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Fluoro-Containing Complexes of Chromium(III). VI. Preparation and Characterization of Some Mixed Acido-Mixed Diamine Complexes[1]

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A well-characterized salt of the cation in the complex *cis*-difluorobis(propanediamine)chromium(III) tetrafluoro(propanediamine)chromate(III) has been isolated. Reactions of the anion in this complex with concentrated hydrohalic acids have been utilized to prepare the chloride, bromide, and iodide salts of the difluorodiaquo(propanediamine)chromium(III) cation. Several new salts of the *trans*-fluoroaquo(propanediamine)(ethylenediamine)chromium(III) and *trans*-fluoroaquo(propanediamine)(trimethylenediamine)chromium(III) cations have been prepared and characterized. The thermal dehydration of the chloride and bromide salts has been utilized to prepare the previously unknown *cis*-fluorobromo and -fluorochloro complexes. The reaction of *trans*-fluoroaquo(propanediamine)(ethylenediamine)chromium(III) perchlorate with ammonium chloride in methyl alcohol solution has been used to prepare the new *trans*-fluorochloro complex. A new method has been developed for the synthesis of the *trans*-dibromo(propanediamine)(ethylenediamine)chromium(III) cation. Assignments of cis or trans structures were made by studies of the electronic absorption spectra of the complexes.

Introduction

In 1908 Pfeiffer, *et al.*,[3] reported the first known complexes of chromium(III) where the central atom was coordinated by two different bidentate amine ligands. The five salts reported by Pfeiffer all contained the propanediaminebis(ethylenediamine)chromium(III) cation and the counterions were bromide, thiocyanate, iodide, tris(oxalato)chromate(III), or hexacyanochromate(III).

There are a number of chromium(III) complexes which contain two identical bidentate and two other identical monodentate ligands. In comparison, there is a relatively small number of chromium(III) compounds in which the two bidentate ligands are the same and the two monodentate ligands are different. These two types of complexes can be represented by the general formulas $[Cr(AA)_2X_2]^{n+}$ and $[Cr(AA)_2XY]^{n+}$ where (AA) is the bidentate ligand, X and Y are monodentate ligands, and *n* is the charge on the complex.

The purpose of this research was to prepare and characterize new complexes of the type $[Cr(AA)(BB)FX]^{n+}$ which contain two nonidentical bidentate ligands, (AA) and (BB), and two nonidentical monodentate ligands one of which is the fluoro group.

Such complexes should be potentially useful in kinetic studies of fluoride ion release and Cr–N bond rupture.

Experimental Section

Preparation of Difluorobis(propanediamine)chromium(III) Tetrafluoro(propanediamine)chromate(III). This complex was prepared essentially by the method of Vaughn and Marzowski.[1]

Final purification was achieved by grinding a 5-g sample of the crude material with 50 ml of 95% ethanol, filtering, and repeating the process four times. Prior to analysis, the product was dried at 140° for 48 hr. Analytical data for the new compounds prepared in this study are in Table I.

Difluorodiaquo(propanediamine)chromium(III) iodide-1.5-water was isolated from the double complex as described previously.[1]

Isolation of *cis*-$[Cr(pn)_2F_2](C_6H_5)_4B\cdot1.5H_2O$. A 2.0-g (0.055-mol) sample of recrystallized $[Cr(pn)_2F_2][Cr(pn)F_4]$ was dissolved in the minimum amount of water at room temperature and the solution was filtered. To the well-stirred filtrate was added *ca.* 1.5 ml of a saturated aqueous solution of sodium tetraphenylborate; the insoluble pink precipitate was collected by filtration and discarded. The filtrate was treated with an additional 1 ml of tetraphenylborate solution; the precipitate was collected and discarded. The filtrate was treated with 10 ml of sodium tetraphenylborate solution; the precipitate was collected, washed with 5 ml of ice water, and air-dried. The yield by this method was 0.1 g.

The compound was dried *in vacuo* over anhydrous magnesium perchlorate for 2 days at room temperature. During the drying the compound lost 4.3% of its weight and for complete dehydration the calculated weight loss was 4.6%. The electronic spectral data for all the new complexes prepared in this study are in Table II. The assignments of a structure as cis or trans will be discussed later.

Synthesis of $[Cr(pn)F_2(OH_2)_2]Cl\cdot0.5H_2O$. Difluorodiaquo(propanediamine)chromium(III) iodide-1.5-water (25.0 g, 0.071 mol) was ground with 50 ml of concentrated (37%) hydrochloric acid at room temperature for 3–4 min and the solution was filtered. To precipitate the desired product, the filtrate was added with stirring to 1.5 l. of cold acetone (*ca.* 8–10°). The purple product was collected by filtration and immediately washed with anhydrous ether. Since the compound was very hygroscopic and tended to oil on drying, the final drying was in a bell jar under vacuum for 24 hr at room temperature. This procedure gave 64% (2.8 g) of product based on the starting complex.

Synthesis of $[Cr(pn)F_2(OH_2)_2]Br\cdot H_2O$. This material was prepared in the same fashion as the corresponding chloride except that concentrated hydrobromic acid was used in the synthesis. The desired product was obtained in 57% yield.

The complex, $[Cr(pn)F_2(OH_2)_2]Br\cdot H_2O$, was also prepared by a different route. A 20-g (0.045-mol) sample of the double complex was ground to a fine powder, 45 ml of 48% hydrobromic acid was added, and the grinding was continued for a time period not exceeding 1 min, before the solution was filtered through a large filter (7.0–9.0 cm in diameter) so that filtration could be completed before crystallization began. After filtration, the filtrate was immediately transferred to a beaker and cooled in an ice bath for 1 hr before the purple crystals were collected. Excess acid was removed by washing the fine crystals with 200 ml of absolute ethanol and the final product was air-dried. This method gave 6.8 g (51%) of product.

Recrystallization was accomplished by dissolving the crude product in a minimum amount of water at room temperature and filtering to remove any undissolved material. The filtrate was acidified with 2 ml of 48% hydrobromic acid and the solution was cooled in an ice bath for 1 hr. The crystals which had precipitated were collected, washed with absolute alcohol, and air-dried.

Synthesis of *trans*-$[Cr(pn)(en)F_2]Br$. This complex was prepared in 92% yield by the literature method.[1]

Purification of the complex was accomplished by stirring 4.0 g of the crude reaction product with 100 ml of 95% ethanol for 1 hr at room temperature and filtering. The filtrate was saved for the isolation of the cis isomer described below.

The slurring of the crude material with 100 ml of 95% ethanol was repeated. The alcohol insoluble fraction was dissolved in a mixture of 25 ml of 95% ethanol and 12 ml of water. The alcohol-water solution was cooled in ice; the precipitate was collected, washed with acetone, and air-dried. A 52% recovery was obtained by this method. The final product was dried at 120° for 48 hr prior to analysis.

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[1] For the previous publication in this series see J. W. Vaughn and J. Marzowski, *Inorg. Chem.*, **12**, 2346 (1973).

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

[3] P. Pfeiffer, T. Gassman, and H. Pietch, *Z. Anorg. Chem.*, **57**, 312 (1908).

Table I. Analytical Data (%) for the New Complexes of Chromium(III) Prepared in This Study

	Theory							Found						
Compd	C	H	N	Br	Cr	Cl	F	C	H	N	Br	Cr	Cl	F
cis-$[Cr(pn)_2F_2](C_6H_5)_4B \cdot 1.5H_2O$	61.7	7.4	9.6		8.9		6.4	61.9	7.6	9.2		8.9		6.4
$[Cr(pn)F_2(OH_2)_2]Cl \cdot 0.5H_2O$	14.7	6.1	11.4			14.5	15.5	14.7	6.3	11.0			14.6	15.2
$[Cr(pn)F_2(OH_2)_2]Br \cdot H_2O$	12.1	5.4	9.4	26.8	17.5			12.1	5.3	9.3	26.8	17.2		
cis-$[Cr(pn)(en)F_2]Br$	19.7	5.9	18.4	26.4	17.3		12.5	19.4	5.8	18.0	26.2	17.3		12.4
trans-$[Cr(pn)(en)Br_2]ClO_4 \cdot 0.5H_2O$	13.2	4.2	12.3	35.2	11.5			13.1	4.0	12.7	35.6	11.3		
trans-$[Cr(pn)(en)F(OH_2)]I_2 \cdot 1.5H_2O$	11.9	4.6	11.2				3.8	11.7	4.3	11.7				4.0
trans-$[Cr(pn)(en)F(OH_2)]Cl_2 \cdot H_2O$	19.2	7.1	18.0		16.7	22.8		18.5	7.0	18.0		17.1	23.4	
trans-$[Cr(pn)(en)F(OH_2)]Br_2 \cdot 0.5H_2O$	15.3	5.4	14.3	40.9	13.3		4.9	15.4	5.5	14.5	41.1	13.5		4.8
cis-$[Cr(pn)(en)FCl]Cl$	21.8	6.6	20.3		18.9	25.7	6.9	21.8	6.6	20.0		19.0	25.3	6.8
cis-$[Cr(pn)(en)FBr]Br$	16.5	4.9	15.4	43.8	14.2		5.2	16.6	5.1	15.7	43.4	14.5		5.1
trans-$[Cr(pn)(en)FCl]ClO_4$	17.7	5.3	16.5		15.3	10.5	5.6	17.6	5.5	16.2		15.5	10.0	5.8
trans-$[Cr(pn)(tmd)F(OH_2)]Cl_2 \cdot 0.75H_2O$	22.4	7.3	17.4		16.2	22.0	5.9	22.7	7.7	17.6		16.1	21.9	5.8
trans-$[Cr(pn)(tmd)F(OH_2)]Br_2 \cdot 0.5H_2O$	17.8	5.7	13.8		12.8		4.7	17.7	5.9	13.8		12.9		4.6
trans-$[Cr(pn)(tmd)F(OH_2)]I_2 \cdot 0.5H_2O$	14.4	4.6	11.2				3.8	14.2	4.6	11.0				3.7
trans-$[Cr(pn)(tmd)F(OH_2)](NO_3)_2$	20.0	6.1	23.2		14.4		5.3	20.0	6.2	23.4		14.7		5.4
cis-$[Cr(pn)(tmd)FCl]Cl$	24.8	6.9	19.3		18.0	24.6	6.6	25.1	7.1	19.1		18.2	24.1	6.2
cis-$[Cr(pn)(tmd)FBr]Br$	19.0	5.3	14.8	42.3	13.8		5.0	19.1	5.5	15.0	42.9	13.8		5.0

A thin-layer chromatographic study indicated that this product may contain more than one isomer with the predominant species being the trans isomer.

Isolation of *cis*-$[Cr(pn)(en)F_2]Br$. The filtrate from the alcohol extraction of crude *trans*-$[Cr(pn)(en)F_2]^+$ was placed in an evaporating dish and the alcohol and water were evaporated at room temperature by a stream of air. The residue was further dried at 140° for 1 hr and the "crusty" product was ground into a fine powder before analysis.

Synthesis of *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2 \cdot H_2O$ and *trans*-$[Cr(pn)(en)Br_2]ClO_4 \cdot 0.5H_2O$. An 11.0-g (0.036-mol) sample of *trans*-difluoro(propanediamine)(ethylenediamine)chromium(III) bromide was dissolved in 25 ml of *cold* 72% perchloric acid, the solution was filtered, and the filtrate was allowed to stand at room temperature for 1 hr. After 1 hr, 5 ml of cold water was added dropwise to the reaction mixture with stirring and scratching the side of the beaker. The reaction mixture was cooled in ice for 30–40 min in order to precipitate a small amount of a green solid. The green product was collected by filtration and the filtrate was allowed to sit overnight at 8°. The green product was washed with 2–3 ml of cold water, followed by 2–3 ml of anhydrous ether, and air-dried.

The light pink precipitate which had formed in the filtrate overnight was collected, washed with 15 ml of absolute ethanol, followed by 5 ml of acetone, and air-dried. This procedure yielded 4.0 g of the pink $[Cr(pn)(en)F(OH_2)](ClO_4)_2 \cdot H_2O$ and 0.85 g of the green $[Cr(pn)(en)Br_2]ClO_4 \cdot 0.5H_2O$.

The green product was dried over anhydrous magnesium perchlorate *in vacuo* at 0.05 mm for 18 hr at room temperature.

Anion Replacement Reactions. Fluoroaquo(propanediamine)(ethylenediamine)chromium(III) perchlorate-1-water (1.0 g, 2.3 mmol) was dissolved in 4–5 ml of water at room temperature and filtered. The filtrate was treated with 4.0 g of sodium iodide with stirring to precipitate a pink, crystalline solid. The solution was filtered and the crystals were washed with 50–75 ml of 95% ethanol, followed by 20 ml of acetone, and air-dried. This method gave 0.40 g (33%) of fluoroaquo(propanediamine)(ethylenediamine)chromium(III) iodide-1.5-water.

Fluoroaquo(propanediamine)(ethylenediamine)chromium(III) perchlorate-1-water (1.5 g, 0.0034 mol) was dissolved in 5 ml of water and passed through a column of Dowex 1-X10 anion-exchange resin (50–100 mesh, Cl^-, 1 × 15 cm). Elution through the column was accomplished with 100–150 ml of water. Precipitation of the desired product was effected by dripping the eluent into 900 ml of a 1:2 mixture of absolute ethanol and anhydrous ether. The fluffy precipitate was collected, washed with 40–50 ml of anhydrous ether, and placed in a bell jar under vacuum for 24 hr at room temperature. If this compound is allowed to stand for a period of time greater than 48 hr, a noticeable change in color from pink to purple occurs. A 74% yield (0.79 g) was obtained by the above procedure.

A solution of fluoroaquo(1,2-propanediamine)(ethylenediamine)chromium(III) perchlorate-1-water, 1.5 g (3.4 m*M*) in 5 ml of water, was passed through a column of 1-X10 Dowex anion-exchange resin in Br^- form. Elution, percipitation, and drying were the same as described previously for the chloride salt. This procedure resulted in a 73% recovery (0.98 g).

Synthesis of *cis*-$[Cr(pn)(en)ClF]Cl$. A 0.5-g (1.6-mmol) sample of orange fluoroaquo(propanediamine)(ethylenediamine)chromium(III) chloride–1-water was heated at 110° in air for 18 hr before the partially dehydrated material was transferred to an Aberhalten apparatus and heated an additional 2 hr at 118° and 0.05 mm, to produce the anhydrous salt. Since the purple product was very hygroscopic, anhydrous conditions were utilized for all weighings.

Synthesis of *cis*-$[Cr(pn)(en)BrF]Br$. This purple compound was prepared in a manner similar to that of the chloride homolog previously described.

Synthesis of *trans*-$[Cr(pn)(en)ClF](ClO_4)$. This new complex was prepared by the method utilized by Vaughn, DeJovine, and Seiler for the synthesis of *trans*-$[Cr(en)_2FCl](ClO_4)$.[4]

To remove any water or organic solvent, the product was dried over anhydrous magnesium perchlorate *in vacuo* (0.05 mm) at room temperature for 20 hr prior to analysis.

Synthesis of *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2 \cdot 1.5H_2O$. This complex was prepared as described in the literature,[1] except that the acid solution was cooled in ice for 5 hr before the product was collected.

Anion Replacement Reactions Using *trans*-Fluoroaquo(propanediamine)(trimethylenediamine)chromium(III) Perchlorate. The *trans*-fluoroaquo(propanediamine)(trimethylenediamine)chromium(III) cation was isolated as its chloride or bromide salts by the ion-exchange procedure previously described. The chloride salt was precipitated from 700 ml of a 1:5 absolute alcohol–ether mixture while a 2:7 mixture was necessary to precipitate the bromide salt. The chloride was obtained in 74% yield and the bromide in 88% yield.

A sample (2.0 g, 4.3 mmol) of fluoroaquo(propanediamine)(trimethylenediamine)chromium(III) perchlorate was dissolved in 8–10 ml of water, the solution was filtered, and solid sodium iodide was added. Upon the addition of the sodium iodide, pink crystals of the iodide salt began to form. The mixture was stirred for 10 min, filtered, and washed with cold 95% ethanol. Since the complex exhibited an appreciable solubility in 95% ethanol, only a small volume of alcohol was used (10–15 ml) before the product was washed with acetone and air-dried. This method gave the desired iodide in 18% yield. The corresponding nitrate was obtained in 35% yield by the above procedure using 1.0 g of the perchlorate salt of the cation and 4.0 g of sodium nitrate.

Synthesis of *cis*-$[Cr(pn)(tmd)FCl]Cl$. This complex was prepared from *trans*-fluoroaquo(propanediamine)(trimethylenediamine)chromium(III) chloride–0.75-water by the method described for *cis*-$[Cr(pn)(en)FCl]Cl$.

Synthesis of *cis*-$[Cr(pn)(tmd)FBr]Br$. The preparation of bromofluoro(propanediamine)(trimethylenediamine)chromium(III) bromide is analogous to the synthesis of chlorobluoro(propanediamine)(trimethylenediamine)chromium(III) chloride.

Chromatographic Studies. Thin-layer chromatographic studies of all difluoro complexes were made by the method of Swain and Sudmeier.[5]

Separation of an Equimolar Mixture of *trans*-Difluorobis(ethylenediamine)chromium(III) Bromide and *trans*-Difluorobis(propane-

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(4) J. Vaughn, J. DeJovine, and G. Seiler, *Inorg. Chem.*, **9**, 684 (1970).

(5) J. L. Swain and J. L. Sudmeier, *Anal. Chem.*, **40**, 418 (1968).

diamine)chromium(III) Bromide. A mixture of 0.01 mol (2.90 g) of *trans*-difluorobis(ethylenediamine)chromium(III) bromide and 0.01 mol (3.18 g) of *trans*-difluorobis(propanediamine)chromium(III) bromide was separated by the procedure used for the recrystallization of *trans*-difluoro(propanediamine)(ethylenediamine)chromium(III) bromide. The crystals which precipitated on cooling were collected, washed with acetone, and air-dried. The recrystallized material was heated at 120° for 24 hr prior to analysis. *Anal.* Calcd for *trans*-difluorobis(ethylenediamine)chromium(III) bromide: C, 16.5; H, 5.5; N, 19.3; Cr, 17.9. Found: C, 16.4; H, 5.6; N, 19.9; Cr, 17.8.

The electronic spectrum of a 0.01 *M* aqueous solution of the product isolated by this procedure [assuming the molecular weight to be that of *trans*-difluorobis(ethylenediamine)chromium(III) bromide] was in agreement with that previously reported for an authentic sample of *trans*-difluorobis(ethylenediamine)chromium(III) bromide.

Analytical Methods and Instrumentation. All microanalyses were preformed by Huffman Laboratories, Inc., Wheatridge, Colo.

Chromium was determined by alkali peroxide oxidation to CrO_4^{2-} and spectrophotometric determination at 372 nm. Halogen analyses were made by standard potentiometric titration with 0.01 *M* silver nitrate.

All ultraviolet-visible absorption spectra were taken on a Cary Model 14 recording spectrophotometer using 1.0- or 2.0-cm silica cells.

All infrared spectra were taken on a Beckman IR-12 spectrophotometer with the sample in Nujol or hexachlorobutadiene between cesium iodide plates.

Discussion

Previous workers[6] isolated the iodide salt of the $[Cr(pn)_2F_2]^+$ cation but later studies showed the complex to be impure.[7]

The cation has now been isolated as a well-characterized tetraphenylborate salt. The electronic absorption spectrum of the complex in acetone solution exhibited the two-band spectrum characteristic of a cis complex of the type $[Cr(AA)_2X_2]^{n+}$; however instead of widely differing values for the molar absorptivities as is usually found for cis complexes this particular material was characterized by both absorption maxima having the same molar absorptivities. The enhancement of the high-energy band is due to the fact that the tetraphenylborate anion of the complex has considerable absorption at 370 nm. As would be expected the absorption maxima are near those reported for the authentic cis complex difluorobis(ethylenediamine)chromium(III) iodide.[6] The initial pink product isolated in the synthesis was apparently contaminated with some amine salt and did not give reproducible analytical results; however, the electronic spectrum was in qualitative agreement with the pure compound.

The previously unknown complex difluorodiaquo(propanediamine)chromium(III) chloride-0.5-water was isolated during this investigation. This particular complex is much more hygroscopic than the previously reported bromide and iodide salts.[1] From the similarity of the electronic absorption spectra all of the salts of this cation have the same unknown configuration and in the absence of more definitive structural data further speculation about which isomer was prepared is not warranted at this time.

The complexes $[Cr(AA)(BB)FX]^+$ (AA and BB represent two nonidentical bidentate ligands and $X^- = Cl^-$ or Br^-) prepared in this study appear to be the first reported complexes of this type. The synthetic method developed for these new complexes involved the use of a monodiamine complex of chromium(III) whose chemical properties under the proper experimental conditions would favor the addition of another different diamine over all other reaction possibilities.

In the present study a diaquo species difluorodiaquo(propanediamine)chromium(III) bromide was utilized as the starting material. Although this complex contains two strong $Cr-OH_2$ bonds and the possibility of forming hydroxo polymers exists, the diaquo complex could be effectively utilized as a starting material in alcohol solution. Chromium-nitrogen bond rupture did not appear to be important in the synthesis.

The reaction of $[Cr(pn)F_2(OH_2)_2]Br \cdot H_2O$ with ethylenediamine, propanediamine, or trimethylenediamine in refluxing absolute alcohol produced two products. In all cases the alcohol-insoluble product consisted chiefly of the corresponding *trans*-difluoro mixed diamine complex while the more soluble fraction is apparently the cis isomer. It was possible to isolate *cis*-difluoro(propanediamine)(ethylenediamine)chromium(III) bromide from one of the reaction mixtures but the low molar absorptivities indicate that this complex is not pure. The existence of two different geometrical isomers in the same reaction mixture requires that the reaction of the difluorodiaquochromium(III) ion with another diamine in refluxing absolute alcohol either proceeds without complete retention of configuration or involves a subsequent isomerization in a second step after the initial process has gone with retention. The possibility of a trans-cis isomerization is currently being investigated.

Acid hydrolysis of the *trans*-$[Cr(pn)(BB)F_2]^+$ complexes proceeded as expected to produce the corresponding *trans*-$[Cr(pn)(BB)F(OH_2)]^{2+}$ products with one exception. In the case of $[Cr(pn)(en)F_2]Br$ two products could be isolated from the reaction mixture. One of these products was the anticipated cation and the other was the green *trans*-$[Cr(pn)(en)Br_2]^+$ cation. The green cation is thought to arise in the following fashion. The acid-catalyzed fluoride ion release from *trans*-$[Cr(pn)(en)F_2]Br$ is accomplished in 72% perchloric acid and at this acid concentration essentially all of the water present is associated with the acid and is not present as "free" water. This supposition is supported by the observation that *trans*-fluoroaquobis(diamine)chromium(III) salts do not precipitate from the acid hydrolysis reaction mixture until the system is diluted with water. With one of the possible entering ligands, in this case water, not available for coordination to the chromium(III) ion, it is not surprising that the complex adds the free bromide ligand instead of water.

It appears that solubilities play an important role in the isolation of the dibromo complexes and it could well be that these complexes are formed in all cases of acid hydrolysis of the difluoro complexes which contain bromide as the counterion but their solubilities are such that they have escaped detection until the present time.

The trans geometry was assigned to the dibromo complex on the basis of its characteristic green color and the similarity of its electronic absorption spectrum to those of previously reported *trans*-dibromobis(diamine)complexes of chromium(III) (see Table II). The high-energy transition in the mixed ligand complex is shifted considerably with respect to the corresponding transition in the bis(ethylenediamine) and bis(propanediamine) complexes.

The anion replacement reactions using *trans*-fluoroaquo(propanediamine)(ethylenediamine)chromium(III) perchlorate as the starting material proceeded as expected. The perchlorate, iodide, chloride, and bromide salts were all characterized by similar colors and electronic absorption spectra. However, the electronic absorption spectra did vary slightly with the nature of the anion. The discrepancies in the electronic spectra were greatest for those salts (chloride

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

(7) J. W. Vaughn, unpublished observation.

Table II. Electronic Spectral Data for Some Complexes of Chromium(III)

Compd	λ_{max}[a] (ϵ)[b]	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)
cis-$[Cr(pn)_2F_2](C_6H_5)_4B\cdot 1.5H_2O$[f]	530 (88.6)	452 (43.8)	370 (88.6)				
cis-$[Cr(en)_2F_2]I$[d,e]	516 (75.5)		378 (39.5)				
$[Cr(pn)F_2(OH_2)_2]Cl\cdot 0.5H_2O$	545 (38.2)		415[h]	454 (12.5)	374 (18.5)		
$[Cr(pn)F_2(OH_2)_2]Br\cdot H_2O$[g,i]	545 (35.0)		415[h]	454 (7.2)	373 (12.2)		
$[Cr(pn)F_2(OH_2)_2]Br\cdot H_2O$[g,j]	545 (36.1)		415[h]	451 (6.6)	373 (11.9)		
trans-$[Cr(pn)(en)F_2]Br$[d,c]	525[h] (18.0)		465 (22.4)	413 (19.3)	395 (14.6)	375 (13.9)	350 (16.0)
cis-$[Cr(pn)(en)F_2]Br$[d]	515 (40.6)	430 (16.4)	377 (26.8)				
cis-$[Cr(pn)_2F_2]Br$[c,d]	517 (45.0)		375 (33.5)				
trans-$[Cr(pn)(en)Br_2]ClO_4$[g]	602 (32.3)	526 (11.0)	455[h] (28.4)		389 (36.8)		
trans-$[Cr(en)_2Br_2]Br$[k]	607 (34.9)		460[h] (24.0)		406 (30.7)		
trans-$[Cr(pn)_2Br_2]Br$[l]	606 (36.9)		460[h] (27.9)		406 (34.0)		
trans-$[Cr(en)_2F(OH_2)](ClO_4)_2$[d,m]	519 (22.4)		454 (25.6)		371 (31.2)		
trans-$[Cr(en)(pn)F(OH_2)](ClO_4)_2$[g]	518 (27.8)	494(24.4)	458 (27.2)	418 (21.2)	369 (33.3)		
trans-$[Cr(en)(pn)F(OH_2)]I_2$[d]	516 (24.2)	493 (22.7)	456 (26.4)	416 (19.9)	368 (33.0)		
trans-$[Cr(pn)(en)F(OH_2)]Cl_2$[g]	527 (30.6)		460[h] (22.5)	430 (20.5)	380 (23.8)		
trans-$[Cr(pn)(en)F(OH_2)]Br_2$[g]	522 (27.4)		460[h] (24.6)	421 (20.9)	372 (30.2)		
trans-$[Cr(pn)(en)FCl]ClO_4$[d]	549 (20.4)	508 (14.2)	458 (22.6)	435 (18.1)	378 (31.2)		
trans-$[Cr(en)_2FCl]ClO_4$[d,n]	553 (19.9)		460 (21.5)		381 (27.4)		
trans-$[Cr(tmd)_2FCl]ClO_4$[d,o]	564 (19.6)		460 (20.0)		386 (31.8)		
trans-$[Cr(pn)(tmd)F_2]Br$[d]	530[h] (18.9)		465 (27.1)	418 (19.8)	395[h] (20.9)		355 (27.6)
trans-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2$[g]	523 (23.8)	500 (22.8)	457 (30.7)	418 (23.0)	369 (44.2)		
trans-$[Cr(pn)(tmd)F(OH_2)]Cl_2$[g]	522 (23.0)	500 (22.5)	457 (29.0)	418 (20.9)	370 (42.3)		
trans-$[Cr(pn)(tmd)F(OH_2)]Br_2$[g]	523 (23.1)	500 (21.4)	458 (27.8)	420 (19.7)	371 (40.6)		
trans-$[Cr(pn)(tmd)F(OH_2)]I_2$[d]	523 (23.2)	503 (17.5)	456 (30.1)	418 (22.2)	369 (44.5)		
trans-$[Cr(pn)(tmd)F(OH_2)](NO_3)_2$[g]	521 (26.2)	500 (21.8)	457 (29.0)	420 (21.3)	370 (43.3)		
cis-$[Cr(en)_2FCl]Cl$[d,m]	518 (62.4)		387 (42.8)				
cis-$[Cr(en)_2FBr]Br$[d,m]	512 (61.2)		381 (37.6)				
cis-$[Cr(en)(pn)FCl]Cl$[d]	512 (57.5)	443 (20.3)	385 (39.0)				
cis-$[Cr(en)(pn)FBr]Br$[d]	518 (52.4)	437 (20.5)	384 (35.2)				
cis-$[Cr(pn)(tmd)FCl]Cl$[d]	523 (43.0)	440 (17.8)	375 (37.7)				
cis-$[Cr(pn)(tmd)FBr]Br$[d]	513 (49.7)	436 (17.9)	382 (34.6)				

[a] Wavelengths in nanometers. [b] Molar absorptivities in cm^{-1} M^{-1}. [c] J. W. Vaughn and J. A. Marzowski, *Inorg. Chem.*, 12, 2346 (1973). [d] Solvent was water. [e] J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, 4, 1077 (1965). [f] Solvent was acetone. [g] Solvent was 0.1 *M* perchloric acid. [h] Band present as a shoulder. [i] Prepared from $[Cr(pn)F_2(OH_2)_2]I$ by treatment with hydrobromic acid. [j] Prepared from $[Cr(pn)_2F_2][Cr(pn)F_4]$ by treatment with hydrobromic acid. [k] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, 3, 1348 (1964). [l] J. A. McLean and R. I. Goarman, *Inorg. Nucl. Chem. Lett.*, 7, 12 (1971). [m] J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968). [n] J. W. Vaughn, J. M. DeJovine and G. J. Seiler, *ibid.*, 9, 684 (1970). [o] J. W. Vaughn, *Inorg. Nucl. Chem. Lett.*, 4, 183 (1968).

and bromide) which were prepared by ion-exchange techniques and required prolonged drying to obtain good samples. The chloride and bromide salts appeared to be slightly unstable and discolored on drying. The color changes noted are consistent with the loss of a coordinated water molecule and subsequent replacement by the anion. In the two cases (iodide and perchlorate) where the solid salts could be isolated directly without prolonged drying the electronic spectra matched well.

Previous workers have unequivocally assigned a cis geometry[8] to the purple isomer of $[Cr(en)_2FCl]Cl$ *via* resolution of the complex into *d* and *l* forms. Thus the electronic spectra (Table II) and purple colors of $[Cr(pn)(en)FCl]Cl$, $[Cr(pn)(en)FBr]Br$, $[Cr(pn)(tmd)FCl]Cl$, and $[Cr(pn)(tmd)FBr]Br$ are consistent with a cis geometry. The trans geometry for one of the isomers of $[Cr(en)_2FCl]Cl$ has been established *via* a comparison of elemental analyses and electronic and far-infrared spectra with those of the authentic cis isomer. Thus the isomer of $[Cr(pn)(en)FCl]ClO_4$ prepared from alcohol solution at room temperature must involve a trans arrangement of halo ligands.

During the course of this investigation several new salts of the cation *trans*-$[Cr(pn)(tmd)F(OH_2)]^{2+}$ were prepared. Chloride, bromide, and iodide salts were obtained as hydrates; however it was possible to obtain the nitrate salt in the anhydrous form. This is not surprising since the chloride and bromide anions tend to replace the water molecule coordinated to the chromium(III) ion and form the corresponding *cis*-fluorochloro and -fluorobromo complexes. Since nitrate does not strongly coordinate to Cr(III) it was possible to prepare the anhydrous nitrate salt without removing the mole of coordinated water per mole of complex.

The synthetic methods employed for the preparation of *trans*-$[Cr(pn)(en)F_2]Br$ and *trans*-$[Cr(pn)(tmd)F_2]Br$ suggest that, instead of the mixed ligand complexes, the product could be an equimolar mixture of *trans*-$[Cr(pn)_2F_2]Br$ and *trans*-$[Cr(en)_2F_2]Br$. There are two different pieces of evidence that suggest that an equimolar mixture was not produced: (1) by thin-layer chromatography studies of equimolar mixtures of *trans*-$[Cr(en)_2F_2]Br$ and *trans*-$[Cr(pn)_2F_2]Cl$ could be separated into two distinct spots with different R_f values while the mixed complex chromatographed as essentially a single spot with R_f value intermediate between those of the mixture; (2) it was possible to separate an equimolar mixture of the two trans complexes by fractional recrystallization whereas the mixed ligand complex gave only a single fraction when subjected to the same process.

Registry No. *cis*-$[Cr(pn)_2F_2](C_6H_5)_4B$, 49634-00-6; $[Cr(pn)F_2(OH_2)_2]Cl$, 49634-01-7; $[Cr(pn)F_2(OH_2)_2]Br$, 40902-39-4; *cis*-$[Cr(pn)(en)F_2]Br$, 49634-03-9; *trans*-$[Cr(pn)(en)Br_2]ClO_4$, 49634-04-0; *trans*-$[Cr(pn)(en)F(OH_2)]I_2$, 49634-05-1; *trans*-$[Cr(pn)(en)F(OH_2)]Cl_2$, 49634-06-2; *trans*-$[Cr(pn)(en)F(OH_2)]Br_2$, 49634-07-3; *cis*-$[Cr(pn)(en)FCl]Cl$, 49634-08-4; *cis*-$[Cr(pn)(en)FBr]Br$, 49634-09-5; *trans*-$[Cr(pn)(en)FCl]ClO_4$, 49634-10-8; *trans*-$[Cr(pn)(tmd)F(OH_2)]Cl_2$, 49634-11-9; *trans*-$[Cr(pn)(tmd)F(OH_2)]Br_2$, 49634-12-0; *trans*-$[Cr(pn)(tmd)F(OH_2)]I_2$, 49634-13-1; *trans*-$[Cr(pn)(tmd)F(OH_2)](NO_3)_2$, 49634-14-2; *cis*-$[Cr(pn)(tmd)FCl]Cl$, 49634-15-3; *cis*-$[Cr(pn)(tmd)FBr]Br$, 49634-16-4; $[Cr(pn)F_2(OH_2)_2]Br$, 40902-39-4; *trans*-$[Cr(en)(pn)F(OH_2)](ClO_4)_2$, 40902-45-2; *trans*-$[Cr(pn)(tmd)F_2]Br$, 40902-42-9; *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2$, 40902-46-3.

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(8) J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968).