TABLE I

$Zn_2(RCO_2)$-$(C_5H_7O_2)_3$, R =	Yield, %	M.p., °C.	Mol. wt.			% C		% H	
			Calcd.	Found[a] in C_6H_6	Found[a] in $CHCl_3$	Calcd.	Found	Calcd.	Found
CH_3	78	198–200	487.14	*b*	319	41.92	42.31	4.97	5.06
CH_3CH_2	67	159–160	501.17	528	328	43.14	43.95	5.23	5.23
$CH_2{=}C(CH_3)$	55	193–194	513.18	498	446	44.47	44.03	5.11	4.99
C_6H_5	88	243–245 dec.	549.21	*b*	340	48.11	49.12	4.77	4.79
m-$CH_3C_6H_4$	72	219–220	563.24	*b*	422	49.05	50.94	5.01	4.95
p-$CH_3C_6H_4$	83	244 dec.	563.24	*b*	397	49.05	50.78	5.01	4.87
p-ClC_6H_4	80	257 dec.	583.66	*b*	*b*	45.27	45.35	4.32	4.12
p-BrC_6H_4	91	251 dec.	628.12	*b*	*b*	42.07	41.74	4.01	3.93

[a] Mechrolab vapor pressure osmometer. [b] Insoluble.

solutions of sodium acetylacetonate and zinc acetate according to the procedure given by Dwyer and Sargeson.[3] The desired compound was obtained in poor yield; the major product was a compound of the empirical formula $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$ and unknown structure.

It was not possible to carry out any further reactions with the sodium tris(acetylacetonato)zincate(II) thus prepared, due to its low solubility in alcohol and instability in the presence of water.

Experimental

Anhydrous Bis(acetylacetonato)zinc(II).—Reports about this product in the literature are rather inconsistent.[2,4] We prepared it in large runs *via* the unstable methanol adduct of bis(acetylacetonato)zinc(II).

Bis(acetylacetonato)zinc(II) hydrate (100 g.) was dissolved in 600 ml. of methanol. The flask containing the solution was packed in Dry Ice and stored with occasional shaking, until the temperature dropped to −50°. The crystals formed were filtered rapidly through a precooled Büchner funnel and transferred to a round-bottom flask; extended contact with moist air was avoided. After 24 hr. drying under high vacuum 80 g. of anhydrous bis(acetylacetonate)zinc(II), m.p. 127°, was obtained. Unlike the monohydrate, this product dissolved readily in common organic solvents.

Preparation of Compounds $Zn_2(RCO_2)(C_5H_7O_2)_3$. General Procedure.—Anhydrous bis(acetylacetonato)zinc(II) (10.5 g., 40 mmoles) was dissolved in benzene. A solution of 20 mmoles of the acid in benzene was added and the mixture allowed to stand overnight. The resulting crystals were filtered, washed with benzene and petroleum ether, and dried. Recrystallization did not significantly improve the elemental analyses.

When the acid is not sufficiently soluble in benzene, as in the case of *p*-chloro- and *p*-bromobenzoic acids, the components could be dissolved in hot xylene before being poured together.

Preparation of $NaZn(C_5H_7O_2)_3$ and $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$.—Methanol solutions of sodium acetylacetonate (0.32 mmole) and zinc acetate (0.16 mmole) were combined. Sodium acetylacetonatozincate(II) (11.5 g., 0.03 mmole) precipitated immediately and was filtered and dried. The mother liquor, set aside in a freezer overnight, precipitated a crystalline colorless compound (decomposes above 225°); the yield was 31.1 g. or 0.082 mole. The formula $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$ was established by elemental analysis, by potentiometric titration of acetylacetone and acetic acid after aqueous phosphoric acid decomposition and steam distillation, and by v.p.c. detection of methanol in the decomposed aqueous solution.

Anal. Calcd. for $ZnNaC_{13}H_{20}O_7$: C, 41.34; H, 5.60; Zn, 17.31; Na, 6.09. Found: C, 41.05; H, 5.30; Zn, 17.17; Na, 5.69.

Acknowledgment.—We are indebted to Mr. Carmine DiPietro of these laboratories for carrying out the microanalysis and to the National Academy of Sciences for the opportunity given to G. R. to work at the U. S. Army Natick Laboratories.

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[4] D. P. Graddon and D. G. Weeden, *Australian J. Chem.*, **16**, 980 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Synthesis and Resolution of *cis*-Difluorobis(ethylenediamine)chromium(III) Iodide

BY JOE W. VAUGHN AND BARBARA J. KRAINC[1]

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In 1960 Fehrmann and Garner[2] reported the first successful synthesis of *cis*-difluorobis(ethylenediamine)-chromium(III) iodide. The assignment of the *cis* arrangement of the fluoro ligands was on the basis of the color of the complex, its visible absorption spectrum, and the behavior of the complex on ion-exchange columns. Absolute proof of the *cis* structure was not presented by these authors and, in addition, the synthesis, while ultimately yielding a pure product, was tedious and gave the desired compound in a low yield.

During the course of stereochemical studies in this laboratory, it was necessary to prepare *cis*-difluorobis(ethylenediamine)chromium(III) iodide in quantity and to establish unequivocally the *cis* configuration of the complex.

Experimental

Preparation and Source of Starting Materials.—Aqueous (95%) ethylenediamine, 1,2-propanediamine, and 1,3-propanediamine were dried according to the method of Putnam and Kobe.[3] Anhydrous chromium(III) fluoride was used as received.[4]

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[1] Taken in part from a thesis submitted by B. J. K. to the Graduate School of Northern Illinois University in partial fulfillment of the requirements for the degree of Master of Science.

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

[3] G. L. Putnam and K. A. Kobe, *Trans. Am. Electrochem. Soc.*, **74**, 609 (1934).

[4] Available from Alpha Inorganics, Inc., Beverly, Mass.

l-Dibenzoyl-*d*-tartaric acid monhydrate was prepared according to the procedure of Butler and Cretcher.[5] A sample for analysis was dried *in vacuo* over P_2O_5 at 56° for 3 hr. Under these drying conditions the compound loses 0.5 mole of water per formula weight. *Anal.* Calcd. for $C_{18}H_{14}O_8 \cdot 0.5H_2O$: C, 59.0; H, 4.1. Found: C, 58.91; H, 4.31. The specific rotation at the sodium D-line was $-113°$ and at the mercury line (5461 Å.) it was $-114°$. The literature values are $-116°$[5] and $-114.8°$[6] at the sodium D-line.

The procedure given by Coyne, McEwen, and VanderWerf[6] for the synthesis of silver *l*-dibenzoyl-*d*-hydrogen tartrate was modified to obtain disilver *l*-dibenzoyl-*d*-tartrate. The modification involved the addition of 2 equiv. of silver nitrate. *Anal.* Calcd. for $C_{18}H_{12}O_8Ag_2$: Ag, 37.8. Found: Ag, 37.5. The specific rotation at the mercury line was $-108°$.

Synthesis of *cis*-Difluorobis(ethylenediamine)chromium(III) Tetrafluoroethylenediaminechromate(III) Monohydrate.—In a 250-ml. flask were placed 27.2 g. (0.25 mole) of commercial anhydrous chromium(III) fluoride and 44 ml. (0.66 mole) of dry ethylenediamine. An air condenser equipped with a calcium chloride drying tube was attached, and the flask was heated on a steam bath for 4 hr. The color change from the green of the chromium(III) fluoride to a deep purple was quite rapid and the contents of the flask turned to a purple pasty solid after 30–45 min. At the end of 4 hr. the product was worked up from 95% ethanol and filtered. The product was washed three more times with alcohol, once with ether, collected by filtration, and air-dried. The yield of the crude complex was 33.6 g. (64% based on chromium(III) fluoride).

The complex was purified by dissolving 8 g. (0.019 mole) of the crude product in 30 ml. of water at 50°. A finely divided water-insoluble green solid was removed by filtration. The filtrate was acidified with 6.5 ml. of 48% hydrofluoric acid and refiltered, and the complex was precipitated by the addition of 100 ml. of absolute alcohol to the filtrate. The product was filtered off, washed with absolute alcohol and then ether, and air-dried. The procedure yielded 5.3 g. (0.0127 mole) of the recrystallized compound.

A second recrystallization indicated the presence of only a very small amount of the water-insoluble green solid.

A sample for elemental analysis was dried for 1 hr. at 90°. *Anal.* Calcd. for $[Cr(en)_2F_2][Cr(en)F_4] \cdot H_2O$: C, 17.3; H, 6.25; N, 20.1; F, 27.4; Cr, 25.0. Found: C, 16.95; H, 6.08; N, 20.1; F, 27.84; Cr, 24.98.

Titration of a sample of once recrystallized product with standard base indicated the presence of approximately 0.10 mole of occluded HF per mole of complex.

Conductance measurements of a 10^{-3} *M* aqueous solution of the complex at 25° gave a molar conductance of 100, which is well within the range for a uni-univalent electrolyte. An aqueous solution of the complex exhibited absorption maxima at 384 and 528 mμ; the molar absorptivities are approximately 45.5 and 85.0 l. mole^{-1} cm.$^{-1}$, respectively.

The green solid which was removed from the crude double complex gave a negative test for nitrogen, and the infrared absorption spectrum had a relatively strong band at 1050 cm.$^{-1}$. The X-ray data for the water-insoluble green solid did not agree with those for anhydrous chromium(III) fluoride.

The presence of a complex anion in the double complex was convincingly demonstrated by the following ion-exchange experiments. A concentrated aqueous solution of the double complex was passed through a Dowex 50W-X4 cation-exchange resin (hydrogen form, 20–50 mesh). The effluent was a deep blue and the resin turned red due to the retention of the cation. Similar exchange experiments utilizing the anion-exchange cotton, cellulose N,N-diethylaminoethyl ether, perchlorate form, completely eliminated the possibility of the blue fraction being due to a neutral molecule since the blue color could be retained on the column.

The complex anion could not be precipitated from the deep blue effluent obtained from the cation-exchange columns by the addition of silver nitrate, ammonium nitrate, potassium acetate, strychnine, brucine sulfate, or tris(ethylenediamine)cobalt(III) chloride. The following method was utilized to isolate the sodium salt of the anion in a rather impure form.

A sample of the double complex was passed through a Dowex 50W-X4 cation-exchange resin (sodium form, 20–50 mesh), and the column was eluted with one column volume of distilled water. Alcohol–ether mixtures were ineffectual in precipitating the desired product; however, a blue oil formed on the addition of acetone to the effluent. This oil solidified when worked up from acetone, and the infrared absorption spectrum clearly indicated the presence of ethylenediamine in the blue solid. Titration of weighed samples of the sodium salt after passing the compound through a cation-exchange resin in the hydrogen form invariably gave low equivalent weights for the anionic complex, probably due to the presence of occluded acetone in the sodium salt. Attempts to isolate the sodium salt by concentration of the blue solutions at steam bath temperatures resulted in decomposition of the material.

Concentrated aqueous solutions of the complex anion obtained from passing the double complex through a cation-exchange column in the hydrogen form are not stable. The absorption maximum shifted from 572 to 550 mμ in 24 hr. and the solution acquired a bluish purple color. A red color was retained on a cation-exchange resin (hydrogen form) when these aged solutions were passed through the column. When the complex anion was in the form of the sodium salt, the shift in the absorption maximum was not as pronounced, as evidenced by the fact that the absorption maximum shifted from 572 to 560 mμ in 24 hr. The shift in the absorption maximum in acid solution is apparently due to acid hydrolysis of the anion, and in neutral solutions hydrolysis does not occur to the same extent.

Isolation of *cis*-Difluorobis(ethylenediamine)chromium(III) Iodide.—To isolate the desired cation 30 g. (0.072 mole) of the crude double complex was dissolved in 90 ml. of water at room temperature and filtered. The filtrate was acidified with 40 ml. of 48% hydriodic acid and the solution refiltered. Addition of three volumes of absolute alcohol and two volumes of ether precipitated the complex iodide. The crystals were collected by filtration, washed with absolute alcohol and then acetone, and air-dried. This procedure yielded 14 g. (58% based on the double complex) of a rose-red solid. This entire yield was dissolved in 125 ml. of water at room temperature and acidified with 16 ml. of hydriodic acid, and the iodide was precipitated by the addition of two volumes of absolute alcohol. The yield was 8 g. of shiny rose-red crystals. A sample for analysis was dried at 95° for 3 hr. *Anal.* Calcd. for *cis*-$[Cr(en)_2F_2]I$: C, 14.2; H, 4.75; N, 16.6; F, 11.2; I, 37.7. Found: C, 14.41; H, 4.76; N, 16.40; F, 11.11; I, 37.9.

In aqueous solution at room temperature the molar absorptivities at the wave lengths of maximum absorption, 378 and 516 mμ, are 39.5 and 75.5 l. mole^{-1} cm.$^{-1}$, respectively, which are in fair agreement with those previously reported (37.0 and 75).[2]

Resolution of the *cis*-Difluorobis(ethylenediamine)chromium(III) Ion.—The following resolving agents were not successful in effecting the resolution: potassium antimony-*d*-tartrate, ammonium *d*-camphor-π-sulfonate, and ammonium *d*-α-bromocamphor-π-sulfonate. Resolution was effected, however, by the use of the disilver salt of *l*-dibenzoyl-*d*-tartaric acid.

A solution of the complex cation was prepared by dissolving 8 g. (0.0237 mole) of recrystallized racemic *cis*-difluorobis(ethylenediamine)chromium(III) iodide in 80 ml. of water at room temperature and filtering. The solution was kept in a mortar on ice while 6.778 g. (0.0118 mole) of solid disilver *l*-dibenzoyl-*d*-tartrate was added in small portions. The mixture was ground for 15 min., and the precipitated silver iodide was removed by filtration. The crude diastereoisomer was precipitated by the slow addition of small portions of acetone. The acetone was added to the ice-cold solution with constant stirring over a period of 45 min. Precipitation started after the addition of

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(5) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **55**, 2605 (1933).

(6) D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **78**, 3063 (1956).

three to four volumes of acetone and was essentially complete when ten volumes of acetone had been added. The crude product was collected by filtration, washed with acetone, and air-dried. This procedure yielded 9 g. (88% based on the racemic mixture) of pink crystals. A sample for analysis was dried at 90° for 1 hr. *Anal.* Calcd. for $[Cr(en)_2F_2]_2C_{18}H_{12}O_8 \cdot 5H_2O$: C, 36.0; H, 6.24; N, 12.9; F, 8.78. Found: C, 35.66; H, 6.26; N, 12.86; F, 9.25. The specific rotations at the sodium D-line and mercury line were −73° and −53°, respectively.

The diastereoisomers were separated by fractional recrystallization from water. Due to the high solubility of the diastereoisomers in water, solubility losses are appreciable during the recrystallization.

The crude diastereoisomers, 6.5 g. (0.0075 mole), were dissolved in 5 ml. of water at 50° and the solution immediately cooled to 0°. This recrystallization produced 1.73 g. of product whose specific rotations at the sodium and mercury lines were −54.6° and +171°, respectively. Continued recrystallization from water ultimately yielded 0.210 g. of a product whose specific rotations were constant at the sodium and mercury lines at −25.2° and +275°, respectively.

The optical form was freed of the resolving agent by grinding 0.160 g. (0.000185 mole) of the recrystallized diastereoisomer for 5 min. with 10 ml. of absolute alcohol acidified with 0.3 ml. of 48% hydriodic acid. This procedure yielded 0.110 g. of pink product whose specific rotations at the sodium and mercury lines were +27.5° and +440°, respectively. Recrystallization did not raise the rotation values. Dilute aqueous solutions of the active compound showed no change in rotation on standing 1 hr. at room temperature. The optical rotation remained unchanged after a sample of the solid had been heated at 100° for 1 hr. *Anal.* Calcd. for *d-cis*-$[Cr(en)_2F_2]I$: C, 14.2; H, 4.75; N, 16.6; F, 11.2. Found: C, 14.47; H, 4.85; N, 16.36; F, 11.39.

cis-Difluorobis(ethylenediamine)chromium(III) iodide did not react when boiled with excess ethylenediamine for 10 hr. The double complex exhibited similar behavior. However, substitution in the complex cation did occur upon heating an aqueous solution of the complex containing sodium oxalate.

Propylenediamine Complexes.—1,3-Propanediamine produced only purple oils and gums when allowed to react with anhydrous chromium(III) fluoride. Racemic 1,2-propanediamine reacted as did ethylenediamine. The propylenediamine double complex was prepared as described for the ethylenediamine analog. A sample for analysis was dried for 1 hr. at 90°. *Anal.* Calcd. for $[Cr(pn)_2F_2][Cr(pn)F_4] \cdot 3.5H_2O \cdot 0.5HF$: C, 21.1; H, 7.3; N, 16.35; F, 24.1. Found: C, 21.0; H, 7.13; N, 16.15; F, 24.36. A 10^{-3} M aqueous solution of the complex had a molar conductance of 103, which indicated the presence of a 1–1 electrolyte. Absorption maxima were found at 384 and 528 mμ in aqueous solution; approximate molar absorptivities are 45 and 78 l. mole^{-1} cm.$^{-1}$, respectively. Ion-exchange experiments similar to those described previously indicate a complex anion to be present.

The double complex was converted to the corresponding iodide and dried at 100° for 1 hr. *Anal.* Calcd. for $[Cr(pn)_2F_2]I$: I, 34.8. Found: I, 34.9. The compound is somewhat unstable and decomposed in a desiccator after a few days.

Absorption maxima were found at 380 and 522 mμ in aqueous solution; the molar absorptivities are 31.5 and 55 l. mole^{-1} cm.$^{-1}$, respectively.

Analytical Methods and Instrumentation.—All microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

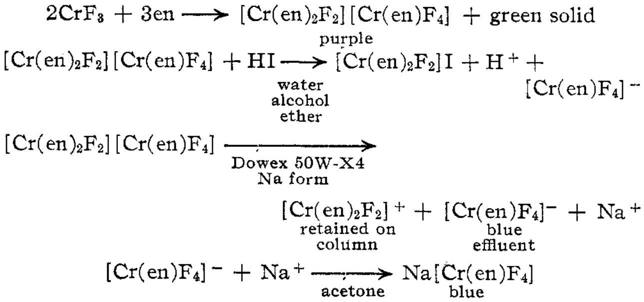
Optical rotations were taken on a Bendix-Ericsson U. K. Ltd. Type 143A ETL-NPL automatic polarimeter coupled to a Sargent SR 1/4% recorder. Appropriate filters were used to isolate the desired wave lengths and all measurements were at room temperature. Syringe type cells with 40-mm. path lengths were used.

Ultraviolet–visible spectra were taken at room temperature on a Beckman DU spectrophotometer using matched 1.0-cm. silica cells.

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

Discussion

The experimental studies indicate that the syntheses of *cis*-$[Cr(en)_2F_2]I$ and $Na[Cr(en)F_4]$ occur according to the following sequence of reactions.



$$2CrF_3 + 3en \longrightarrow \underset{\text{purple}}{[Cr(en)_2F_2][Cr(en)F_4]} + \text{green solid}$$

$$[Cr(en)_2F_2][Cr(en)F_4] + HI \xrightarrow[\substack{\text{water}\\ \text{alcohol}\\ \text{ether}}]{} [Cr(en)_2F_2]I + H^+ + [Cr(en)F_4]^-$$

$$[Cr(en)_2F_2][Cr(en)F_4] \xrightarrow[\substack{\text{Dowex 50W-X4}\\ \text{Na form}}]{} \underset{\substack{\text{retained on}\\ \text{column}}}{[Cr(en)_2F_2]^+} + \underset{\substack{\text{blue}\\ \text{effluent}}}{[Cr(en)F_4]^-} + Na^+$$

$$[Cr(en)F_4]^- + Na^+ \xrightarrow[\text{acetone}]{} \underset{\text{blue}}{Na[Cr(en)F_4]}$$

Anhydrous chromium(III) chloride and anhydrous chromium(III) sulfate react smoothly with ethylenediamine to yield the corresponding tris(ethylenediamine) complexes. This, however, is not the case with chromium(III) fluoride, where the reaction yields the double complex, difluorobis(ethylenediamine)chromium(III) tetrafluoroethylenediaminechromate(III). At no time during the reaction was there evidence for the presence of tris(ethylenediamine)chromium(III) fluoride or *cis*-difluorobis(ethylenediamine)chromium(III) fluoride. There appear to be at least two reasons for this behavior. First, the structure of chromium(III) fluoride is quite similar to the three-dimensional framework structure of rhenium oxide,[7] whereas chromium(III) chloride is known to have a two-dimensional layer structure. Second, the chromium–fluorine bond is apparently much stronger than a chromium–chlorine bond. The difference of the metal–ligand bond strength is supported by the fact that *cis*-difluorobis(ethylenediamine)chromium(III) iodide cannot be converted to the tris complex by boiling with excess ethylenediamine; however, the *cis*-dichloro compound is converted to the corresponding tris compound by boiling with ethylenediamine monohydrate.

cis-Difluorobis(ethylenediamine)chromium(III) iodide is apparently the first complex which has been resolved that contains chromium–fluorine bonds. It is not, however, the first optically active coordination compound isolated that contains a metal–fluorine bond, for Matoush and Basolo[8] were able to resolve *cis*-difluorobis(ethylenediamine)cobalt(III) iodide. The specific rotation of the chromium complex at the sodium line is approximately one-sixth that of the corresponding cobalt complex. This would appear to be unusually low since the specific rotations of the chromium complexes are usually one-third to one-fourth that of the cobalt analogs. The relative stabilities of the dichloro and difluoro complexes of chromium(III) show the lability of the chromium–halogen bond to parallel the lability of the cobalt–halogen bond, which decreases in the order chloride > fluoride.

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(7) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, p. 340.

(8) W. R. Matoush and F. Basolo, *J. Am. Chem. Soc.*, **78**, 3972 (1956).

Application of the solubility rules of Werner[9] to the analogous chromium and cobalt fluoro complexes indicates both of these to have the same relative generic configuration. This is further supported by the observation that both complexes have similarly shaped rotatory dispersion curves. Thus *d-cis*-$[Cr(en)_2F_2]I$, *d-cis*-$[Co(en)_2F_2]I$, and *l-cis*-$[Co(en)_2Cl_2]Cl$ all have the same relative configurations.

The formation of the complex anion is probably dependent upon the following factors. First, there is a difference in the structures of solid chromium(III) fluoride and solid chromium(III) chloride. The three-dimensional structure of chromium(III) fluoride could possibly facilitate the transfer of a fluoro ligand between adjacent metal ions more easily than could a two-dimensional structure. Second, chromium(III) resembles aluminum(III) and it is known that the affinity of an aluminum(III) halide for another halogen drops off markedly with increasing atomic weight of the halogen. Anionic fluoro complexes of chromium(III) such as $M_3[CrF_6]$ and $M_2[CrF_5H_2O]$ are known, but apparently the only example of an anionic complex involving ethylenediamine similar to the one found in the study is $M[Cr(en)(SCN)_4]$.[10] A similar complex involving ethylenediamine and chlorine is apparently not known.

The instability of the tetrafluoroethylenediaminechromate(III) anion in acid solution is probably due to reactions of the type

$$[Cr(en)F_4]^- + H_3O^+ \rightleftharpoons [Cr(en)(H_2O)F_3] + HF$$
$$[Cr(en)(H_2O)F_3] + H_3O^+ \rightleftharpoons [Cr(en)(H_2O)_2F_2]^+ + HF$$

Such reactions would explain the observed shifts in the absorption spectra and the formation of a new cationic species as the solutions were allowed to age at room temperature.

On the basis of the limited amount of data available the 1,2-propanediamine complex of chromium(III) fluoride would appear to involve a *cis* arrangement of the fluoro ligands. Resolution of the complex cation is currently underway in this laboratory.

[9] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 229.

[10] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green, and Co., London, 1948, p. 410.

CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION,
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Reactions of Thorium Carbides with Aqueous Sodium Hydroxide Solutions[1]

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The reactions of thorium mono- and dicarbides with aqueous sodium hydroxide solutions were investigated as part of a continuing program on the chemistry of the heavy metal carbides. The reactions of the thorium carbides with water were studied previously.[2] No reference to their behavior toward basic solutions could be found.

Experimental

Preparation and Characterization of Carbides.—The carbide specimens were prepared by arc melting high purity thorium metal with spectroscopic grade carbon using graphite electrodes, as described previously.[2] Only thorium monocarbide or thorium dicarbide was detected in the X-ray diffraction powder patterns. Metallographic examination of the thorium monocarbide specimens showed 5 to 8% thorium dicarbide impurity. No free metal was observed, indicating that thorium monocarbide is a carbon-deficient compound.[3] The thorium dicarbide specimen was nearly single-phase dicarbide with a small amount of graphite inhomogeneously dispersed throughout the carbide. No thorium monocarbide impurity was observed in the dicarbide specimen by metallographic examination.

Sodium Hydroxide Solutions.—The sodium hydroxide solutions were prepared by the standard method for carbonate-free base[4] using reagent grade sodium hydroxide pellets and boiled distilled water. At the conclusion of the experimental program the solutions contained an average of 0.4 mg. of CO_3^{2-} per ml.

Procedure.—The apparatus, analytical techniques, and experimental procedures used were similar to those described previously.[2,5] When the reaction was complete, 12 *M* HCl was added to neutralize the sodium hydroxide and dissolve the thorium oxide.

Results

Thorium Monocarbide.—The reaction of thorium monocarbide with 0 to 18 *M* NaOH solutions at 80° produced thorium oxide (identified by X-ray diffraction analysis) and 90 ml. (STP) of gas per gram of carbide consisting of 83 vol. % methane and 13% hydrogen with small quantities of C_2 to C_8 hydrocarbons (Table I). The reaction with 6 *M* NaOH gave the same products at 40 and 80°. Of the total carbon present initially in the carbide, 79% was found as methane, 12% as gaseous C_2 to C_8 hydrocarbons, 2% in a hydrochloric acid insoluble residue, and 7% was unaccounted for. There may have been a trace of wax deposited on the surface of the reaction vessel; however, the amount was too small to recover. The thorium oxide dissolved readily in hydrochloric acid; material balances for thorium ranged from 97 to 100%.

After dissolving the thorium oxide, a small amount of an insoluble white solid remained (about 0.1 g./g. of carbide). Semiquantitative emission spectroscopy showed that it consisted mainly of sodium (10 to 100%) and silicon (10 to 100%) with a little boron (1 to 10%), indicating that it probably resulted from a reaction between the sodium hydroxide and the Pyrex reaction flask and possibly also the silicone stopcock grease.

The rate of reaction was not affected by the sodium hydroxide concentration. At 80°, 95% of the gas was evolved within the first 4 hr.; the reaction was complete in about 6 hr. The reaction with 6 *M* NaOH at

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] M. J. Bradley and L. M. Ferris, *J. Inorg. Nucl. Chem.*, in press.

[3] M. J. Bradley and T. M. Kegley, manuscript in preparation.

[4] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 108.

[5] M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **3**, 189 (1964).