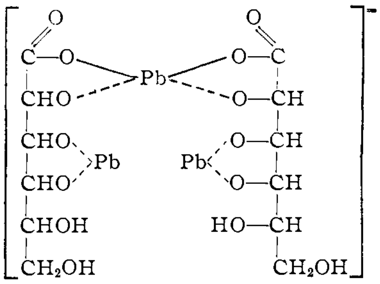
has been determined from polarographic data at ionic strengths from 3.0 to 0.15. The equation

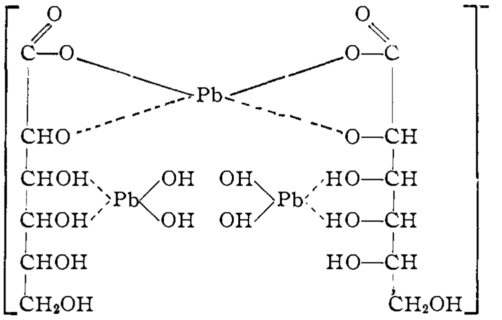
$$pK = \frac{(E_{1/2})_c - (E_{1/2})_s}{-0.02957} - \log\left(C_{GH_4^-} + \frac{C_{complex}}{2}\right)(OH^-)^2 + \log\frac{(i_d)_s}{(i_d)_c} \quad (14)$$

may be used to determine the pK for reaction 13.[2a] Five determinations of the pK were made in each case. The average pK value and the standard deviation is: $\mu = 3.0$, $pK = 16.39 \pm 0.05$; $\mu = 2.0$, $pK = 16.26 \pm 0.03$; $\mu = 1.0$, $pK = 16.17 \pm 0.05$; $\mu = 0.55$, $pK = 16.09 \pm 0.05$; $\mu = 0.30$, $pK = 15.92 \pm 0.06$; $\mu = 0.15$, $pK = 15.71 \pm 0.09$.

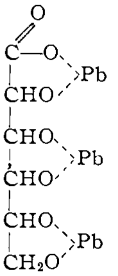
Probable Structure.—The evidence presented above suggests the following types of structures for the 3:2 complex present at pH 11.5. The state of hydration cannot be determined from our data.



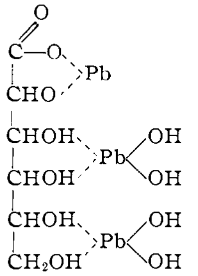
or



The most probable structure of the 3:1 solid which precipitates at pH 11.5 is



or



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Synthesis and Properties of Some Fluoro-bis-(ethylenediamine)-cobalt(III) Complexes[1-3]

BY WILLIAM R. MATOUSH AND FRED BASOLO

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A somewhat different approach to the synthesis of fluoroamminecobalt(III) salts is presented. Preparation of five new complexes is described and the isolation of optically active compounds containing a metal–fluoride bond is reported for the first time. Isolation of such optically active forms provides a proof of structure for three different pairs of geometric isomers. Reactions of *dextro*-$[Coen_2F_2]^+$ give no evidence for a Walden inversion type reaction as is known for *levo*-$[Coen_2Cl_2]^+$.

Extensive investigations[4] have been carried out on the synthesis and properties of chloroamminecobalt(III) complexes, whereas relatively few[5] studies are reported on the corresponding fluoro compounds. However, the role of fluoride ion in these complexes is of interest with regard to metal-ligand bonding in coördination compounds.[6] Magnetic data suggest that the cobalt(III)–fluoride bond is "ionic" in $[CoF_6]^{-3}$ but "covalent" in partially substituted cobalt(III) ammines. Except for the fact that the latter complexes are diamagnetic, little is known about the nature of the Co–F bond in these compounds. It is, therefore, the purpose of this paper to describe some of the properties of fluoro-bis-(ethylenediamine)–cobalt (III) complexes with specific reference to methods of synthesis, reactions and resolution of *racemic* compounds.

Experimental

Preparation of Compounds.—The fluoro-bis-(ethylenediamine)–cobalt(III) salts were generally prepared from the corresponding chloro or carbonato complexes. These starting materials were synthesized by standard procedures described in the literature.[4]

***trans*-Difluoro-bis-(ethylenediamine)-cobalt(III) Salts.**—The method of Seibt[5a] was used to prepare the bifluoride salt of this complex. However, large quantities of this com-

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[1] Previous communication, W. R. Matoush and F. Basolo, THIS JOURNAL, **77**, 1072 (1955).

[2] Investigation supported by a National Science Foundation Grant (NSF-G58) and in part by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

[3] Presented in part at the International Conference on Coördination Compounds in Amsterdam, April, 1955.

[4] "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie G. M. B. H., Berlin, 1930, Vol. 58B, pp. 1–376.

[5] (a) H. Seibt, Dissertation University of Zurich, 1913; (b) M. Linhard and M. Weigel, *Z. anorg. allgem Chem.*, **271**, 101 (1952).

[6] (a) W. C. Fernelius, *Rec. Chem. Progr.* (*Kresge Hooker Sci. Lib.*), **2**, 17 (1950); (b) H. Taube, *Chem. Revs*, **50**, 69 (1952); (c) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

pound were obtained by the procedure described here. A suspension of 125 g. of cobalt(II) carbonate in 1 l. of water in a polythene container was treated with 100 ml. of 48% hydrofluoric acid. This mixture was heated on a steam-bath until evolution of carbon dioxide subsided and then 6 l. of water was added and the heating continued. After the cobalt(II) fluoride had largely dissolved, the solution was cooled to room temperature and 400 ml. of 20% ethylenediamine was added. Air was bubbled through the solution for 12 hr. after which 150 ml. of 48% hydrofluoric acid was added and the solution then concentrated to dryness on a steam-bath. The solid residue was further dried in an oven at 85° and then extracted with small (100 ml.) portions of water. Addition of alcohol, acetone and ether to the aqueous extracts fractionally precipitated a small quantity of cobalt(II) fluoride followed by the desired *trans* salt. When collected on a filter, washed with alcohol and air-dried, the product weighed 105 g. (39% yield).

Anal. Calcd. for $[\mathrm{Coen_2F_2}]\mathrm{HF_2}$: ionic F, 14.84; total F, 29.67. Found: ionic F, 15.3; total 30.1.

The bifluoride was readily converted to the nitrate by the addition of an excess of ammonium nitrate to a concentrated solution of the bifluoride. The nitrate was collected on a filter and recrystallized by dissolving it in a minimum amount of water and slowly adding methanol to the cold solution.

Anal. Calcd. for $[\mathrm{Coen_2F_2}]\mathrm{NO_3}$: Co, 21.14; C, 17.20; H, 5.79; N, 25.09; F, 13.62. Found: Co, 21.0; C, 17.68; H, 5.81; N, 25.77; F, 13.45.

The *trans*-nitrate salt was also prepared by the reaction of 14 g. of *trans*-$[\mathrm{Coen_2Cl_2}]\mathrm{NO_3}$ suspended in 150 ml. of 1:2 methanol–hydrofluoric acid with 15 g. of silver carbonate. The cold (−70°) reaction mixture was allowed to reach room temperature and during this period of 30 min. the color changed from green to violet. Silver chloride was removed on a hardened filter paper using a polythene funnel. The filtrate was collected in 1 l. of ether cooled by the addition of Dry Ice. The precipitate that formed, essentially a mixture of *cis*- and *trans*-difluoro salts, was collected on a filter. These solids were then dissolved in a minimum amount of water and excess solid ammonium nitrate was added. Fractional crystallization was carried out by the gradual addition of methanol, acetone and ether. A yield of 6 g. of *trans*-$[\mathrm{Coen_2F_2}]\mathrm{NO_3}$ was obtained in the less soluble fraction and 5 g. of *cis* isomer in the more soluble fraction.

***cis*-Difluoro-bis-(ethylenediamine)-cobalt(III) Salts.**—The rearrangement of *trans*-$[\mathrm{Coen_2F_2}]\mathrm{F}$ into the *cis* isomer described by Seibt[5a] has been adapted to the synthesis of salts of this complex. An aqueous solution containing 40 g. of *trans*-$[\mathrm{Coen_2F_2}]\mathrm{HF_2}$ was evaporated almost to dryness on a steam-bath. Sufficient water was added to dissolve the residue and the solution was again concentrated almost to dryness. It was necessary to repeat this process a number of times in order to get an appreciable conversion of the *trans* isomer to the *cis* salt, as many as six such evaporations being required. The tacky mass of solid was then extracted with 10 ml. of cold water and the undissolved *trans* isomer was removed on a filter. Addition of alcohol and acetone to this filtrate yielded first, residual *trans* isomer and then the desired *cis* salt. Following the appearance of the reddish-pink *cis* salt, the remaining mother liquor was treated with an excess of a methanol solution of ammonium nitrate, thereby yielding a precipitate of *cis* and *trans* nitrates. These were separated by fractional crystallization from a concentrated aqueous solution upon addition of alcohol and acetone. The proportions of solid products isolated in such a transformation are *trans*-$[\mathrm{Coen_2F_2}]\mathrm{HF_2}$, 20 g.; mixture of *cis* and *trans*-$[\mathrm{Coen_2F_2}]\mathrm{HF_2}$, 3 g.; *cis*-$[\mathrm{Coen_2F_2}]\mathrm{F}$, 6 g.; *cis*-$[\mathrm{Coen_2F_2}]\mathrm{NO_3}$, 4 g. It should be pointed out that at this stage the "*cis*" salts were not rigorously free of *trans* isomer, which would have required further fractionation to remove completely.

Anal. Calcd. for *cis*-$[\mathrm{Coen_2F_2}]\mathrm{F}$: F, 24.14. Found: F, 24.1.

Preparation of the pure *cis* isomer was accomplished most readily in the form of the nitrate or iodide salt. Thus, a concentrated aqueous solution of the "*cis*" fluoride described above was treated with either ammonium nitrate or ammonium iodide. On fractionally precipitating the solution with acetone or with alcohol and ether, the *trans* isomer separated first. Subsequent fractions of the *cis* complex were redissolved and the precipitation repeated until the *trans* impurity was effectively eliminated.

Anal. Calcd. for *cis*-$[\mathrm{Coen_2F_2}]\mathrm{NO_3}$: F, 13.62; N, 25.09. Found: F, 13.6; N, 25.14.

Anal. Calcd. for *cis*-$[\mathrm{Coen_2F_2}]\mathrm{I}$: F, 11.04; I, 37.18; Co, 17.16; N, 16.29. Found: F, 11.1; I, 37.3; Co, 17.2; N, 16.24.

dextro-cis-Difluoro-bis-(ethylenediamine)-cobalt(III) nitrate was prepared by the reaction of 2.2 g. of *levo-cis*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ in 25 ml. of 1:1 ethanol–hydrofluoric acid with 4 g. of $\mathrm{Ag_2CO_3}$. The reaction mixture was removed from the Dry Ice–acetone bath and allowed to come to room temperature over a period of approximately 30 min. The silver chloride was removed on a filter and the product was fractionally precipitated from the filtrate by addition of acetone and ether. Two optically inactive fractions were followed by a more soluble active fraction (0.53 g.) with $[\alpha]^{28}\mathrm{D}$ +220° and fluoride analysis corresponding to $[\mathrm{Coen_2F_2}]\mathrm{NO_3}$. The color of the two optically inactive fractions suggests these were a mixture of *racemic cis*- and *trans*-$[\mathrm{Coen_2F_2}]\mathrm{NO_3}$.

***cis*-Fluoroammine-bis-(ethylenediamine)-cobalt(III) Bromide.**—The method of Seibt[5a] was repeated but in our hands it was not too satisfactory and the yield of desired complex was small. Attempts to prepare this compound by the reaction of *trans*-$[\mathrm{Coen_2F_2}]\mathrm{HF_2}$ with ammonia were also not entirely successful. The desired complex was conveniently prepared by the reaction of 12 g. of *cis*-$[\mathrm{Coen_2NH_3Cl}]\mathrm{Cl_2}$ in 200 ml. of 1:2 ethanol–hydrofluoric acid with 19 g. of silver oxide. The procedure described above was followed and the bromide salt isolated after treatment of the reaction mixture with an excess of ammonium bromide. The salmon-pink micro-crystalline product weighed 14.5 g. (98% yield).

Anal. Calcd. for $[\mathrm{Coen_2NH_3F}]\mathrm{Br_2}$: F, 5.07; Br, 42.62; C, 12.81; H, 5.11. Found: F, 4.98; Br, 42.4; C, 12.72; H, 5.24.

By this same procedure, 1 g. of *dextro-cis*-$[\mathrm{Coen_2NH_3Cl}]\mathrm{Cl_2}$ yielded 1.05 g. (94% yield) of *dextro-cis*-$[\mathrm{Coen_2NH_3F}](\mathrm{NO_3})_2$, with $[\alpha]^{28}\mathrm{D}$ +140°. Fractional crystallization of this material effected only a superficial change in optical activity: $[\alpha]^{28}\mathrm{D}$ +170°.

***trans*-Fluoronitro-bis-(ethylenediamine)-cobalt (III) Nitrate.**—Three grams of *trans*-$[\mathrm{Coen_2NO_2Cl}]\mathrm{NO_3}$ was added to 60 ml. of 1:2 ethanol–hydrofluoric acid to which had previously been added 1.4 g. of silver oxide. After a few minutes the reaction mixture was removed from the Dry Ice–acetone bath and allowed to come to room temperature. The usual procedure was followed to isolate the nitrate salt, which was then recrystallized by dissolution in 20 ml. of water followed by the addition of 90 ml. of ethanol and 60 ml. of acetone at −10°. The yellow-brown needles that separated were air-dried and found to weigh 1.45 g. (51% yield).

Anal. Calcd. for $[\mathrm{Coen_2NO_2F}]\mathrm{NO_3}$: F, 6.21; N, 27.45. Found: F, 6.24; N, 27.24.

***cis*-Fluoronitro-bis-(ethylenediamine)-cobalt(III) Nitrate.**—The method of synthesis of this salt was essentially the same as that just described for the preparation of *trans*-$[\mathrm{Coen_2NO_2F}]\mathrm{NO_3}$ except that the starting material is *cis*-$[\mathrm{Coen_2NO_2Cl}]\mathrm{Cl}$. Three grams of this salt gave 1.3 g. (42% yield) of the desired product.

Anal. Calcd. for $[\mathrm{Coen_2NO_2F}]\mathrm{NO_3}$: F, 6.21; N, 27.45. Found: F, 6.20; N, 27.12.

The above procedure was carried out using 1 g. of *dextro-cis*-$[\mathrm{Coen_2NO_2Cl}]\mathrm{I}$ ($[\alpha]^{28}\mathrm{D}$ +106°) and two crops (0.4 and 0.15 g. for an over-all yield of 66%) of *dextro-cis*-$[\mathrm{Coen_2NO_2F}]\mathrm{NO_3}$ were isolated. The $[\alpha]^{28}\mathrm{D}$ of a 0.3% solution of these salts were +150° and +120°, respectively, and the fluoride and nitrogen analyses corresponded to $[\mathrm{Coen_2NO_2F}]\mathrm{NO_3}$.

Fluoroaquo-bis-(ethylenediamine)-cobalt(III) Sulfate.—The preparation of this compound followed Werner's method[7] for the synthesis of *cis*-$[\mathrm{Coen_2H_2OCl}]\mathrm{SO_4}$. Ten grams of *trans*-$[\mathrm{Coen_2F_2}]\mathrm{HF_2}$ was covered with 10 ml. of water and the mixture was heated to boiling over an open flame. To the dark red solution was added 7 g. of finely ground solid ammonium sulfate and after thorough agitation the mixture was allowed to stand at room temperature for three days. The crystalline product was collected and washed with three 5-ml. portions of cold water followed by

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(7) A. Werner, *Lieb. Ann.*, **386**, 122 (1912).

methanol and acetone. For analysis, this product was recrystallized from 50 ml. of water by slow addition of 80 ml. of methanol. The air-dried, pink crystalline product weighed 5 g. (39% yield). Heating this compound at 105° resulted in the loss of two molecules of water and the formation of [Coen$_2$FSO$_4$].

Anal. Calcd. for [Coen$_2$H$_2$OF]SO$_4$·H$_2$O: F, 5.75; N, 16.97; H$_2$O, 10.91. Found: F, 5.69; N, 17.0; H$_2$O, 10.9.

It is believed that this is the *cis* isomer but there is at present no proof as to whether or not this is correct. The *cis* configuration is preferred to the *trans* because of the method of synthesis, known in the chloro complex to yield the *cis* isomer, and also because the solid fluoroaquo salts lose water to form *cis*-[Coen$_2$F X]X as described below.

***cis*-Fluorobromo-bis-(ethylenediamine)-cobalt(III) Bromide.**—One gram of [Coen$_2$H$_2$OF]SO$_4$·H$_2$O and 3 g. of barium bromide dihydrate were mixed in 25 ml. of water. The barium sulfate was removed and addition of acetone to the filtrate gave a pink precipitate of the fluoroaquo bromide, which, however, turned to violet in color upon standing overnight in the cold mother liquor. The violet solid was collected and recrystallized from water by the addition of alcohol and acetone. The air-dried salt weighed 0.6 g. (55% yield) and contained no ionic fluoride.

Anal. Calcd. for [Coen$_2$FBr]Br: F, 5.31. Found: F, 5.40.

***cis*-Fluorochloro-bis-(ethylenediamine)-cobalt(III) Chloride.**—Two grams of [Coen$_2$H$_2$OF]SO$_4$·H$_2$O in 10 ml. of water was treated with 4 g. of barium sulfate, and the precipitated solids were removed on a filter. Methanol and acetone were added to the filtrate and the pink precipitate was allowed to stand in the mother liquor for one week. During this time the pink solid turned violet and the violet product was recrystallized by addition of acetone to its concentrated aqueous solution. A yield of 0.4 g. (49%) was obtained and the salt contained no ionic fluoride.

Anal. Calcd. for [Coen$_2$FCl]Cl: F, 7.06. Found: F, 6.4.

Attempted Synthesis of Fluorothiocyanato-bis-(ethylenediamine)-cobalt(III) Salts.—Two different approaches were used in an attempt to prepare salts of this complex. Equimolar quantities of potassium thiocyanate and *trans*-[Coen$_2$F$_2$]HF$_2$ in water were allowed to react on a steam-bath. The red solution, upon addition of alcohol and acetone, yielded a red-violet powder which did not give the correct analysis for the desired product and appeared to be a mixture. A second attempt was to carry out the reaction between *trans*-[Coen$_2$NCSCl]NCS and silver fluoride in 1:2 ethanol–hydrofluoric acid. This resulted in the precipitation of the silver addition complex [Coen$_2$(NCSAg)Cl](HF$_2$)$_2$ and there was no detectable replacement of chloride by fluoride ion.

Miscellaneous Reactions in Liquid Hydrofluoric Acid.—The addition of [Coen$_2$CO$_3$]X, where X = Cl$^-$ or Br$^-$, to liquid hydrofluoric acid resulted in the formation of primarily the chloro or bromo complexes. It was also observed that when *cis*-[Coen$_2$Cl$_2$]Cl was added to liquid hydrofluoric acid, it isomerized rapidly to the *trans*-isomer and separated as the sparingly soluble acid salt. In still another instance a hydrofluoric acid solution of *trans*-[Coen$_2$F$_2$]Br was allowed to stand several minutes after which time the original compound was recovered. These observations suggest that either chloride or bromide ions react more readily than does fluoride, but the Co–F bond is the least labile.

Resolution of *racemic-cis*-Difluoro-bis-(ethylenediamine)-cobalt(III) Ion.—Several unsuccessful attempts were made to resolve *racemic-cis*-[Coen$_2$F$_2$]$^+$ using as resolving agents ammonium α-bromo-*dextro*-camphor-π-sulfonate, potassium antimonyl *dextro*-tartrate, *dextro*-tartaric acid, *levo*-mandelic acid, *dextro*-camphor-10-sulfonic acid, potassium *levo*-tris-(oxalato)-cobaltate(III) and optically active quartz. The method that finally was successful is described. Seven grams of dibenzoyltartaric acid, 4 g. of silver carbonate and 100 ml. of water were ground in a mortar surrounded by an ice-bath. To the mixture was added gradually, with stirring and grinding, a solution of 10 g. of *cis*-[Coen$_2$F$_2$]I in 100 ml. of cold water. After grinding for 15 min. the silver iodide was removed on a filter and the filtrate was kept in an ice-bath. Addition of 2 l. of acetone in small portions to the cold filtrate gave a precipitate that was collected on a filter and air-dried. This 11 g. of material was dissolved in 25 ml. of water and the solution was cooled in an ice–salt-bath. The crystals that separated were collected and washed with methanol and acetone and weighed 4 g. The [α]^{28}D of a 0.1% solution was raised from 70 to 120° by this recrystallization but additional recrystallization has no further effect on the optical rotation.

Two grams of the diastereomer *d-cis*-[Coen$_2$F$_2$]$_2$*l*-(C$_{18}$H$_{12}$O$_8$) was converted into the nitrate salt by treatment with 100 ml. of acetone containing 5 ml. of concentrated nitric acid. The diastereomer was triturated with successive 25-ml. portions of the acidified acetone and finally washed with several portions of acetone. The yield of *d-cis*-[Coen$_2$F$_2$]NO$_3$ remaining was 1.25 g., with [α]^{28}D +220° (0.1% solution).

Resolution of *racemic-cis*-Fluoronitro-bis-(ethylenediamine)-cobalt(III) Ion.—The resolution of this salt was readily accomplished by the use of ammonium α-bromo-*d*-camphor-π-sulfonate. A solution containing 300 mg. of *cis*-[Coen$_2$NO$_2$F]NO$_3$ in 3 ml. of water was treated with 170 mg. of the resolving agent. The mixture was cooled in an ice-bath and the orange crystals were collected and washed with small amounts of methanol and acetone. A yield of 165 mg. of diastereomer was obtained which gave [α]^{28}D +100° for a 0.5% solution. One hundred milligrams of the diastereomer contained in 130 ml. of water was converted into the sparingly soluble reineckate upon the addition of 100 mg. of NH$_4$[Cr(NH$_3$)$_2$(SCN)$_4$]. The reineckate salt is too insoluble to permit polarimetric measurements and was, therefore, converted to the nitrate. A mixture of 15 mg. of *d-cis*-[Coen$_2$F$_2$][Cr(NH$_3$)$_2$(SCN)$_4$], 65 mg. of silver nitrate and 3 ml. of water was agitated for several minutes and then centrifuged. A portion of the clear yellow supernatant solution was used to determine the optical rotation of *d-cis*-[Coen$_2$NO$_2$F$_2$]NO$_3$ found to be [α]^{28}D +92° (0.272% solution). This optical rotation is perhaps low because of the entrainment of some active complex in the pink precipitate of the centrifuged mixture.

Reactions of *dextro-cis*-Difluoro-bis-(ethylenediamine)-cobalt(III) Nitrate.—The reaction of *dextro-cis*-[Coen$_2$F$_2$]NO$_3$ with a number of reagents was investigated to determine whether optically active products are obtained and if there is any evidence for inversion of configuration. Particular attention was paid to the reaction with carbonate ion to see if the inversion reported by Bailar and Auten[8] might be duplicated with the analogous fluoro complex. The results of these reactions are shown in Table I. Since the procedures were similar, only the general method is described. The solid reactants were dry blended, then a small amount of water was added and the resulting mixture was thoroughly ground. The pasty solids were either heated on a steam-bath or allowed to stand at room temperature with intermittent stirring. Sufficient water was then added to give a 0.1% solution on the basis of the original complex and the insoluble materials removed on a filter. The rotation of the filtrate was determined. Since there was insufficient material to isolate the products and the extent of reaction was not known, only qualitative significance can be attached to these results.

The *dextro*-[Coen$_2$CO$_3$]NO$_3$ was isolated from a reaction mixture composed of 0.250 g. of *dextro-cis*-[Coen$_2$F$_2$]NO$_3$ and 0.125 g. of potassium carbonate in 0.5 ml. of water. This mixture was heated on a steam-bath for 5 min. during which time the solution solidified to a crystalline mass. A yield of 0.215 g. of crude product with [α]^{28}D +560° (0.1% solution) was obtained from the cooled mixture. Extraction of the solid with 0.5 ml. of cold water followed by addition of excess alcohol to the extract gave *dextro*-[Coen$_2$CO$_3$]NO$_3$, [α]^{28}D +890° (0.1% solution).

Investigations in liquid ammonia[9] revealed that there was little or no reaction of either the *cis*- or *trans*-[Coen$_2$F$_2$]$^+$ with the solvent. The addition of carbon to the mixture did not promote reaction.[10] The apparent inertness of these complexes is perhaps largely due to their not being soluble in liquid ammonia. It was, therefore, decided to attempt the reaction in ethylene glycol saturated with ammonia. Ten grams of *trans*-[Coen$_2$F$_2$]HF$_2$ was dissolved in 150 ml. of 1:2 ammonia–ethylene glycol. The green colored solution was allowed to stand at room temperature in a stoppered

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(8) J. C. Bailar, Jr., and W. Auten, THIS JOURNAL, **56**, 774 (1934).

(9) J. C. Bailar, Jr., J. H. Haslam and E. M. Jones, *ibid.*, **58**, 2226 (1936).

(10) J. C. Bailar, Jr., and J. B. Work, *ibid.*, **67**, 176 (1945).

TABLE I

REACTION OF *d-cis*-DIFLUORO-BIS-(ETHYLENEDIAMINE)-COBALT(III) NITRATE WITH REAGENTS YIELDING THE CARBONATO COMPLEX

Reagent	Complex (g.)	Reagent (g.)	Reaction time (min.)[a]	Temp., °C.	$[\alpha]^{28}\text{D}$[b]
$CaCO_3$	0.1	0.1	30	28	+220°
$MgCO_3$	.015	.09	20 (hrs.)	28	+300°
$MgCO_3$	.1	.1	3–4	28	+410°
$Ce_2(CO_3)_3 \cdot 5H_2O$	.015	.1	30	28	+310°
Thorium carbonate[c]	.015	....	15	28	+480°
K_2CO_3	.250	.125	3–5	80	+560°
K_2CO_3	.110	15	2	28	+230°
K_2SO_3	.018	4.0	2–3	100	+170°
K_2CO_3	.016	10	2–3	28	+300°

[a] Reaction time = period during which mixture was a concentrated paste and the indicated conditions of temperature were maintained. Excepted are the last three cases, when reaction was in a more dilute aqueous medium, *i.e.*, 0.1% aqueous solutions were prepared directly from the intimately ground *solids*. [b] Specific rotation of 0.1% solution after indicated reaction time; concentration based on amount of difluoro nitrate taken, for which $[\alpha]\text{D}$ +220° (0.1% solution). [c] Thorium carbonate prepared *in situ* from $Th(NO_3)_4 \cdot 12H_2O$ (0.042 g.) and excess K_2CO_3 (0.023 g.).

flask for one week. During the first day the color changed to red. Successive additions of alcohol, acetone and ether to the reaction mixture yielded first a fraction of colorless crystals followed by a yellow oil. Both of these were discarded and the more soluble pink product was isolated upon addition of more ether to the mother liquor. Nitrate and iodide salts were prepared by combining an alcohol solution of the pink compound with an alcoholic solution of the appropriate ammonium salt. The final products are unstable in acid and contain no fluorine.

Anal. Calcd. for $[Coen_2OCH_2CH_2O]NO_3$: N, 23.25. Found: N, 23.2.

Anal. Calcd. for $[Coen_2OCH_2CH_2O]I$: I, 34.67. Found: I, 34.3.

Polarimetric Measurements.—Measurements of optical rotation were made with a Bellingham and Stanley polarimeter using a 1-dm. light path. A sodium vapor lamp was generally the light source but in a few cases a mercury lamp was used in conjunction with a prismatic eye-piece on the polarimeter. Rotational readings reported are an average of 5–10 trials and all measurements were made at approximately 28°.

Measurements of optical rotation at various wave lengths were kindly made by Dr. B. Das Sarma at the University of Illinois through the coöperation of Professor John C. Bailar, Jr. The rotatory dispersion curves plotted from these data are compared to the analogous chloro complexes in Fig. 1 and 2.

Discussion

The methods described for the synthesis of fluoroamminecobalt(III) complexes employ aqueous reaction mixtures. These methods are often satisfactory but better yields and more desirable results are obtained if one uses either liquid hydrogen fluoride or the liquid diluted with a 1–2 fold volume of methanol. In general good yields of the desired fluorocomplex are obtained by the reaction of the corresponding chloro complex with an excess of silver ion in a mixture of hydrogen fluoride and methanol. The reaction times are short and the conditions relatively mild. Under these conditions it is expected that there is little or no opportunity for secondary rearrangements and therefore the configuration of the product is determined primarily by the reaction path for the replacement of chloride by fluoride.

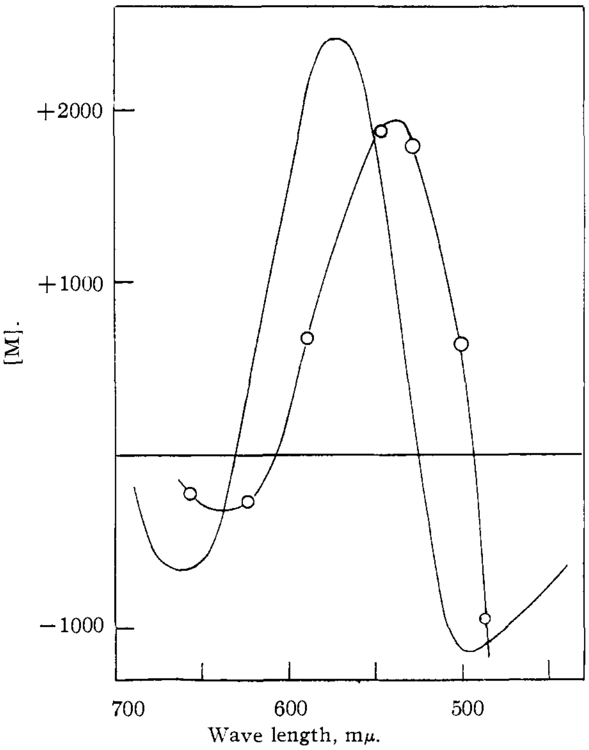

Fig. 1.—Rotatory dispersion curves: *d-cis*-$[Coen_2F_2]NO_3$ O-O-; *l-cis*-$[Coen_2Cl_2]Cl$ (Mathieu[11]) —.

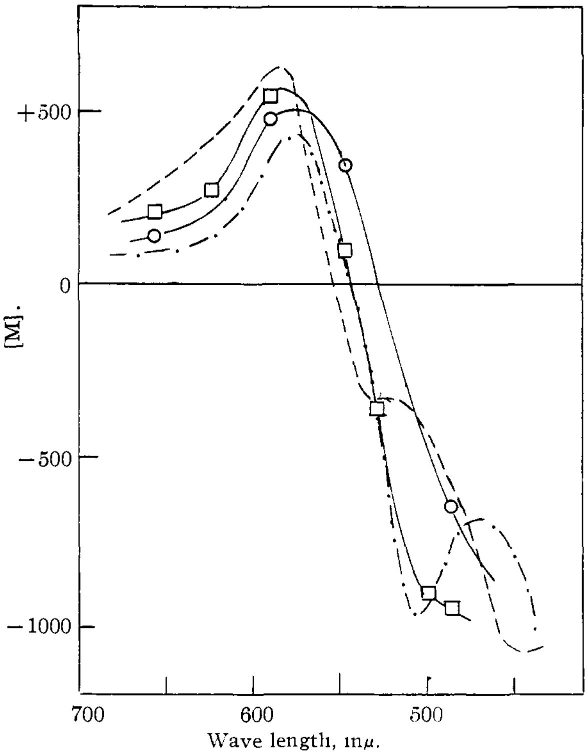

Fig. 2.—Rotatory dispersion curves: *d-cis*-$[Coen_2NO_2F]NO_3$ -O-O-; *d-cis*-$[Coen_2NH_3F](NO_3)_2$ -□-□-; *d-cis*-$[Coen_2NO_2Cl]Cl$ (Mathieu[11]) —·—·—; *d-cis*-$[Coen_2NH_3Cl]Cl_2$ (Mathieu[11]) — — —.

No attempt was made to determine the extent of rearrangement during these reactions but the qualitative results show that there is in large part a retention of configuration. For example *trans*-$[\mathrm{Coen_2NO_2Cl}]^+$ gives almost a quantitative yield of *trans*-$[\mathrm{Coen_2NO_2F}]^+$. Furthermore, optically active chloro complexes yield the corresponding optically active fluoro complex accompanied by a minimum amount of racemization. Although *dextro*-$[\mathrm{Coen_2F_2}]^+$ salts are readily prepared in good yield from *levo*-$[\mathrm{Coen_2Cl_2}]^+$ the reaction of *dextro*-$[\mathrm{Coen_2CO_3}]^+$ with liquid hydrogen fluoride under similar conditions yields *racemic*-$[\mathrm{Coen_2F_2}]^+$. That rearrangements can occur during these reactions is also demonstrated by the reaction of *trans*-$[\mathrm{Coen_2Cl_2}]^+$ to produce almost equal quantities of the *cis*- and *trans*-difluoro isomers.

The asymmetric synthesis of fluoro complexes from the analogous optically active chloro complexes raises the question of whether a retention or inversion of configuration accompanies the transformation. There is no proof of which is involved but two pieces of experimental evidence do support a retention of configuration. In the first place the rotatory dispersion curves of the starting materials are very similar to those of the reaction products as shown in Fig. 1 and 2. Such an observation for analogous compounds like these is said to be an indication of their having the same generic configuration.[11] Another method used by Werner[12] is based on the assumption that for analogous complex ions the antipodes which form the least soluble salts with the same resolving agent have the same generic configuration. In the present study, the *dextro*-$[\mathrm{Coen_2NO_2Cl}]^+$ reactant and *dextro*-$[\mathrm{Coen_2NO_2F}]^+$ product both yield the least soluble *dextro*-α-bromocamphor-π-sulfonate salts. Similar evidence for the difluoro and fluoroammine complexes is lacking, since these could not be correlated with the respective chloro analogs through a common resolving agent.

The isolation of optically active fluoroamminecobalt(III) complexes is the first time that an optically active compound containing a metal–fluoride bond has been reported. These were obtained by asymmetric synthesis as already described and also by the resolution of the racemic fluoro compounds. It is of interest to note that the optical stability of these compounds is greater than that of the analogous chloro complexes.[13] Except for $[\mathrm{CoF_6}]^{-3}$ almost all of the cobalt(III) complexes studied are found to be diamagnetic. This would suggest that the type of chemical bond in all of these is much the same and if such is the case the optical stability of these fluoro complexes is not unexpected.

The optical activity of the difluoro and fluoroammine complexes definitely establishes that these particular isomers have the *cis* configuration. Seibt had previously assigned these structures correctly on the basis of color and method of synthesis but such evidence cannot be taken as proof of structure. Similarly, the structures of the fluoronitro complexes reported here were determined by the successful resolution of the *cis* isomer.

Bailar and Auten[8] report a Walden inversion reaction starting with *levo*-$[\mathrm{Coen_2Cl_2}]^+$. This complex reacts with silver carbonate in the absence of water to yield *levo*-$[\mathrm{Coen_2CO_3}]^+$ whereas with aqueous potassium carbonate the *dextro*-carbonato complex is obtained. There is some evidence in support of the latter reaction taking place with retention of configuration. The conversion of *dextro*-$[\mathrm{Coen_2F_2}]^+$ into optically active $[\mathrm{Coen_2CO_3}]^+$ was carried out at various reaction conditions as summarized in Table I. In every case a *dextro* rotatory product was obtained. It is not known whether this is a result of inversion or retention of configuration. However, there is some indication that the latter is correct. As has already been mentioned *levo*-$[\mathrm{Coen_2Cl_2}]^+$ and its reaction product *dextro*-$[\mathrm{Coen_2F_2}]^+$ are believed to have the same configuration. It also appears that *dextro*-$[\mathrm{Coen_2CO_3}]^+$ obtained by the reaction of aqueous potassium carbonate with *levo*-$[\mathrm{Coen_2Cl_2}]^+$ has this same generic configuration. Since in all of the reactions of the *dextro*-difluoro complex a *dextro*-carbonato product results these are believed to have the same configuration through their relations with *levo*-$[\mathrm{Coen_2Cl_2}]^+$. What can be said with certainty is that unlike the dichloro complex the difluoro complex in these reactions gives no evidence of reacting by different paths.

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