Contribution from the Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Fluoro-Containing Complexes of Chromium(III). V. Preparation of Some Mixed Diamine Complexes[1]

JOE W. VAUGHN* and JOANNE MARZOWSKI[2]

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The reaction of the previously unreported complex, bromodifluoroaquo(propanediamine)chromium(III), with stoichiometric amounts of ethylenediamine (en), or 1,3-propanediamine (tmd), in refluxing absolute alcohol has been utilized to prepare the new mixed diamine complexes *trans*-$[Cr(pn)(en)F_2]Br$ and *trans*-$[Cr(pn)(tmd)F_2]Br$. Reactions using 1,2-propanediamine under the same conditions produced both *cis*- and *trans*-$[Cr(pn)_2F_2]Br$ as solid products. Reactions using *trans*-1,2-diaminocyclohexane (dach) as the entering bidentate ligand produced the new complex *cis*-$[Cr(pn)(dach)F_2]Br$ as the major product. The geometries of the new complexes were established *via* electronic absorption spectral studies. Reaction of the trans complexes with concentrated perchloric acid produced the new fluoroaquo complexes, *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2$ and *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2$. A new synthetic method was developed for the previously known complex $[Cr(pn)(en)_2]Br_3 \cdot 2H_2O$.

Introduction

In 1908 Pfeiffer, Gassman, and Pietch[3] prepared the first mixed diamine complexes of chromium(III). The five complexes were of the type $[Cr(AA)_2(BB)]^{3+}$ where AA was ethylenediamine and BB was propanediamine. The counteranion was bromide, thiocyanate, iodide, *tris*-oxalatochromate(III), or hexacyanochromate(III). Recently, House, *et al.*,[4,5] reported kinetic studies of the acid hydrolysis reaction of complex $[Cr(AA)(BB)(Cl)_2]^+$ where AA was ethylenediamine and BB was 1,3-propanediamine. Apparently this compound is one of the few known complexes of chromium(III) which contains two acido groups in addition to two different diamines bound to the central ion.

The present research was undertaken to expand the number of mixed diamine complexes of chromium(III) and to include fluoro ligands in the primary coordination sphere, since these complexes could be potentially important in kinetic studies of fluoride ion release.

In addition, some of these complexes could serve as useful starting points for studies of absolute configurations.

Experimental Section

Preparation of Starting Material. In a 500-ml round-bottomed flask equipped with an air condenser and a calcium chloride drying tube were placed 43.0 g (0.25 mol) of chromium(III) fluoride 3.5-hydrate and 48.8 g (0.66 mol) of anhydrous propanediamine. The flask and its contents were heated on a steam bath for 3 hr. After about 10–15 min of heating a vigorous reaction took place and the reaction mixture turned from green to purple. At the end of 3 hr the reaction flask was removed from the steam bath and allowed to cool to room temperature, and about 100 ml of absolute alcohol was added. The crude purple product was filtered, slurried several times with more absolute alcohol, filtered, and air-dried. A yield of 57 g [69% based on the chromium(III) fluoride 3.5-hydrate] of a fine purple powder was obtained.

A 5.0-g sample of the crude material was dissolved in a minimum amount of water at room temperature, 5 ml of 48% hydrofluoric acid was added, and the solution was filtered to remove some water-insoluble green solid. The filtrate was treated with absolute alcohol with stirring to reprecipitate the purple solid. The product was collected by filtration, washed with more alcohol, and air-dried. *Anal.* Calcd for $[Cr(pn)_2F_2][Cr(pn)F_4] \cdot 2H_2O$: C, 22.6; H, 7.1; N, 18.0. Found: C, 22.3; H, 6.9; N, 17.9.

Ion exchange studies, with cationic and anionic resins, confirmed the presence of a red cation and a blue anion in the recrystallized purple solid. Due to solubility problems it was not possible to isolate a solid derivative of the cation from aqueous solutions of $[Cr(pn)_2F_2][Cr(pn)F_4]$.

All electronic spectral and conductance data for the complexes investigated in this study are in Table I.

Isolation of $Na[Cr(pn)F_4] \cdot 1.15NaClO_4 \cdot H_2O$. A 2.0-g (4.2 mmol) sample of purified $[Cr(pn)_2F_2][Cr(pn)F_4] \cdot 2H_2O$ was dissolved in 70 ml of water at room temperature, the solution filtered, and 50 ml of a saturated aqueous solution of sodium perchlorate added with constant stirring. The pale blue precipitate was collected by filtration, washed with three 50-ml portions of acetone, and air-dried. This procedure gave 1.1 g (73%) of the desired product. *Anal.* Calcd for $Na[Cr(pn)F_4] \cdot 1.15NaClO_4 \cdot H_2O$: C, 9.4; H, 3.1; N, 7.3; F, 19.8; Cr, 13.6. Found: C, 9.6; H, 3.1; N, 7.3; F, 19.9; Cr, 13.4.

Synthesis of $[Cr(pn)F_2(OH_2)_2]I \cdot H_2O$. A 2.0-g (4.2 mmol) sample of difluorobis(propanediamine)chromium(III) tetrafluoro(propanediamine)chromate(III) 2-hydrate was ground with about 4 ml of concentrated hydriodic acid for 1 min, the solution filtered, and the filtrate cooled in an ice bath. Precipitation of the purple product was complete after 2 min. The solid was collected by filtration, washed three times with 50-ml portions of cold absolute alcohol, and air-dried. A yield of 0.70 g (47%) was obtained by this method. *Anal.* Calcd for $[Cr(pn)F_2(OH_2)_2]I \cdot H_2O$: C, 10.4; H, 4.8; N, 8.2; F, 11.1; I, 36.8. Found: C, 10.6; H, 4.9; N, 8.3; F, 11.3; I, 36.7.

A 1.7-g (4.6 mmol) sample of $Na[Cr(pn)F_4] \cdot 1.15NaClO_4 \cdot H_2O$ was ground with 3 ml of concentrated hydriodic acid for 2–3 min at room temperature. The thick paste was filtered; the crystals were washed with 50 ml of 95% alcohol followed by 5–10 ml of acetone and air-dried. A yield of 0.86 g (53%) of $[Cr(pn)F_2(OH_2)_2]I \cdot 1.5H_2O$ was obtained. The crude compound was recrystallized from a water–hydriodic acid solution. *Anal.* Calcd for $[Cr(pn)F_2(OH_2)_2]I \cdot 1.5H_2O$: C, 10.2; H, 4.8; N, 7.9; I, 35.8. Found: C, 10.5; H, 4.8; N, 8.1; I, 35.7. The electronic spectrum was identical with that of the compound prepared from the double complex.

Synthesis of $[Cr(pn)F_2(OH_2)_2]Br \cdot H_2O$. A 1.0-g (2.9 mmol) sample of $[Cr(pn)F_2(OH_2)_2]I \cdot H_2O$ was ground with about 4 ml of concentrated hydrobromic acid, the solution was filtered, the filtrate was cooled in an ice bath, and 3 vol of cold acetone were added. The purple solid which precipitated on the addition of acetone was collected, washed three times with 15-ml portions of cold acetone, and air-dried. This procedure gave a 47% (0.4 g) yield of $[Cr(pn)F_2(OH_2)_2]Br \cdot H_2O$. *Anal.* Calcd for $[Cr(pn)F_2(OH_2)_2]Br \cdot H_2O$: C, 12.1; H, 5.4; N, 9.4; F, 12.8; Br, 26.8; Cr, 17.5. Found: C, 12.2; H, 5.5; N, 9.5; F, 12.8; Br, 26.8; Cr, 17.4.

The purple complex dried to a pale blue powder after it was heated for 3 hr at 110°. *Anal.* Calcd for $[Cr(pn)F_2(OH_2)Br]$: C, 13.7; H, 4.6; N, 10.7; Br, 30.3. Found: C, 13.2; H, 4.2; N, 10.3; Br, 30.0.

Synthesis of $[Cr(pn)(en)F_2]Br \cdot 0.5H_2O$. The dehydrated complex, $[Cr(pn)F_2(OH_2)Br]$ (5.6 g, 25 mmol), was suspended in 30 ml of absolute alcohol in a 50-ml round-bottomed flask. An equimolar amount of anhydrous ethylenediamine was added, a reflux condenser was attached, and the contents of the flask were refluxed for 3 hr. After about 1 hr of refluxing precipitation of an orange-pink product

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[1] For the previous publication in this series, see J. W. Vaughn, J. M. DeJovine, and G. J. Seiler, *Inorg. Chem.*, 9, 684 (1970).

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

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

[4] M. C. Couldwell and D. A. House, *Inorg. Chem.*, 11, 2024 (1972).

[5] M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, 12, 627 (1973).

Table I. Summary of Electronic Spectral and Conductivity Data for Some Fluoro-Containing Complexes of Chromium(III)

No.	Complex	λ_{max}[a] (ϵ)[b]	λ_{max} (ϵ)	λ_{max} (ϵ)	λ_{max} (ϵ)	Λ[c]
1	$[Cr(pn)_2F_2][Cr(pn)F_4]\cdot H_2O$[d]	380 (63.0)	524 (98.0)			56
2	$Na[Cr(pn)F_4]\cdot 1.15NaClO_4\cdot H_2O$[d]	408 (19.1)	573 (36.4)			226
3	$[Cr(pn)F_2(OH_2)_2]I\cdot H_2O$[d]	372 (19.6)	543 (40.5)	415[e]		99
4	$[Cr(pn)F_2(OH_2)_2]Br\cdot H_2O$[f]	373 (11.9)	545 (36.1)	415[e]		120
5	*trans*-$[Cr(pn)_2F_2]^+$[g]	351 (15.2)	400 (13.9)	467 (23.1)	530 (17.0)	
6	*trans*-$[Cr(en)_2F_2]^+$[g]	351 (14.4)	397 (13.2)	465 (21.0)	530 (16.5)	
7	$[Cr(pn)_2F_2]Br$[d]	348 (15.8)	397 (15.0)	466 (23.0)	522[e] (17.5)	106
8	$[Cr(pn)(en)F_2]Br\cdot 0.5H_2O$[d]	350 (16.0)	395 (14.6)	465 (22.4)	525[e] (18.0)	94
9	$[Cr(pn)(tmd)F_2]Br\cdot H_2O$[d]	353 (26.9)	390 (20.0)	464 (26.1)	525[e] (17.6)	118
10	*cis*-$[Cr(en)_2F_2]I$[d,h]	378 (39.5)	516 (75.5)			
11	$[Cr(pn)_2F_2]Br$[d]	375 (33.5)	517 (45.0)			116
12	$[Cr(pn)(dach)F_2]Br\cdot H_2O$[d]	377 (41.3)	518 (63.3)			123
13	*trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$[d,i]	371 (31.2)	454 (25.6)	519 (24.2)		
14	$[Cr(en)(pn)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$[d]	368 (37.6)	456 (31.0)	519 (28.5)		246
15	$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2\cdot H_2O$[d]	367 (52.7)	460 (40.7)	515 (35.4)		240
16	$[Cr(pn)(en)_2]Br_3\cdot 2H_2O$[d]	348 (66.5)	456 (77.0)			403
17	*trans*-$[Cr(tmd)_2F_2]^+$[g]	360 (16.3)	398 (16.5)	468 (20.7)	538 (16.8)	

[a] Wavelength in nanometers. [b] Molar absorptivities in l. M^{-1} cm^{-1}. [c] Calculated from resistance measurements on a 1 mM aqueous solution of the complex at room temperature, units are cm^2 ohm^{-1} M^{-1}. [d] Spectrum taken in aqueous solution at room temperature. [e] This band present as a shoulder. [f] Spectrum taken in 0.1 M aqueous perchloric acid at room temperature. [g] J. Glerup, J. Josphensen, K. Mickelsen, E. Pederson, and C. Schaffer, *Acta Chem. Scand.*, 24, 247 (1970). [h] J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, 4, 1077 (1965). [i] J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968).

was noted. At the end of the reflux period the reaction mixture was cooled in ice; the product was collected by filtration, washed three times with 10-ml portions of absolute alcohol, and air-dried. This procedure gave 6.7 g (81%) of an orange-pink product. The crude material was dissolved in a minimum of water at room temperature and filtered, and the solid reprecipitated by the addition of cold absolute alcohol to the filtrate. The sample was collected and dried at 100° for 1 hr prior to analysis. *Anal.* Calcd for *trans*-$[Cr(pn)(en)F_2]Br\cdot 0.5H_2O$: C, 19.2; H, 6.1; N, 17.9; F, 12.4; Br, 25.5; Cr, 16.6. Found: C, 19.0; H, 5.6; N, 18.5; F, 12.4; Br, 26.0; Cr, 16.6. The demonstration of the assigned structure will be discussed later in the paper.

A weighed sample of *trans*-$[Cr(pn)(en)F_2]Br\cdot 0.5H_2O$ was dried *in vacuo* over anhydrous magnesium perchlorate at 125° for 18 hr. *Anal.* Calcd for *trans*-$[Cr(pn)(en)F_2]Br$: C, 19.4; H, 5.9; N, 18.4; Br, 26.3. Found: C, 19.8; H, 6.0; N, 18.6; Br, 25.9.

Synthesis of $[Cr(pn)_2F_2]Br\cdot H_2O$. A 0.4-g (1.9 mmol) sample of $[Cr(pn)F_2(OH_2)Br]$ was suspended in 15 ml of absolute alcohol in a 50-ml round-bottomed flask, an equimolar amount of anhydrous propanediamine was added, and the mixture was refluxed for 3 hr. The sample was purified and dried as described for the complex $[Cr(pn)(en)F_2]Br$. *Anal.* Calcd for *trans*-$[Cr(pn)_2F_2]Br\cdot H_2O$: C, 21.4; H, 6.5; N, 16.7; F, 11.3; Br, 23.8; Cr, 15.5. Found: C, 21.7; H, 6.5; N, 16.9; F, 11.6; Br, 23.8; Cr, 15.5.

Isolation of *cis*-$[Cr(pn)_2F_2]Br$. After the isolation of the *trans*-$[Cr(pn)_2F_2]Br$ from the alcohol reaction, the filtrate was diluted with 3 vol of anhydrous ether. The flocculent pink precipitate was collected and dried *in vacuo* at room temperature for 18 hr. This procedure produced the cis isomer in 20% yield (0.12 g). *Anal.* Calcd for *cis*-$[Cr(pn)_2F_2]Br\cdot H_2O$: C, 21.4; H, 6.5; N, 16.7; F, 11.3; Br, 23.8. Found: C, 21.9; H, 6.5; N, 16.1; F, 10.7; Br, 23.4.

The mole of water of hydration per formula weight of the complex was removed by drying the complex at 0.05 mm, 120°, for 48 hr. *Anal.* Calcd for *cis*-$[Cr(pn)_2F_2]Br$: C, 22.7; H, 6.3; N, 17.6; F, 11.9. Found: C, 22.9; H, 6.4; N, 17.1; F, 11.9. The low values for the molar absorptivities of this complex (see Table I) suggest that this product is impure and could possibly be a cis-trans mixture.

Synthesis of $[Cr(pn)(tmd)F_2]Br\cdot H_2O$. This material was prepared by the method described for $[Cr(pn)(en)F_2]Br$, except that trimethylenediamine, 1,3-propanediamine, was used in place of ethylenediamine. *Anal.* Calcd for *trans*-$[Cr(pn)(tmd)F_2]Br\cdot H_2O$: C, 21.4; H, 6.5; N, 16.7; F, 11.3; Br, 23.8; Cr, 15.5. Found: C, 21.3; H, 6.8; N, 16.8; F, 11.4; Br, 23.6; Cr, 15.3.

Synthesis of $[Cr(pn)(dach)F_2]Br\cdot H_2O$. This complex was prepared in the same fashion as $[Cr(pn)(en)F_2]Br$ except that *trans*-1,2-diaminocyclohexane was used in place of ethylenediamine. The yield by this method was 1.1 g (89%).

Anal. Calcd for *cis*-$[Cr(pn)(dach)F_2]Br\cdot H_2O$: C, 28.6; H, 6.9; N, 14.9; F, 10.1; Br, 21.3; Cr, 13.8. Found: C, 28.8; H, 6.8; N, 14.8; F, 10.1; Br, 21.3; Cr, 14.2.

Synthesis of *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$. A 0.5-g (1.5 mmol) sample of *trans*-$[Cr(en)(pn)F_2]Br\cdot 0.5H_2O$ was slowly added to 2.5 ml of ice-cold 72% perchloric acid with constant stirring. The red-orange solution was filtered to remove a small amount of undissolved material and the filtrate was allowed to stand at room temperature for 1 hr. The solution was cooled in an ice bath and about 0.75 ml of water was added dropwise. After 1 hr of cooling, precipitation began and was complete after 4 hr. The orange crystals were collected by filtration, washed with absolute alcohol, and air-dried. This procedure gave the desired product in 32% (0.21 g) yield. *Anal.* Calcd for *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$: C, 13.9; H, 4.9; N, 13.0; F, 4.4; Cr, 12.4. Found: C, 13.7; H, 4.9; N, 13.4; F, 4.4; Cr, 12.7.

Synthesis of *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2\cdot H_2O$. This complex was prepared by the method described for the complex *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$. *Anal.* Calcd for *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2\cdot H_2O$: C, 15.8; H, 5.3; N, 12.3; F, 4.2; Cr, 11.2. Found: C, 15.9; H, 5.0; N, 12.4; F, 4.1; Cr, 11.4.

Synthesis of $[Cr(pn)(en)_2]Br_3\cdot 2H_2O$. A sample of $[Cr(pn)F_2(OH_2)Br]$ was dissolved in absolute alcohol, a 10 molar excess of ethylenediamine was added, and the reaction mixture was refluxed for 18 hr. The yellow solid that formed during the reflux period was collected, washed, recrystallized, and dried in the manner previously described for the mixed diamine complexes. *Anal.* Calcd for $[Cr(pn)(en)_2]Br_3\cdot 2H_2O$: C, 16.1; H, 5.7, N, 16.4; Br, 49.4; Cr, 10.7. Found: C, 16.0; H, 5.3; N, 16.1; Br, 49.4; Cr, 10.8.

Chromatographic Separation. The existence of a true mixed diamine complex rather than equimolar mixtures of two different bis(diamine) complexes was established *via* thin-layer chromatography. The method of Swain and Sudmeier[6] was utilized.

Approximately 1 μl of 5×10^{-2} M aqueous solutions of the complexes were spotted on prewashed Eastman Kodak silica gel (No. 6061) plates and eluted upward with a mixture of absolute alcohol, acetic acid, and water (70:20:10). Development was in an iodine chamber. Equimolar mixtures of *trans*-$[Cr(pn)_2F_2]Br$ and *trans*-$[Cr(en)_2F_2]Br$ separated into two spots with different R_f values; the mixed complex *trans*-$[Cr(pn)(en)F_2]Br$ gave essentially a single spot with an R_f value between those of the equimolar mixture. All other complexes reported here as mixed ligand complexes behaved in a similar fashion. Therefore, the products were not mixtures of bis(diamine) complexes.

Analytical Methods and Instrumentation. Carbon, hydrogen, nitrogen, and fluorine analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Halogen other than fluorine was determined by potentiometric titration with 0.1 M silver nitrate solution using a Sargent LS pH meter.

Chromium was determined by oxidation of the complexes with basic hydrogen peroxide and subsequent measurement of the absorption of the resulting chromate solution at 373 nm.

Resistance measurements were obtained at room temperature using a Lectro Mho-meter Model 11000 conductivity bridge.

Ultraviolet-visible spectra were obtained from a Cary Model 14 spectrophotometer using matched 1.0-cm cells. All spectra were measured at room temperature.

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

Discussion

The preparation of the new compounds utilized the complex difluorobis(propanediamine)chromium(III) tetrafluoro(propanediamine)chromate(III) as the starting material. Ion exchange studies confirmed the presence of a red cation and a blue anion in the starting compound. Since propanediamine complexes of chromium(III) tend to be much more soluble than the corresponding ethylenediamine analogs, it was not possible to isolate well-characterized solid derivatives of the cation *via* the methods used for the ethylenediamine complexes.[7]

The gross features of the electronic absorption spectrum of an aqueous solution of the cation $[Cr(pn)_2F_2]^+$ compare favorably with those found in solutions of *cis*-$[Cr(en)_2F_2]^+$. Thus, the cation $[Cr(pn)_2F_2]^+$ is assigned a cis geometry. Attempts to isolate stable solid derivatives of $[Cr(pn)_2F_2]^+$ are still underway.

Treatment of the complex $[Cr(pn)_2F_2][Cr(pn)F_4]$ with hydriodic acid produced $[Cr(pn)F_2(OH_2)_2]I \cdot H_2O$ as an insoluble product. This product could arise in one of two ways: (1) the cation in the double complex could undergo rapid Cr–N bond rupture with the complete loss of a propanediamine ligand, or (2) the complex anion could undergo the rapid loss of two fluoro ligands to form the observed diaquo product. The loss of two fluoro ligands from the anion appears to be the main if not only source of the difluorodiaquochromium(III) cation. This conclusion is supported by the observation that recrystallized samples of the sodium salt of the anion react in the same time interval as does $[Cr(pn)_2F_2][Cr(pn)F_4]$ with concentrated hydriodic acid; if the product were formed *via* Cr–N bond breaking, one would reasonably expect a difference in rates. If the cation was reacting, the sodium salt of the anion should not react on the same time scale.

Fluoride ion replacement in the anion in strong acid solution would result in the formation of weakly dissociated hydrogen fluoride molecules which would serve as an additional driving force for the reaction.

The cation, $[Cr(pn)F_2(OH_2)_2]^+$, is a good starting material for the preparation of other complexes of chromium(III). The obvious advantage is that the complex already contains two fluoro groups bound to Cr(III) and the difficulties of inducing fluoride to coordinate to Cr(III) can be avoided. The Cr–F bonds are sufficiently strong to remain intact during normal synthetic procedures so long as contact with strong acid solutions is avoided.

It is tempting to suggest that after the initial rapid loss of two fluoro ligands from the tetrafluoro complex, the rate of fluoride ion release decreases to the point that the remaining fluoro groups become relatively inert. However, the iodide salt of difluorodiaquo(propanediamine)chromium(III) has a low solubility in concentrated hydriodic acid and it may be that the diminished solubility of the complex becomes dominant at this point.

Reaction of the previously unreported complex bromodifluoroaquo(propanediamine)chromium(III) with ethylenediamine, propanediamine, or trimethylenediamine in boiling absolute alcohol produced at least two products. The major fraction of the pink-orange alcohol-insoluble product was identified as *trans*-$[Cr(pn)(AA)F_2]Br$, where AA was ethylenediamine, propanediamine, or trimethylenediamine.

The nature of the products was established *via* electronic absorption spectra, thin-layer chromatography, and additional synthetic investigations. The synthetic methods employed would suggest that one possible product of the reaction of the chromium(III) complex with ethylenediamine in alcohol would be an equimolar mixture of *trans*-$[Cr(pn)_2F_2]Br$ and $[Cr(en)_2F_2]Br$. Reaction of the starting complex, bromodifluoroaquo(propanediamine)chromium(III), with a tenfold excess of ethylenediamine for 18 hr (six times longer than that used in the preparative scheme and ten times as much diamine) produced only $[Cr(pn)(en)_2]Br_3$ as an alcohol-insoluble material. Thus, replacement of propanediamine coordinated to Cr(III) was not possible under the reaction conditions utilized in the preparative method. This result effectively excludes the possibility of the product being an equimolar mixture of bis(propanediamine) and bis(ethylenediamine) complexes.

Thin-layer chromatographic studies on the alcohol-insoluble fraction by the method of Swain and Sudmeyer indicated the presence of two products. The minor fraction could be greatly reduced by repeated recrystallization of the crude material from alcohol–water, but it was not possible to obtain a sample which chromatographed as a single spot. The inability to obtain a chromatographically pure sample is not too surprising since fluoride ion release from complexes of this type is known to be acid catalyzed.[8]

Known mixtures of *trans*-$[Cr(pn)_2F_2]^+$ and *trans*-$[Cr(en)_2F_2]^+$ could be separated *via* thin-layer chromatography and the R_f values of these materials did not agree with that of the impurity in the reaction mixture.

The electronic spectra of the samples obtained by repeated recrystallization from alcohol–water mixtures exhibited four bands in the 350–600-nm range. Such multiband spectra are consistent with a trans arrangement of the two fluoro ligands in complexes where the symmetry of the complex can be approximated as D_{4h}.

Table I gives the results of the electronic spectral studies. From Table I it is evident that complexes 5–9 have similar structures. Dubicki, Hitchman, and Day[9] using the complex *trans*-$[Cr(en)_2F_2]^+$ assigned the electronic transitions responsible for the observed spectral bands. In order of increasing energy these transitions are ${}^4B_{1g} \to {}^4E_g({}^4T_{2g})$, ${}^4B_{1g} \to {}^4B_{2g}({}^4T_{2g})$, ${}^4B_{1g} \to {}^4E_g({}^4T_{1g(a)})$, and ${}^4B_{1g} \to {}^4A_{2g}({}^4T_{1g(a)})$.

For trans complexes which contain two identical bidentate ligands, the transition ${}^4B_{1g} \to {}^4B_{2g}$ is characterized by the highest intensity. When the electronic spectra of *trans*-difluorobis(diamine)chromium(III) complexes of ethylenediamine and 1,2-propanediamine are compared in the range 350–700 nm and the transitions are arranged in order of decreasing molar absorptivities the following arrangement is found: ${}^4B_{1g} \to {}^4B_{2g}$, ${}^4B_{1g} \to {}^4E_g({}^4T_{2g})$, ${}^4B_{1g} \to A_{2g}({}^4T_{1g(a)})$, ${}^4B_{1g} \to {}^4E_g({}^4T_{1g(a)})$. Upon replacement of ethylenediamine by 1,3-propanediamine to yield the corresponding bis(trimethylenediamine) complex, all transitions other than ${}^4B_{1g} \to {}^4B_{2g}$ have very nearly the same molar absorptivities (see Table I).

For the mixed diamine complex *trans*-$[Cr(pn)(en)F_2]Br$, the order of molar absorptivities is identical with that found in the bis(ethylenediamine) and bis(1,2-propanediamine) complexes. This is not surprising since all the complexes contain five-membered chelate rings, and the ligand field strengths of ethylenediamine and 1,2-propanediamine are similar.

However, when the complex contains two different bidentate amine ligands, one capable of forming a five-membered chelate ring and one capable of forming a six-membered chelate ring, the transition ${}^4B_{1g} \to {}^4A_{2g}({}^4T_{1g(a)})$ is characterized

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

[8] J. M. DeJovine, W. R. Mason III, and J. W. Vaughn, unpublished data.

[9] L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, 9, 188 (1970).

by the greatest molar absorptivity and thus becomes "more allowed" than the $^4B_{1g} \rightarrow {}^4B_{2g}$ transition.

In the case where propanediamine was the ligand added to the starting material, an alcohol-soluble product could also be isolated. This material analyzed the same as the trans isomer insoluble in alcohol, but the electronic absorption spectrum consisted of only two bands and the molar absorptivities were about twice those exhibited by the trans isomer. The two-band spectrum and enhanced molar absorptivities are consistent with a cis structure. Thus complexes 11 and 12 are assigned cis structures since the spectra are consistent with that of *cis*-$[Cr(en)_2F_2]I$ which has been shown by other methods to have a cis arrangement of the two fluoro ligands.[7]

The amount of trans isomer formed in the synthetic scheme appeared to vary with the nature of the diamine being added to the starting complex. When ethylenediamine was used, an 80% yield of trans isomer was obtained; the percentage of trans isomer decreased to 56% with propanediamine and to 30% with trimethylenediamine.

Treatment of *trans*-$[Cr(pn)(en)F_2]Br$ or *trans*-$[Cr(pn)(tmd)F_2]Br$ with 72% perchloric acid produced the corresponding fluoroaquo complexes, *e.g.*, *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2$, as orange products, along with some green solid. The nature of the green product will be discussed in a following publication. The fluoroaquo complexes all chromatographed as single spots and the electronic spectra of three bands are consistent with a trans structure. Thus, the replacement of one fluoro ligand in the mixed ligand complexes by concentrated perchloric acid takes place with retention of configuration.

Registry No. $[Cr(pn)_2F_2][Cr(pn)F_4]$, 40946-18-7; $Na[Cr(pn)F_4]\cdot 1.15NaClO_4$, 40961-77-1; $[Cr(pn)F_2(OH_2)_2]I$, 40902-38-3; $[Cr(pn)F_2(OH_2)_2]Br$, 40902-39-4; *trans*-$[Cr(pn)_2F_2]Br$, 40902-40-7; *trans*-$[Cr(pn)(en)F_2]Br$, 40902-41-8; *trans*-$[Cr(pn)(tmd)F_2]Br$, 40902-42-9; $[Cr(pn)_2F_2]Br$, 40902-44-1; $[Cr(pn)(dach)F_2]Br$, 40902-43-0; *trans*-$[Cr(en)(pn)F(OH_2)](ClO_4)_2$, 40902-45-2; *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2$, 40902-46-3; $[Cr(pn)(en)_2]Br_3$, 40902-47-4; $[Cr(pn)F_2(OH)_2Br]$, 40902-48-5; en, 107-15-3.

Contribution from the Metcalf Research Laboratory, Department of Chemistry,
Brown University, Providence, Rhode Island 02912

Spectroscopic Studies of Metal-Metal Bonding. IV. Absorption and Laser Raman Spectra and Vibrational Analyses of $[(OC)_5Mn\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W)[1]

JOHN R. JOHNSON,[2] ROBERT J. ZIEGLER, and WILLIAM M. RISEN, Jr.*

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The infrared (33-2200 cm^{-1}), laser Raman (0-2200 cm^{-1}), and uv-visible (20,000-35,000 cm^{-1}) spectra of the compounds $A[MnM'(CO)_{10}]$, where M' = Cr, Mo, W and $A^+ = (C_6H_5)_4As^+$ or $(C_2H_5)_4N^+$, are reported. The vibrational spectra have been assigned on the basis of C_{4v} symmetry, normal-coordinate analyses based on these assignments have been performed, and the values of k(Mn-M') have been found to be in the order k(Mn-W) > k(Mn-Mo) > k(Mn-Cr). For isoelectronic pairs, k(Mn-Re) > k(Mn-W), and k(Mn-Mn) > k(Mn-Cr). The resultant appropriate eigenvectors show that currently employed simplified models for estimation of intermetallic forces are inadequate to predict correctly the magnitude of k(Mn-M'). The bonding implications of these variations in metal-metal bond strengths are discussed.

Introduction

The monoanions $[(OC)_5Mn\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W) prepared by Anders and Graham[3] form part of the $MM'(CO)_{10}$ series of metal-metal bonded compounds in which changes in metal-metal bond strength, k(M-M'), can be studied as a function of both M and M'. The complete series includes $M_2(CO)_{10}$ (M = Mn, Tc, Re), $MM'(CO)_{10}$ (M = Re; M' = Mn), $MM'(CO)_{10}^-$ (M = Mn, Re; M' = Cr, Mo, W), and $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W), among which there are a number of useful relationships to study. For example, $MnCr(CO)_{10}^-$ is isoelectronic with both the neutral $Mn_2(CO)_{10}$ and the dianion $Cr_2(CO)_{10}^{2-}$, and $MnW(CO)_{10}^-$ is isoelectronic and isostructural with $MnRe(CO)_{10}$. Through vibrational analysis of the anions presented here we may expect then to observe how changing the nuclear charge distribution affects k(Mn-M') in several cases and how strong is the effect on k(Mn-M') on going from first- to second- to third-row transition metal, M', bound to the same metal, Mn. To develop this approach more fully, the vibrational analysis of the series $[(OC)_5Re\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W) will be reported in a subsequent publication.[4]

Several spectroscopic investigations of metal-metal bonded carbonyls of the type $MM'(CO)_{10}$ have been reported.[3,5-20]

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(2) Abstracted in part from the Ph.D. thesis of J. R. Johnson, Brown University, which is to be submitted for publication.

(3) U. Anders and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 539 (1967).

(4) J. R. Johnson and W. M. Risen, Jr., to be submitted for publication.

(5) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

(6) D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc. A*, 1, 71 (1971).

(7) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2363 (1969).

(8) I. J. Hyams, D. Jones, and E. R. Lippincott, *J. Chem. Soc. A*, 1987 (1967).

(9) D. M. Adams and A. Squire, *J. Chem. Soc. A*, 2817 (1968).

(10) D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc. A*, 695 (1966).

(11) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965).

(12) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

(13) R. W. Cattrall and R. J. H. Clark, *J. Organometal. Chem.*, **6**, 167 (1966).

(14) R. J. H. Clark and B. C. Crosse, *J. Chem. Soc. A*, 224 (1969).

(15) J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and F. Nyman, *Nature (London)*, **207**, 142 (1965).

(16) D. M. Adams, M. A. Hooper, and A. Squire, *Chem. Commun.*, 1188 (1970).

(17) G. O. Evans, W. T. Wozniak, and R. K. Sheline, *Inorg. Chem.*, 9, 979 (1970).

(18) A. Davison and J. W. Faller, *Inorg. Chem.*, **6**, 845 (1967).

(19) P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 1889 (1967).

(20) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, 92, 3653 (1970).