137 spectrometer using NaCl optics. Nujol mulls and KBr disks were employed in determining these spectra.

Conductivity Measurements.—Conductivity determinations were performed using an Industrial Instruments Model 16B2 conductivity bridge. Molar conductivities were determined at 25° and concentrations of $10^{-3}\ M$.

Paper Chromatography.—Paper chromatograms were obtained according to the method of Stefanovic and Janjic[7] using 1 × 12 in. strips of Whatman No. 1 chromatography paper. The eluting solution consisted of concentrated HCl in water-saturated 1-butanol (5 ml of concentrated HCl/100 ml of solution).

Results and Discussion

Two isomers of $[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$ have been isolated and characterized. The green isomer, which shows only one spot with paper chromatographic separation, has been assigned the *trans* configuration on the basis of its visible absorption spectrum. In its visible spectrum there is a maximum at 623 mμ and a shoulder at 410 mμ having extinction coefficients of 35.2 and 35 $M^{-1}\ \mathrm{cm}^{-1}$, respectively. These values compare well with the spectra for the *trans* isomers of the corresponding en, trien, and cyclam complexes as shown in Table I.

TABLE I

VISIBLE SPECTRAL DATA

Complex	λmax, mμ	ε, M^{-1} cm^{-1}	λmax, mμ	ε, M^{-1} cm^{-1}
trans-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$[a]	625	34.7	450	25.2
trans-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$[b]	615	36.3	454	33.9
trans-$[\mathrm{Co(cyclam)Cl_2}]\mathrm{Cl}$[c]	635	32	435	42
trans-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$	623	35.2	410[e]	35
cis-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$[a]	540	100	390	77.6
cis-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$[d]	540	105	379	87.1
cis-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$	540	103	390[e]	85

[a] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950). [b] See ref 4. [c] See ref 1. [d] E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1120 (1966). [e] Observed as shoulders.

The other isomer, which is violet in color, is assigned the *cis* configuration. This isomer was formed in small yields from what is believed to be the carbonato complex. The visible spectrum of the *cis* isomer displays a maximum at 540 mμ having an extinction coefficient of 103. An additional shoulder is observed at 390 mμ. As indicated in Table I, these values are also in line with corresponding data for analogous *cis* complexes.

Additional evidence concerning the configurations of these complexes has been obtained through study of their infrared spectra. As with the octahedral complexes of trien, beap should give rise to *trans*, *cis*-α, and *cis*-β isomers. Since the differences in the two ligands are slight, they would be expected to yield very similar infrared spectra when coordinated in the same configuration. This expected similarity is borne out for the *trans* isomers. As with *trans*-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$,[8] *trans*-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$ displays four absorption bands in the N–H stretching region of 3000–3300 cm^{-1} and yields only one band at 1600 cm^{-1} resulting from an $\mathrm{NH_2}$ bending mode. The *cis* complex isolated in this study has an infrared spectrum quite similar to the *cis*-α trien complex and on this basis we have reason to believe the complex is of the *cis*-α configuration. Major factors which lead to assigning this structure include the presence of only three sharp absorptions in the N–H stretching region, the presence of only one band at 1600 cm^{-1}, and the presence of two strong absorptions in the region 990–1090 cm^{-1}. The positions and intensities of these bands correspond to those of *cis*-α trien complex and are in contrast to the spectrum of the *cis*-β trien complex where 4, 2, and 4 bands populate the respective areas.[8]

It is of interest to consider relative stabilities of the *cis*- and *trans*-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$ isomers. Preparation of the dichloro complex by conventional air oxidation proceeds with exclusive formation of the *trans* isomer. All attempts to prepare the *cis* complex by prolonged heating of an aqueous solution of the *trans* isomer have been unsuccessful. This behavior parallels that of the corresponding cyclam complex[1] and is in strict contrast to the behavior of the trien system. In methanolic solution isomerization of *cis*-α-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$ to the *trans* isomer proceeds to completion proving the greater stability of the *trans* isomer. Although, it is apparent that the *trans* configuration is preferred for beap complexes, the stereospecificity is not so pronounced as in the cyclam case since Bosnich, *et al.*,[1] unsuccessfully attempted to prepare *cis* cyclam complexes using methods quite similar to ours for *cis*-α-$[\mathrm{Co(beap)Cl_2}]\mathrm{Cl}$. The close similarity between the beap and cyclam systems and the marked divergence of the beap and trien systems suggest that the nature of the group(s) bridging the ethylenediamine residues, rather than linear or macrocyclic character, determines the stereochemistry.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Fluoro-Containing Complexes of Chromium(III). II. The Reaction of Sodium Tetrafluoroethylenediaminechromate(III) Monohydrate with Ethylenediamine[1]

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The anion tetrafluoroethylenediaminechromate(III) was first prepared by Dahme[2,3] in 1957 and isolated as

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[1] For the first paper in this series, see J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, **4**, 1077 (1965).

[2] W. Dahme, Thesis, Bergakademie Clausthal, 1957.

[3] "Gmelins Handbuch der Anorganischen Chemie," Chrom, Part C, Vol. 52, 1965, p 274.

either $Na[Cr(en)F_4]\cdot 0.5NaClO_4$ or $(en\text{-}H_2)[Cr(en)F_4]ClO_4$. While this paper was in preparation, House and Garner[4] reported the isolation and characterization of ammonium tetrafluoroethylenediaminechromate(III).

This anion is of interest since its stereochemistry is such that it could possibly serve as a starting point for the synthesis of presently unknown fluoro complexes of Cr(III). Most of the previous work with this anion was concerned with its characterization and not with its application to synthetic chemistry. However, House and Garner reported that the anion is slowly aquated in dilute acid at 25° and Dahme[5] used $Na[Cr(en)F_4]\cdot 0.5NaClO_4$ to prepare $[Cr(en)(OH_2)_2F_2]Cl$ by adding the sodium salt to a 1:1 solution of hydrochloric acid at $-5°$.

The major purpose of this investigation was to study the reaction of sodium tetrafluoroethylenediaminechromate(III) monohydrate with ethylenediamine under different conditions. Since previous work in this laboratory[1] was concerned with the synthesis and characterization of *cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$, part of the present research dealt with the isolation of the complex anion from this double salt.

Experimental Section

Isolation of Sodium Tetrafluoroethylenediaminechromate(III) Monohydrate.—The double complex $[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ was prepared as described previously[1] and air dried but not recrystallized. Recrystallization was omitted since the complex always occludes some hydrofluoric acid when recrystallized from aqueous hydrofluoric acid solution, and, further, the anion hydrolyzes to some extent under these conditions.

A 1.0-g (2.1×10^{-3} mole) sample of the crude product was dissolved in 15 ml of water at room temperature and passed through an ion-exchange column of Dowex 50W-X4 (sodium form, 20–50 mesh) at the rate of 1.5–2 ml/min. Elution was with one column volume of distilled water. The blue eluate was collected in one fraction and added with constant stirring to 150 ml of ice-cold acetone. The acetone solution turned cloudy and the turbid solution was kept in an ice bath for an additional 15 min. At the end of this time, the flocculant blue precipitate was filtered off, washed with 15 ml of acetone, and sucked dry. The formation of a precipitate does not always occur, and sometimes the product will form an oil. However, crystallization can be induced by grinding the oil with fresh acetone.

The product was somewhat gummy after filtration and a lumpy solid resulted when the product was dried for 1 hr at 110°. The solid was pulverized and dried for an additional 12 hr. The yield of final product was 0.300 g (68% based on the double complex) of a blue powder. *Anal.* Calcd for $Na[Cr(en)F_4]\cdot H_2O$: C, 10.48; H, 4.36; N, 12.2; Cr, 22.7. Found: C, 10.71; H, 4.36; N, 11.8; Cr, 22.9.

A sample of this material was ion exchanged a second time through an identical column, and a small red unknown fraction was retained on the column.

Conductance measurements on a 10^{-3} M aqueous solution of the sodium salt at 25° gave a molar conductance of 100 which is well within the range of a 1–1 electrolyte.

The molar absorptivities of a 10^{-2} M aqueous solution at the wavelengths of maximum absorption, 572 and 412 mμ, are 34.0 and 18.5 M^{-1} cm^{-1}, respectively.

Several attempts were made to determine the equivalent weight of the sodium salt by passing the compound through an ion-exchange column in the hydrogen form and potentiometrically titrating the eluant with standard base. The equivalent weights determined in this manner ranged from 190 to 200, and a red fraction was always retained on the column. This fraction was eluted with cold perchloric acid–water (1 ml of 72% perchloric acid–1 ml of water) and its absorption spectrum determined. The spectrum was not the same as that of $[Cr(en)_2F_2]^+$.

X-Ray powder data on the sodium salt indicated sodium fluoride to be present [d (A), I/I_0]: NaF: 2.33, 100; 1.64, 90; 1.33, 50; 1.16, 15; 1.04, 40; 0.95, 40; $Na[Cr(en)F_4]\cdot H_2O$: 4.78, 100; 3.79, 25; 3.39, 10; 2.71, 5; 2.26, 50; 2.09, 50; 1.81, 20; 1.60, 10; 1.32, 5.

Reaction of Sodium Tetrafluoroethylenediaminechromate(III) Monohydrate with Ethylenediamine.—A 0.76-g (3.3×10^{-3} mole) sample of sodium tetrafluoroethylenediaminechromate(III) monohydrate was placed in a glass ampoule of 30-ml volume and 1.75 g (2.9×10^{-2} mole) of anhydrous ethylenediamine was added. The loaded ampoule was frozen in liquid nitrogen, sealed under vacuum, placed inside a high-pressure stainless steel bomb, and heated for 36 hr at 150°. At the end of this time the ampoule was opened and the product washed onto a filter with absolute alcohol. The pasty material was washed several times with absolute alcohol, followed by acetone and finally by ether. The final product was dried at 110° for 2 hr. *Anal.* Calcd for $[Cr(en)_2F_2][Cr(en)F_4] + 2NaF$: Cr, 21.6. Found: Cr, 21.6.

The presence of the cation, difluorobis(ethylenediamine)-chromium(III) was confirmed by dissolving 100 mg of the double complex in 6 drops of water acidified with 1 drop of 48% hydriodic acid and precipitating the product as the iodide with absolute alcohol. The final product was dried for 24 hr at 110°. *Anal.* Calcd for $[Cr(en)_2F_2]I$: C, 14.2; H, 4.75; F, 11.2; I, 37.7. Found: C, 14.4; H, 4.96; F, 10.9; I, 38.2.

The *cis* configuration of the cation was established by the following methods. (1) The physical properties were the same as that of an authentic sample of *cis*-difluorobis(ethylenediamine)-chromium(III) iodide. (2) A weighed sample (50 mg) was dissolved in 10 ml of water and passed over a column of Dowex 50W-X4 (20–50 mesh, H^+ form) and eluted with one column volume of water. The blue eluate was diluted to 25 ml with water and the absorption spectrum was determined. This spectrum was essentially identical with that of the tetrafluoroethylenediaminechromate(III) ion. The column was then eluted with 150 ml of 0.3 F perchloric acid followed by 150 ml of 0.6 F perchloric acid. The eluate was completely colorless when the column was eluted with the 0.3 F acid and the red fraction did not move off the column until the acid concentration was raised to 0.6 F. This was taken to indicate that the *trans* isomer was not present in the complex.[6]

The anion–cation ratio in the complex was established in the following manner. A 50-mg sample of the double complex was passed over a column of Dowex 2X-8 (20–50 mesh, Cl^- form); the eluate was diluted to 25 ml and the absorption spectrum was determined. Another 50-mg sample was passed over Dowex 50W-X4 (20–50 mesh, Na^+ form); the eluate was diluted to 25 ml and the absorption spectrum was determined. Calculations based on the spectral data indicated that the anion–cation ratio in the double complex was 1.031:1.

A 1.0-g (4.3×10^{-3} mole) sample of sodium tetrafluoroethylenediaminechromate(III) monohydrate was heated with a large excess of dry ethylenediamine on a steam bath for 18 hr. The product was treated as described previously and the ion-exchange procedures were repeated. The reaction proceeded in the same way as described previously but the anion–cation ratio was 2.4:1, which would indicate incomplete reaction. Again it was not possible to detect the presence of any *trans* isomer.

Analytical Methods and Instrumentation.—All microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Chromium was determined by first oxidizing the Cr(III) to dichromate with hot perchloric acid followed by titration with standard Fe(II) solution to the ferroin end point.

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(4) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).

(5) Reference 3, p 208.

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

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. Absorption spectra were obtained on a Beckman DU spectrophotometer using matched 1-cm quartz cells.

Discussion

The formula of the sodium salt, $Na[Cr(en)F_4]\cdot H_2O$, is consistent with that of a compound derived from the double complex, $[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$. Since the sodium salt was isolated as a hydrate, this would indicate the complex anion is the group which contains the water of hydration in the double complex.

The formation of the red cationic species in the ion-exchange experiments, the presence of sodium fluoride in the final product, and the low equivalent weights all appear to be due to hydrolysis of the anion during the exchange reactions. Previous work in this laboratory has shown aqueous solutions of $[Cr(en)_2F_2]I$ to be sufficiently stable toward hydrolysis not to cause these effects.

The molar absorptivities of $Na[Cr(en)F_4]$ at the wavelengths of maximum absorption are roughly half that of *cis*-$[Cr(en)_2F_2]I$ at its maximum. The value at 572 mμ (34.0 M^{-1} cm^{-1}) agrees with the 32.9 M^{-1} cm^{-1} found by House and Garner for the corresponding ammonium salt; however, the values at the "blue" peak differ by 4 units with the value obtained in this investigation the larger.

The reaction of sodium tetrafluoroethylenediaminechromate(III) monohydrate with excess dry ethylenediamine at 150° produces the double complex, *cis*-difluorobis(ethylenediamine)chromium(III) tetrafluoroethylenediaminechromate(III). This reaction can be described by the equation

$$2Na[Cr(en)F_4]\cdot H_2O + en \longrightarrow [Cr(en)_2F_2][Cr(en)F_4] + 2NaF + 2H_2O$$

The double complex has a very low solubility in anhydrous ethylenediamine and this would appear to be one reason the reaction does not proceed beyond this point.

If the reaction of the sodium salt with ethylenediamine followed simple statistics the reaction product should contain 80% *cis* and 20% *trans* isomer. However, it was not possible to detect the presence of any *trans* isomer in the product. One possible explanation for the lack of the *trans* isomer is that the *trans* product isomerized during the reaction.

Another explanation is based on the fact that the fluoro groups are not equivalent in the starting material. In the complex anion two of the fluoro ligands are *trans* to each other and the other pair is *cis* to each other but *trans* to the nitrogen of the ethylenediamine. Hence, these ligands are not necessarily equally labile. If rearrangement does not occur during reaction, then the replacement of two fluoro ligands by ethylenediamine involves one fluoro group from each nonequivalent pair.

The reaction proceeds in the same fashion at steam bath temperatures so the more drastic conditions employed in the bomb reaction are not responsible for the nature of the final product. Hence, the same effect or combination of effects is operating in both cases.

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The 1,5-Cyclooctadiene Complex of Copper(I) Perchlorate

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Olefinic and acetylenic hydrocarbons are known to form complex compounds with copper(I) chloride and copper(I) bromide.[1] A great deal of interest has recently been shown in the use of cyclic olefins as ligands in copper(I) complexes.[2-5] Methods for synthesizing a number of cyclic olefin complexes of CuCl and CuBr have been reported.[4]

The cyclic olefin complexes of CuCl and CuBr are not very stable. It has been noted[4] that the "relatively stable" ones may be stored at 0° in an inert atmosphere over calcium sulfate. This instability is probably due in part to the strong complexation of copper(I) by halide ions. Even in acetonitrile, a solvent which specifically solvates copper(I),[6] the over-all formation constant[7] of $CuCl_2^-$ is 10^{10}.[8] It is apparent, therefore, that in solution in a halide medium (and presumably in the solid state as well) halide ions compete very strongly with olefins for the copper(I) ligand sites.

We have succeeded in preparing the 1,5-cyclooctadiene (cyc) complex, $Cu(cyc)_2ClO_4$, of copper(I) perchlorate by electrolysis at copper electrodes of a solution containing copper(II) perchlorate and cyc in methanol. The cyc in solution stabilizes the +1 oxidation state of copper so that the reaction at the cathode is $Cu^{2+} + 2cyc + ClO_4^- + e = Cu(cyc)_2ClO_4\downarrow$ and the anode reaction is $Cu + 2cyc + ClO_4^- = Cu(cyc)_2ClO_4\downarrow + e$.

The complex is moderately soluble (*ca.* 5×10^{-3} M) in acetone. The voltammetric behavior of the compound was studied in this solvent in order to determine the formula and stability of the Cu(I)–cyc complex ion in acetone solution. The rotating platinum electrode was used for the voltammetric studies because

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