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Synthesis and Spectrum of *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Iodide[1]

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RECEIVED APRIL 18, 1960

The previously unknown cation *cis*-$[Cr(en)_2F_2]^+$ has been synthesized and characterized as the iodide salt. Various methods of preparation, including methods similar to some used for the *cis* and *trans* cobalt(III) analogs, were unsuccessfully attempted before a useable method was found. Differences between the visible absorption spectra of *cis*-$[Cr(en)_2F_2]^+$ and *cis*-$[Cr(en)_2Cl_2]^+$ are considered in terms of crystal-field effects.

In connection with a comparison of the kinetics of substitution reactions of cobalt(III) and chromium(III) complexes, the synthesis and characterization of a compound of the previously unknown *cis* - difluoro - bis - (ethylenediamine) - chromium(III) cation was attempted with ultimate success. The visible absorption spectrum of aqueous solutions of the complex has been compared with the spectra of the *cis*- and *trans*-dichloro analogs and differences between the two *cis* complexes considered in the light of crystal-field theory.

Attempts to prepare the desired cation by a variety of other methods including a number similar to some previously developed[2] for the *cis* and *trans* isomers of the cobalt(III) analog were unsuccessful, not necessarily because none of the sought-for complex was produced, but largely because the products were oily smears from which crystals could not be obtained.

Experimental

Unsuccessful Attempts to Synthesize a *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Compound.—The approaches outlined below were unsuccessful in our hands.

The preparation of $[Cr(en)_3]F_3$ was attempted since, if it could be obtained, it might yield the desired difluoro complex by thermal decomposition, in analogy with the synthesis[3] of *cis*-$[Cr(en)_2Cl_2]Cl$ by thermal decomposition of $[Cr(en)_3]Cl_3$. Four methods were tried, all unsuccessful: (a) admixture of concentrated aqueous solutions of $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ and AgF, followed by evaporation or addition of ethanol, *i*-propanol, dioxane, acetone or ether; (b) HF was condensed onto $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ and the mixture warmed to 100°; (c) crude $[Cr(en)_3]_2(SO_4)_3$ was metathesized with $Ba(OH)_2$, the product treated with 48% HF, and *ca.* 10 volumes of methanol added—the yellow precipitate ultimately obtained was not $[Cr(en)_3]F_3$ according to analyses for Cr, C, N and H; (d) green $CrF_3 \cdot xH_2O$ was refluxed with an excess of ethylenediamine, with the hope that a reaction would occur analogous to that between $Cr_2(SO_4)_3 \cdot xH_2O$ and ethylenediamine, but only a violet solution was obtained with a large proportion of unreacted $CrF_3 \cdot xH_2O$.

Saturated aqueous solutions of *cis*-$[Cr(en)_2Cl_2]Cl$ were treated with varying proportions of saturated AgF solution, and after the AgCl was filtered off, varying proportions of ethanol, acetone or ether were added without producing crystals (only smears were obtained).

Violet $[Cr(py)_4F_2]NO_3$ was prepared as described by Costachescu[4] and mixed in aqueous solution with ethylenediamine, then evaporated to a syrupy consistency. When HF was added a violent reaction occurred, resulting in complete decomposition of the complex. Attempts to moderate the reaction failed. This attempted method was patterned generally after the synthesis of *cis*$[Cr(en)_2Br_2]Br$ by Pfeiffer.[5]

Attempts were made to prepare a trifluoro-tris-(dimethylformamide)-chromium(III) compound (for subsequent reaction with ethylenediamine) by refluxing $CrF_3 \cdot 3.5H_2O$ (tech. grade) or $CrF_3 \cdot 9H_2O$ (purified grade) with dimethylformamide and benzene in a manner analogous to the reported[6] formation of the trichloro-tris complex from $CrCl_3 \cdot 6H_2O$. There was never any evidence of reaction. It was learned later[7] that the apparent success of the experiments of Rollinson and White was associated with the presence of a catalytic impurity.

Successful Synthesis of *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Iodide.—In outline this method consisted of treating dry ethylenediamine with chromium(II) fluoride suspended in dry ethereal solution of hydrogen fluoride, converting the crude *cis*-difluoro-bis-(ethylenediamine)-chromium(III) fluoride to the iodide salt and purifying the latter through recrystallization from *ca.* 1% HI and finally from water at 60°.

1. Preparation of Chromium(II) Fluoride.—917 grams of $CrCl_3 \cdot 6H_2O$ was dissolved in enough water to give 1 l. of solution, which was shaken vigorously with twice the theoretical amount of Zn dust and enough conc. HCl to cause bubbles of H_2 to appear. More Zn and HCl were added from time to time, and the mixture cooled to keep it below 50°. After the solution became blue it was filtered into 2 l. of a saturated solution of NaOAc, and the precipitated $Cr(OAc)_2 \cdot xH_2O$ washed 4 times with 200-ml. portions of 3% NaOAc, air being excluded from all solutions by a layer of ligroin on top. The solid acetate was divided into 2 equal portions and each half separately converted to fluoride by slurrying in an equal volume of water, stirring in 230 g. of 48% HF, then, after the red slurry had turned blue, filtering off the residue and washing it 3× with 100-ml. portions of water and finally drying with ethanol and ether, then in a desiccator over Drierite. These operations were carried out in polyethylene containers and filters under an atmosphere of N_2.

2. Dry Ethylenediamine.—Eastman "white label" 95% ethylenediamine was dried by heating 1 kg. on a steam-bath with 150 g. of NaOH pellets overnight, decanting and then distilling the ethylenediamine.

3. Preparation of *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Iodide.—In a typical synthesis, 200 g. of $CrF_2 \cdot xH_2O$ (produced as above and possibly anhydrous) in a 2-l. beaker were stirred with 300 ml. of dry ether containing *ca.* 20 ml. of HF (condensed from a tank), and 180 g. of dry ethylenediamine added. If the reaction did not start spontaneously the beaker was gently warmed. After the reaction began ether was added as fast as

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(1) This investigation was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-34, Project 12.

(2) W. R. Matoush and F. Basolo, THIS JOURNAL, **78**, 3972 (1956).

(3) C. L. Rollinson and J. C. Bailar, Jr., *ibid.*, **66**, 641 (1944); "Inorganic Syntheses," Vol. 11, W. C. Fernelius, editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, pp. 196–200.

(4) N. Costachescu, *Chem. Zentr.*, **83**, 1, 1970 (1912).

(5) P. Pfeiffer, *Ber.*, **37**, 4255 (1904), *Z. anorg. Chem.*, **56**, 279 (1908).

(6) C. L. Rollinson and R. C. White, *Abstracts*, A.C.S. Meeting, Fall 1958.

(7) C. L. Rollinson, private communication.

it boiled off to keep the reaction temperature at 40–50°. The originally blue suspension soon turned deep violet. After 1 hr. 1 l. of dry ether was added and the mixture stirred thoroughly and allowed to stand at room temperature for 1 day, then the crystals filtered off and washed 3× with 500-ml. portions of ethanol to remove most of the excess ethylenediamine. The remainder, together with ethylenediammonium carbonate, was removed by dissolution of the solid in the minimum volume of water at 50°, 20 ml. of 48% HF added, the mixture filtered through a fine-pore paper to remove an unknown finely dispersed green solid, then the crude complex fluoride precipitated by addition of 4 volumes of absolute ethanol and 2 volumes of ether to the filtrate. The voluminous precipitate was filtered off, washed with ethanol and ether and dried at 90° to avoid hydrolysis on storage. Yield of the dry crude complex fluoride is *ca.* 40 g. The preparation up to this point is not completely controllable—sometimes a high percentage of the violet complex fluoride consists of oils and smears which fail to give an easily filterable solid on precipitation with ethanol and ether. The presence of too much water tends to give smears, but traces of water appear to be essential inasmuch as better results were obtained with ethylenediamine dried as above than with ethylenediamine dried additionally by distillation off of metallic sodium. Attempts to purify the crude complex fluoride by fractional precipitation with ethanol and ether, by fractional crystallization from hot water or by adsorption on Dowex 50W-X8 cation-exchange resin and elution with various eluting agents were unsuccessful.

The above product was dissolved in the minimum volume of water and 200 ml. of 48% HI were added and the crude complex iodide precipitated with 4 volumes of ethanol and 2 volumes of ether. The filtered solid was washed with ethanol and ether and the precipitation repeated from 100 ml. of 48% HI. The solid was next dissolved in the minimum volume (*ca.* 50 ml.) of water at 65°, 1 ml. of 48% HI added, then the solution filtered and the filtrate kept at 0° for 1 day. The resulting crystals were recrystallized 3× from water at 60°, then dried in a desiccator over Drierite. Yield was 4 g. of reddish-purple iridescent plates.

Anal. Calcd. for $[Cr(en)_2F_2]I$: Cr, 15.43; F, 11.27; I, 37.65; C, 14.25; H, 4.78. Found: Cr, 15.18; F, 11.46; I, 37.38; C, 14.34; H, 4.54.

Fluorine was determined by the method of Willard and Winter,[8] after decomposing 200 mg. of the complex by boiling with 20 ml. of 30% NaOH for 10 min., then acidifying with $HClO_4$, adding 1 ml. of 30% H_2O_2 and boiling to remove iodine and the excess H_2O_2. Sodium alizarin sulfonate was used as indicator for the titration of fluoride with 0.02500 *N* $Th(NO_3)_4$. The method of Lynn and Mason[9] was employed for determining chromium in the distillation residues from the fluoride determinations. Iodine was determined on 30-mg. samples of the complex dissolved in 10 ml. of water and run through a Dowex 50W-X8 column (50- to 100-mesh, in H^+ form) to remove the interfering complex, then the method of Hammock, Beavon and Swift[10] used to titrate iodide in the colorless effluent from the column. Carbon and hydrogen were determined by standard microcombustion methods by Miss Heather King, departmental microanalyst.

Characterization of *cis* Configuration of the New Complex.—A weighed sample of purified complex iodide was dissolved in water and run through a Dowex 2-X8 column (50- to 100-mesh, in Cl^- form) to remove iodide ion (which in certain preliminary experiments was partly oxidized to I_2, which interfered with the spectrum), then adjusted with $HClO_4$ to give a solution 0.00641 *f* in complex and of *p*H 1.16. The visible absorption spectrum of this solution was recorded immediately (other solutions made with the iodide directly and with HCl in place of $HClO_4$ gave essentially the same spectrum) for comparison with the spectra of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$. Spectra were taken with a Cary Model 11 recording spectrophotometer, using matched 1.00-cm. quartz cells.

As a better test of the *cis* configuration and to check for the possible presence of some *trans*-$[Cr(en)_2F_2]^+$ in the purified complex iodide, 100 mg. of it was dissolved in 50 ml. of water, and 40 ml. of this immediately adsorbed on an ice-jacketed column of Dowex 50W-X8 cation-exchange resin (100- to 200-mesh, in H^+ form) and 150 ml. of 0.3 *f* HCl allowed to flow through the column under conditions known[11] to elute *trans*-$[Cr(en)_2Cl_2]^+$ quantitatively without eluting *cis*-$[Cr(en)_2Cl]^+$. The column effluent was colorless, indicating the absence of *trans*-$[Cr(en)_2F_2]^+$, assuming that the *trans* isomer would not have hydrolyzed appreciably in the 0.3 *f* HCl during the time involved (aquation of the *cis* isomer was shown to be slow, and generally the *cis* isomer of complexes of this type aquates *ca.* 10× faster than the *trans* isomer at or near room temperature). Next, 150 ml. of 0.6 *f* HCl, known[11] to elute *cis*-$[Cr(en)_2Cl_2]^+$ were allowed to flow through the column; all of the *cis*-$[Cr(en)_2F_2]^+$ was thereby eluted, although there was evidence (development of a reddish coloration in the column and subsequent test experiments) of appreciable aquation of the complex in the 0.6 *f* HCl despite the use of an ice jacket. From experiments[11] with *cis*- and *trans*-$[Cr(en)_2(H_2O)Cl]^{+2}$ and with *trans*-$[Cr(en)_2(H_2O)_2]^{+3}$, one may conclude that any fluoro analogs present as impurities in the new complex would not have been eluted by the 0.6 *f* HCl but would have been eluted (excepting perhaps some of any *trans*-$[Cr(en)_2(H_2O)_2]^{+3}$ present) by 25 ml. of 3 *f* HCl, which when tried were observed to elute the reddish coloration from the column. A control experiment performed on the remaining 10 ml. of the original *cis*-$[Cr(en)_2F_2]^+$ solution indicated that appreciable aquation was occurring in the 0.6 *f* HCl, apparently to the same extent on the resin as in homogeneous solution, and that there was little or no evidence of the above-mentioned impurities in the *cis*-$[Cr(en)_2F_2]I$ preparation.

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[8] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

[9] S. Lynn and D. M. Mason, *Anal. Chem.*, **24**, 1855 (1952).

[10] E. W. Hammock, D. Beavon and E. H. Swift, *ibid.*, **21**, 970 (1949).

[11] D. J. MacDonald and C. S. Garner, unpublished research.

Discussion

The *cis* configuration of the new complex, although requiring the demonstration of the existence of optical isomers for a completely definite proof of configuration, is well supported by these facts: In complexes of the type $[Cr(en)_2XY]Z$, the *cis* isomer usually possesses a red or violet color, whereas the *trans* isomer is green; the new complex iodide is reddish purple in the solid form and purplish violet in aqueous solution. The visible absorption spectrum of the new complex in aqueous solution (Fig. 1) has two absorption maxima (typical of *cis* complexes) rather than the three generally found for *trans* complexes. The sharpness of the absorption peaks suggests that the complex is monomeric. The most convincing evidence is that of the cation-exchange resin experiments described in the Experimental section. Inasmuch as polymeric cations normally require a much higher acid concentration for elution from a cation-exchange resin than do monomers, the elution experiments described further support the conclusion that the new complex isolated is a monomer.

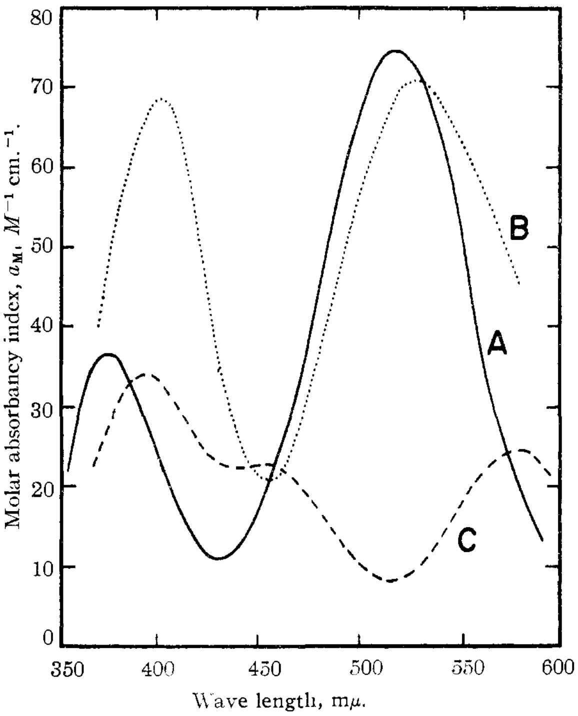

Fig. 1.—Absorption spectra of *cis*-$[Cr(en)_2F_2]^+$ in $HClO_4$ at *p*H 1.16 (A), *cis*-$[Cr(en)_2Cl_2]^+$ in 0.1 *f* HCl (B), *trans*-$[Cr(en)_2Cl_2]^+$ in 0.1 *f* HNO_3 (C).

The difficulties encountered in synthesizing the new complex, in contrast to the relative ease of preparing the cobalt(III) analog, are not fully understood. Perhaps the major source of the difference lies in the greater tendency of chromium(III) to form polynuclear complexes. With the complex in question fluorine may conceivably act as a bridging ligand where oxygen (from solvent water) is absent. In all of the preparations made polynuclear complexes were apparently obtained in high yield as violet oils and smears, from which the monomer was isolated in low yield by repeated fractional crystallizations. Almost certainly, better methods for the synthesis of the *cis*-difluoro complex can be devised. Inasmuch as our purpose was to obtain the complex for kinetic investigation, we have not undertaken a search for a superior synthesis.

It is of interest to consider the visible absorption spectrum of the new complex in terms of crystal-field theory. For chromium(III) and cobalt(III) MA_4B_2 complexes the tetragonal field due to the ligands A and B produces a splitting of the first (long wave length) absorption band, the magnitude of the splitting being dependent upon the relative magnitudes of the crystal-field contributions of the ligands; the splitting is more distinct in *trans* complexes than in the *cis* isomers, where the first band is only broadened. Orgel[12] has shown that the magnitude of the crystal-field effect on the d-electrons of the central M^{+3} ion increases in the order of the spectrochemical series:

$$I^- < Br^- < Cl^- \sim OH^- < NO_3^- < F^- \sim H_2O < NH_3 < en < CN^-.$$

Replacement of the two B ligands by B′ ligands, where B′ is to the right of B in the above series, will therefore shift the first (and often the second) absorption maximum to shorter wave lengths. This effect is apparent in Fig. 1, which includes a comparison of the visible absorption spectra of *cis*-$[Cr(en)_2F_2]^+$ and *cis*-$[Cr(en)_2Cl_2]^+$. Similar agreement with theory has already been reported for the analogous *cis* and *trans* cobalt (III) complexes[13] and for numerous other ethylenediamine and ammine complexes of cobalt(III).[14] The separation between the two bands is smaller for *cis*-$[Cr(en)_2F_2]^+$ than for *cis*-$[Cr(en)_2Cl_2]^+$ (7100 *vs.* 7500 cm.$^{-1}$). As expected from the positions of F^- and H_2O in the spectrochemical series, the spectrum of *cis*-$[Cr(en)_2F_2]^+$ is similar to that[15] of *cis*-$[Cr(en)_2(H_2O)_2]^{+3}$. It is noteworthy that the molar absorbancy index a_M[16] of the second (short wave length) band is roughly half that of the first band at 25° for *cis*-$[Cr(en)_2F_2]^+$ (37 *vs.* 75 M^{-1} cm.$^{-1}$), *cis*-$[Cr(en)_2(H_2O)_2]^{+3}$ (42 *vs.* 77 M^{-1} cm.$^{-1}$)[16] and *cis*-$[Co(en)_2F_2]^+$ (52 *vs.* 82 M^{-1} cm.$^{-1}$),[13] whereas the intensities of the two bands of *cis*-$[Cr(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2Cl_2]^+$ are nearly the same.

(12) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); *J. Chem. Phys.*, **23**, 1004 (1955).

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(14) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **271**, 101 (1952).

(15) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(16) Defined in terms of the molar concentration *c* and optical path length *l* by the expression log $(I_0/I) = a_M cl$.