 1 g (0.0023 mole) of $[Cr(en)_2F(H_2O)](ClO_4)_2 \cdot H_2O$ in 4–5 ml of water was acidified with 2 or 3 drops of 72% perchloric acid and treated with a saturated solution of potassium thiocyanate. It is imperative at this point that the thiocyanate solution contain enough potassium ion to precipitate all of the perchlorate as potassium perchlorate. The solution was cooled to 5° in ice and the insoluble potassium perchlorate was removed by filtration. The deep orange filtrate was treated with solid potassium thiocyanate to precipitate $[Cr(en)_2F(H_2O)](SCN)_2$. The orange solid was collected by filtration, washed with acetone, and air dried. To ensure that the final product was not contaminated with excess potassium thiocyanate, the solid was extracted three times with 30-ml portions of acetone and air dried prior to analysis. This method produced 0.250 g or 26% of an orange powder. *Anal.* Calcd for $[Cr(en)_2F(H_2O)](SCN)_2$: SCN, 35.7; H_2O, 5.5. Found: SCN, 35.2; H_2O, 5.4. A 10^{-3} M aqueous solution of this complex had a molar conductance of 221 at 25° which indicated a 2–1 electrolyte.

This synthesis has produced a few erratic results in that the final product is not always the anhydrous salt; however, we have never found more than 1 mole of occluded or hydrated water.

Sodium thiocyanate is not as good a precipitating agent as the potassium salt, for the compounds so prepared always gave very low values when analyzed for thiocyanate content, apparently owing to perchlorate contamination of the final product.

Synthesis of Complexes of the Type *cis*-$[Cr(en)_2FX]X$.—The same method was used for those complexes where X was chloride, bromide, iodide, or thiocyanate. Essentially the method employed was to remove the coordinated water molecule by heating the corresponding aquo compounds at 110–160°.

A weighed sample of fluoroaquobis(ethylenediamine)chromium(III) chloride monohydrate was heated at 125° for 6 hr. During this time the complex turned from a light pink to a deep purple and this was accompanied by a 11.8% loss in weight. *Anal.* Calcd for $[Cr(en)_2FCl]Cl$: Cr, 19.9; Cl, 27.10; C, 18.3; H, 6.1; N, 21.3; F, 7.3. Found: Cr, 19.4; Cl, 27.1; C, 18.1; H, 6.2; N, 21.2; F, 7.2. A 10^{-3} M aqueous solution of this complex had a molar conductance of 128 at 25°. This indicated the complex to be essentially a 1–1 electrolyte; however, the value of 128 for the molar conductance is slightly higher than that usually found for 1–1 electrolytes. This high value could possibly be due to some contamination of the product or rapid aquation of the complex. An aqueous solution of the complex had absorption maxima at 387 and 518 mμ; the molar absorptivities were 42.8 and 62.4 l. $mole^{-1}$ cm^{-1}, respectively.

This complex appeared to be hygroscopic when exposed to the air for short periods of time. A sample was exposed to the air and then analyzed. *Anal.* Calcd for $[Cr(en)_2FCl]Cl \cdot H_2O$: C, 17.2; H, 6.4; N, 20.0; F, 6.8. Found: C, 17.4; H, 6.3; N, 19.8; F, 6.5.

The above method was repeated with $[Cr(en)_2F(H_2O)]Br_2 \cdot H_2O$ except that the temperature was held at 155° for 8 hr. *Anal.* Calcd for $[Cr(en)_2FBr]Br$: Cr, 14.8; Br, 45.6; C, 13.7; H, 4.6; N, 16.0; F, 5.4. Found: Cr, 14.6; Br, 45.2; C, 14.0; H, 4.8; N, 15.7; F, 5.0. This material did not appear to be as hygroscopic as the FCl complex. An aqueous solution of the complex had absorption maxima at 381 and 512 mμ; the molar absorptivities were 37.6 and 61.2 l. $mole^{-1}$ cm^{-1}, respectively.

A sample of $[Cr(en)_2F(H_2O)](SCN)_2$ was heated for 8 hr at 110°. The complex turned from orange to reddish purple during this time, and there was a 5.4% loss in weight. *Anal.* Calcd for $[Cr(en)_2F(NCS)]SCN$: SCN, 37.7; C, 23.5; H, 5.2; F, 6.2. Found: SCN, 37.2; C, 23.2; H, 5.3; F, 6.1. Although this complex gave good elemental analysis, it appeared to contain a small amount of a material which was more water insoluble than the complex $[Cr(en)_2F(NCS)]SCN$. An aqueous solution of this complex had absorption maxima at 375 and 500 mμ; the molar absorptivities were approximately 52 and 85 l. $mole^{-1}$ cm^{-1}, respectively.

A weighed sample of $[Cr(en)_2(H_2O)F]I_2 \cdot 0.5H_2O$ was heated at 160–170° for 12 hr. During this interval, the solid changed from orange to deep reddish purple; this color change was accompanied by a 5.4% loss in weight. *Anal.* Calcd for $[Cr(en)_2FI]I$: C, 10.8; H, 3.6; N, 12.5; F, 4.3; H_2O, 5.7. Found: C, 10.8; H, 3.7; N, 12.4; F, 3.76; H_2O, 5.4.

Ion-Exchange Experiments with Fluoroaquobis(ethylenediamine)chromium(III) Perchlorate Monohydrate.—In an attempt to gain more information about the geometry of this complex, a solution of 0.425 g (0.001 mole) of the complex was placed on a column of Dowex 50W-X4 (50–100 mesh, H^+ form) and eluted with acid. There was no band movement when 50-ml portions of 0.3, 0.6, or 0.9 *N* acid were used to elute the column. When the acid concentration was increased to 1.2 *N* practically all of the material was eluted. The minimum acid concentration necessary to remove the complex completely from the column was 2.1 *N*. Absorption spectra of the eluted materials were the same as that of the original starting complex.

Reaction of *cis*-Chlorofluorobis(ethylenediamine)chromium(III) Chloride with Silver Ion.—In an attempt to provide more information about the geometry of the starting material, the following experiment was carried out. To a solution of 0.131 g (0.0005 mole) of chlorofluorobis(ethylenediamine)chromium(III) chloride in 30 ml of water at room temperature 1 ml of 72% perchloric acid and 0.209 g (0.0010 mole) of silver perchlorate were added. The solution was allowed to stand for 1 hr at room temperature before the silver chloride precipitate was removed by filtration. The blue-purple filtrate was diluted to 100 ml in a volumetric flask and the absorption spectrum was determined. In the ultraviolet–visible region this solution had absorption maxima at 376 and 506 mμ.

Resolution of Chlorofluorobis(ethylenediamine)chromium(III) Chloride.—To a filtered solution of 6.2 g (0.023 mole) of chlorofluorobis(ethylenediamine)chromium(III) chloride in 20 ml of water at 10° was added 4.0 g (0.012 mole) of solid *d*(+)-ammonium α-bromocamphor-π-sulfonate. The solution was stirred until dissolution was complete and the solution refiltered to remove a small amount of insoluble material. The solution was replaced in the ice bath and stirred frequently. After a period of 15 min had elapsed from the addition of the resolving agent, a precipitate began to form. The solution was kept in the ice bath for a total of 30 min before the crude diastereoisomer was collected and washed with acetone. This crude product weighed 1.39 g and had a specific rotation at 5461 Å of +338°.

The entire crude material was suspended in 4 ml of water at 5–10° and ground in a mortar in an ice bath for 5 min. The product was collected by filtration, washed with acetone, and air dried. This procedure produced 0.84 g of a product whose specific rotation at 5461 Å was +431°.

The entire product was suspended in 2 ml of water at 5–10° and reground for 5 min. At the end of this time, the product was collected by filtration, washed with acetone, and air dried. After the second grinding, 0.67 g of the product was recovered. This product had a specific rotation of +458° for a 0.1% solution at 5461 Å. The entire yield of optically active material was ground a third time with 1.5 ml of 5–10° water for 5 min. The product was collected, washed, and dried as described previously. At this point, 0.56 g of the product was recovered and the specific rotation for a 0.1% solution was 453° at 5461 Å. Since the specific rotations did not change appreciably between the second and third grindings, the sample was assumed to be optically pure and the treatment with cold water stopped. The material had a specific rotation of +155° for a 0.1% solution at the sodium D line. A sample was air dried prior to analysis. *Anal.* Calcd for $[Cr(en)_2FCl]C_{10}H_{15}O_4BrS \cdot 0.5H_2O$: C, 30.8; H, 5.9; N, 10.2. Found: C, 30.8; H, 5.6; N, 10.2.

To isolate *d*-*cis*-chlorofluorobis(ethylenediamine)chromium(III) bromide, 0.500 g of the purified diastereoisomer was ground for 5 min with a solution of 2 ml of 47% hydrobromic acid in 30 ml of absolute alcohol and filtered. The yield of purple dextrorotatory enantiomorph was 0.248 g.

The final product gave a specific rotation of +625° for a 0.1% solution at 5461 Å and +191° at the sodium D line. There was no loss of optical activity on heating a sample of the optically active material for 1 hr at 110°. *Anal.* Calcd for $[Cr(en)_2FCl]Br \cdot 0.25C_2H_5OH$: C, 17.0; H, 5.5; N, 17.6; Cl, 11.1; Br, 25.2; F, 6.0. Found: C, 17.2; H, 5.3; N, 17.3; Cl, 11.3; Br, 25.2; F, 5.9.

We were never able to obtain a product completely free of alcohol. The resolution was repeated using the noncoordinating perchlorate ion in place of bromide with the same results.

For 0.05% aqueous solutions of *d*-*cis*-chlorofluorobis(ethylenediamine)chromium(III) bromide, the half-times for loss of optical rotation were 72 ± 3 min at room temperature.

Analytical Methods and Instrumentation.—All microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Chromium was determined by oxidation to dichromate with a boiling nitric acid–perchloric acid mixture. The dichromate was titrated with a standard iron(II) solution to the ferroin end point.

Optical rotations were taken on a Bendix-Ericsson U.K. Ltd. Type 143A ETL-NPL automatic polarimeter coupled to a Sargent SR $^1/_4$% recorder. Appropriate interference filters were used to isolate the desired wavelengths and all measurements were at room temperature. Syringe-type cells with 40-mm path lengths were used.

Ultraviolet–visible spectra were obtained on either a Beckman DU or a Cary 14 instrument using matched cells. The dimethylformamide was Eastman Spectro Grade and was used without further purification.

Infrared spectra were determined by the KBr pellet method on a Beckman IR-8 spectrophotometer.

X-Ray data were obtained on a Norelco unit using a 114.59-mm diameter camera. All samples were contained in sealed glass capillaries, and the exposure conditions were: molybdenum tube, zirconium filter, 45 kv, and 18 ma for 4 hr. Relative intensities were estimated visually.

Results and Discussion

The reaction of chromium(III) chloride hexahydrate, hydrofluoric acid, and ethylenediamine in aqueous solution was utilized to prepare, as the major product, *trans*-difluorobis(ethylenediamine)chromium(III) chloride. Dahme utilized this reaction under slightly different conditions, more rapid addition of reagents, shorter evaporation times, and different acid concentrations, to prepare what he identified as fluorohydroxobis(ethylenediamine)chromium(III) chloride. In addition to the *trans* complex, the reaction yields at least one minor product which we have not identified at the present time.

The assignment of the *trans* structure is well supported by the visible absorption spectrum which is markedly different from that of the corresponding *cis* isomer. Further, the *trans* isomer can be eluted from a cation-exchange resin with 0.3 *N* perchloric acid while the *cis* isomer is known[7] to require the use of 0.6 *N* acid.

Although the *trans* complex gave a good elemental analysis, the product obtained from the synthesis was shown by ion-exchange methods to be slightly impure. From a consideration of the visible absorption spectrum of what appeared to be the major impurity and the observation that 0.6 *N* acid was necessary to elute this material from an ion-exchange column, it would appear that this substance could well involve a *cis* arrangement of the monodentate ligands. However, the visible absorption spectrum of this impurity is not identical with that of an authentic sample of the *cis*-difluorobis(ethylenediamine)chromium(III) cation.

The *cis–trans* isomers of difluorobis(ethylenediamine)-chromium(III) iodide differ slightly in color, with the *cis* arrangement being slightly reddish purple while the *trans* form is more orange. As would be expected for *cis–trans* isomers, solubility differences exist in aqueous solution with the iodide of the *trans* complex exhibiting a lower solubility than the corresponding *cis* material.

The reaction of *trans*-difluorobis(ethylenediamine)-chromium(III) chloride with 72% perchloric acid at room temperature produces fluoroaquobis(ethylenediamine)chromium(III) perchlorate monohydrate. In the presence of a noncoordinating anion such as the perchlorate ion, the fluoroaquo complex does not undergo complete fluoride release in 12–18 hr at room temperature; however, if the complex is dissolved in concentrated hydrochloric or hydrobromic acid which does contain coordinating anions, the complex undergoes complete fluoride replacement to yield the corresponding *trans*-dichloro- or dibromobis(ethylenediamine)chromium(III) perchlorates in the same length of time. The more insoluble perchlorates are formed rather than the chlorides or bromides although the over-all chloride or bromide concentrations are much higher than that of the perchlorate ion.

From the evidence currently available in this study, it would appear that the replacement of a single fluoro ligand in *trans*-difluorobis(ethylenediamine)chromium-(III) chloride takes place largely if not completely with retention of geometric configuration.

(1) The information obtained by eluting the fluoroaquobis(ethylenediamine)chromium(III) ion from a cation-exchange column strongly indicates a *trans* arrangement of the fluoro and aquo ligands. The complex could be eluted completely from the resin with 50 ml of 2.1 *N* perchloric acid. Other investigators[8] have shown that the *cis* isomer should not elute until the perchloric acid concentration reaches 3 *N*.

(2) The ultraviolet–visible absorption spectrum of the fluoroaquobis(ethylenediamine)chromium(III) ion in aqueous solution contains the three absorption bands characteristic of a *trans* complex.

(3) The acid hydrolysis of *cis*-chlorofluorobis(ethylenediamine)chromium(III) chloride in the presence of Ag(I) produced a product whose absorption spectrum contained only two absorption bands which were widely separated from the peaks in the fluoroaquo complex prepared from the *trans*-difluoro complex.

Assuming on the basis of the preceding evidence that the fluoroaquo complex prepared by acid hydrolysis of the *trans*-difluoro compound does have a *trans* arrangement of the monodentate ligands, the new complex fluoronitritobis(ethylenediamine)chromium(III) perchlorate involves probably a predominantly *trans* arrangement of the fluoro and nitrito groups. This point is supported by the fact that other workers have shown that the reaction of a monoaquo complex of chromium(III) with nitrite ion and acid in buffered solution yields the corresponding nitrito complex with at least 80% of the original chromium–oxygen bonds[9] remaining intact.

In the case under consideration the ambidentate nitrite ligand is in all probability oxygen rather than nitrogen bonded to the chromium(III). Chromium-(III) is an avid oxygen acceptor and bonds more readily to oxygen than nitrogen. The preference of Cr(III) to O rather than N bond is also illustrated by the fact that nitro complexes of Cr(III) have yet to be prepared.[10]

Further, the solution electronic spectrum of $[Cr(en)_2ONOF]ClO_4$ in dimethylformamide at room temperature exhibits considerable vibrational fine structure in the 350–400-mμ region. This vibrational fine structure was first noted by Fee, Garner, and Harrowfield as being characteristic of O rather than N bonding of the NO_2^- ligand. Thus, it would appear that the complex $[Cr(en)_2ONOF]ClO_4$ involves O-bonded nitrite.

The new complexes of the type $[Cr(en)_2FX]^+$ ($X^- = Cl^-, Br^-, I^-, NCS^-$) prepared in this investigation all appear to have the same geometric configuration. In the case of the $[Cr(en)_2FCl]^+$ ion the arrangement of the fluoro and chloro ligands was shown to be unequivocally *cis* since the complex could be resolved into its optical antipodes. The *cis* structure of those complexes where $X^- = Br^-$, I^-, or NCS^- is supported by their similar colors and absorption spectra. In the region of 330–700 mμ in aqueous solution all of these complexes exhibit the two absorption bands characteristic of a *cis* complex.

There are at least two possible ways in which a *cis* product can result from the thermal dehydration of the *trans*-fluoroaquobis(ethylenediamine)chromium-(III) cation. One possibility is the removal of the aquo ligand to produce a five-coordinate square-pyramidal intermediate which then interacts with the incoming anion to yield a *trans* product. This *trans*

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

(8) K. R. A. Fehrmann and C. S. Garner, *ibid.*, **83** 1276 (1961)

(9) R. K. Murmann and H. Taube, *ibid.*, **78**, 4886 (1956).

(10) W. W. Fee, C. S. Garner, and J. N. M. Harrowfield, *Inorg. Chem.*, **6**, 87 (1967).

product is thermally unstable and isomerizes under the reaction conditions to produce what may well be the more stable *cis* product. A second route to the observed product involves collapse of the original *trans*-octahedral structure to a trigonal-bipyramidal intermediate. This intermediate is considered to have the fluoro ligand in an apical position and one of the ethylenediamine ligands in the trigonal plane. The remaining apical and trigonal positions are occupied by the second ethylenediamine molecule.

After the collapse of the octahedron the entering anion attacks in the trigonal plane of the intermediate to produce a *cis* product. At the present time it is not possible to prove or disprove either of the proposed routes to the final product. However, we are currently investigating various synthetic approaches to complexes of the type *trans*-$[Cr(en)_2FX]^{n+}$ which should shed some light on the nature of the intermediates involved in the synthesis of the *cis* complexes.

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The Crystal and Molecular Structure of the High-Spin Square-Planar Complex Triphenylmethylarsonium Bis(toluene-3,4-dithiolato)cobaltate–0.5-Ethanol

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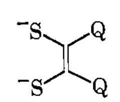
The crystal and molecular structure of the high-spin complex triphenylmethylarsonium bis(toluene-3,4-dithiolato)cobaltate–0.5-ethanol, $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. The structure has been refined by least-squares procedures to a conventional R factor of 0.063 for 1108 nonzero reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system with two molecules in a unit cell of dimensions $a = 18.61 \pm 0.01$, $b = 10.848 \pm 0.006$, $c = 10.206 \pm 0.005$ Å, $\alpha = 112.45 \pm 0.02°$, $\beta = 71.55 \pm 0.02°$, $\gamma = 115.90 \pm 0.02°$, and $V = 1685.4$ Å^3. An observed density of 1.359 ± 0.010 g/cm^3 is in excellent agreement with the calculated value of 1.355 g/cm^3 for $Z = 2$. The $Co(tdt)_2^-$ anions are crystallographically required to have centers of symmetry since the two cobalts per unit cell occupy the (0, 0, 0) and ($^1/_2$, 0, $^1/_2$) special positions of the space group. The S_4 coordination about the cobalts is very nearly square planar with average intra- and interligand S–S distances of 3.098 and 3.028 Å, respectively, and estimated standard deviations for these values of 0.007 Å. The planar $Co(tdt)_2^-$ anions have an ordered *trans* configuration of the tdt ligand methyl groups and thus possess C_{2h} symmetry. The $(C_6H_5)_3(CH_3)As^+$ cation has its expected tetrahedral geometry about arsenic. Ethanol solvent molecules were trapped during crystallization of the complex, presumably because of the asymmetric nature of the cation. These solvent molecules are disordered about the (0, $^1/_2$, 0) center of symmetry with only one molecule per unit cell. Thus, the crystal structure of the complex consists of the packing of essentially planar anions, bulky cations, and trapped solvent molecules. The anions are well separated and exhibit none of the magnetic interactions which characterize the structures of the other related mononegative bis complexes. A ground-state electronic structural assignment for the spin-triplet $Co(tdt)_2^-$ complex is proposed on the basis of molecular orbitals calculated for a closely related nickel complex using the observed structural parameters.

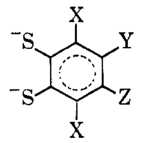
Introduction

The bidentate sulfur-donor ligand systems of types I and II have been found to be excellent stabilizers of the square-planar geometry for a wide variety of metals and ground-state configurations.[2] Although we show I and II in their classical dianion formulation, it is clear from electronic and molecular structural studies that these ligand systems coordinate to form unsaturated five-membered metal–chelate rings in which π bonding plays an important stabilizing role. Complexes of the four ligand systems maleonitriledithiolate (mnt, I with Q = CN), *cis*-stilbenedithiolate ($S_2C_2(C_6H_5)_2$), *cis*-1,2-bis(trifluoromethyl)ethylenedithiolate ($S_2C_2(CF_3)_2$), and toluene-3,4-dithiolate (tdt, II with X = Y = H, Z = CH_3) have received particular attention in these studies.



Q = CH, CF_3, C_6H_5, CH_3, H

I



X = Y = Z = H, CH_3, Cl
X = Y = H, Z = CH_3
X = H, Y = Z = CH_3

II

The considerable interest and activity which de-

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[2] Four of the more recent papers dealing with the synthesis, characterization, and electronic structural properties of the bis square-planar complexes and their oxidation–reduction reactions are: (a) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965); (b) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966); (c) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966); (d) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967). References to earlier studies in this field are given therein.