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Chromium(III) Complexes of the *trans*-Tetraammine Series

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Complexes of the *trans*-tetraamminechromium(III) series *trans*-$[Cr(NH_3)_4AB]^{n+}$ (AB = F_2, Cl_2, Br_2, $F(H_2O)$, $Cl(H_2O)$, $Br(H_2O)$, $(H_2O)_2$, $(H_2O)(OH)$, FCl, FBr) and *cis*-$[Cr(NH_3)_4F_2]^+$ have been prepared and interconversion reactions between them described. *trans*-$[Cr(NH_3)_4BrF]^+$ is new and has been isolated as its perchlorate salt. Pronounced solvent effects upon the d–d spectra, when fluoride is in the coordination sphere, have been associated with varying degrees of hydrogen bonding between the chromophoric ions and the solvent.

Introduction

Chromium(III) complexes of the *cis*-$[Cr(NH_3)_4AB]^{n+}$ series belong to the classical complexes that were known before[1] the time of Soren Mads Jorgensen and Alfred Werner.

One might have thought that there were thermodynamic reasons for the fact that complexes of the corresponding trans series had not been discovered. We mention two factors which are worth considering when metal to ligand binding energies are independent of the atomic configuration. An isolated complex ion belonging to the cis series is statistically 4 times more probable than the corresponding ion of the trans series, and in polar solvents the *cis*-A_2 complex of net polarity might further be stabilized by solvation more than the corresponding trans complex, for which the internal polarities cancel. With a difference in solvation energy of 2 kJ these two factors give an equilibrium constant of 10 in favor of the cis. Electronic causes of cis–trans stability differences may obviously, however, overbear such small energy differences.

These considerations are, however, not necessarily always relevant, since the formation of complexes is in many cases based upon reaction rates[2–4] rather than equilibria.[5–7]

The cis series is prepared by cleavage either of the tetraammineoxalatochromium(III) complex or of suitable polynuclear chromium(III) complexes with strong acids. In both cases the cis configuration is present in the parent complex and advantage is taken of the property of chromium(III) complexes that they do not generally, unlike the corresponding cobalt(III) complexes, easily undergo isomerization reactions.

The trans series was probably first prepared by Schlesinger and Rickles in 1929.[8] However, unsuccessful attempts have been made in this laboratory at repeating Schlesinger and Rickles' procedures and apparently no reports exist in the literature about successful repetitions of their inaccurately described heterogeneous reactions. Further, by their identifications of the *cis*- and *trans*-dichlorotetraamminechromium(III) complexes it can, with the knowledge of their colors, be concluded that they permuted the two isomers. There is, however, a recent report[9] which, by using a procedure similar to that of Schlesinger and Rickles, lends some support to their original claims.

The trans series was discovered (or rediscovered) only recently and curiously enough was prepared almost simultaneously in two different ways. The method of Hoppenjans and Hunt[10] has the beauty of being classical since it involves the cleavage of a bridged complex in which the configuration about the chromium is already trans and remains trans in the mononuclear constituents after the cleavage process. Our[11] method would seem to be rather special since it employs the *trans*-difluorotetrakis(pyridine)chromium(III) ion as an initial reagent. However, this reagent has proved to be of quite general utility[12] in the synthesis of trans complexes of chromium(III), also in amine systems.

The present paper describes the preparation and isolation of the new complex ion *trans*-$[Cr(NH_3)_4BrF]^+$ and details are given for *trans*-$[Cr(NH_3)_4ClF]^+$ and the previously reported[11] series of mainly *trans*-tetraamminechromium(III) complexes. The latter comprises salts of the ions *cis*-$[Cr(NH_3)_4F_2]^+$ and *trans*-$[Cr(NH_3)_4AB]^{n+}$, where AB is F_2, Br_2, Cl_2, $(H_2O)_2$, $F(H_2O)$, $Br(H_2O)$, $Cl(H_2O)$, and $(OH)(H_2O)$, and preparations as well as interconversion reactions are described. The literature[10,13,24] further contains reports of the preparation of the trans ions $[Cr(NH_3)_4BrCl]^+$,[10] $[Cr(NH_3)_4(H_2O)I]^{2+}$ and $[Cr(NH_3)_4ClI]^+$,[13] and $[Cr(NH_3)_4ClF]^+$.[24]

The visible spectra of the present complexes have been parameterized[14,15] in the expanded radial function model[16] which combines the two first-order perturbation models known as the ligand field model and the Slater–Condon–Shortley model of interelectronic repulsion. Further their ESR spectra have been studied and interpreted using the same empirical parameters.[17]

The complexes belong to the class called the orthoaxial[18,19] complexes. These have the peculiarity that no matrix elements[15] of the ligand field connect the $e_g(O_h)$ and the $t_{2g}(O_h)$ orbitals so that the low-symmetry ligand field does not mix the subconfiguration $t_{2g}{}^3$ of the ground level with higher energy subconfigurations. This has the interesting consequence that the magnetic axis of these complexes appears to coincide with the molecular tetragonal axis as opposed to the situation found in the dichlorobis(ethylenediamine)chromium(III) complex.[20]

The present complexes are also of particular interest because they represent the orthoaxial parents[21] of series of complexes which by a small extra nonorthoaxial ligand field, which hardly changes their ligand field spectra, acquire optical activity and thereby circular dichroism. An example would be a complex such as the *trans*-dichlorobis(1(*R*),2(*R*)-cyclohexanediamine)chromium(III) ion.

Similarly the complexes may be considered as the mononuclear parents of bridged complexes whose spectra[22] and magnetic[23] properties are of current interest.

Results and Discussion

The *trans*-difluorotetrakis(pyridine)chromium(III) ion reacts with liquid ammonia at 100 °C to give a mixture of *cis*- and *trans*-difluorotetraamminechromium(III) ions, a mixture which probably approaches equilibrium in the homogeneous solution. When iodide is the anion, the cis complex is soluble in liquid ammonia, in contrast to the trans complex which precipitates from the homogeneous solution. The iodides of the two isomers can easily be separated by washing out the cis complex with liquid ammonia. If the perchlorate is used instead of the iodide, more cis complex is formed, presumably because both perchlorates are soluble in liquid ammonia and the trans complex does not in this case leave the homogeneous reaction mixture. Furthermore, the separation of the cis–trans mixture of perchlorates is not simple either in ammonia or in water solution.

The *cis*-difluoro complex can also be prepared by the action of mercury(II) acetate on a solution of *cis*-

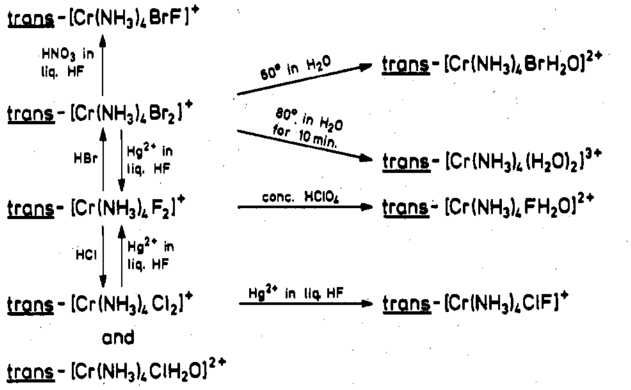

Figure 1. Reactions leading to trans complexes.

aquachlorotetraamminechromium(III) chloride in liquid hydrogen fluoride at −70 °C.

The *trans*-difluorotetraamminechromium(III) ion reacts with concentrated hydrochloric, hydrobromic, and perchloric acids to form the *trans*-dichloro-, *trans*-dibromo-, and *trans*-aquafluorotetraamminechromium(III) complexes, respectively. For the reactions with hydrochloric acid and hydrobromic acid it is convenient to use the usual concentrated acids after they have been saturated at −10 °C with the hydrogen halide gases, in order to minimize the simultaneous formation of *trans*-aquachloro and *trans*-aquabromo complexes. We have found that this is unnecessary with the corresponding reactions of the difluorobis(diamine) complexes when the amines are ethylenediamine, trimethylenediamine, propylenediamine, or *trans*-1,2-cyclohexanediamine, since in these cases the *trans*-aquabromo complexes are much more soluble in the concentrated acids, relative to the corresponding dihalo complexes.

The reverse reactions may also be performed. For example, the replacement of coordinated bromide by fluoride takes place when a solution of the *trans*-dibromotetraamminechromium(III) complex in liquid hydrogen fluoride reacts with mercury(II) acetate.

An interesting reaction is the formation of the complex *trans*-bromofluorotetraamminechromium(III) by dissolution of the *trans*-dibromo nitrate in liquid hydrogen fluoride at −70 °C. Bromine and nitrogen dioxide are formed. We believe that the nitrate ion, which in liquid hydrogen fluoride gives the nitryl ion, oxidizes the coordinated bromide according to

$$\textit{trans}\text{-}[\mathrm{Cr(NH_3)_4Br_2}]^+ + \mathrm{NO_2}^+ + \mathrm{F}^- \rightarrow \textit{trans}\text{-}[\mathrm{Cr(NH_3)_4BrF}]^+ + \mathrm{NO_2} + {}^1/{}_2\mathrm{Br_2}$$

In Figure 1 are shown schematically the reactions which lead to the different trans complexes.

The ligand field spectra have been discussed elsewhere.[14,15] Here we only want to emphasize the fact that a strong solvent effect is observed in the absorption spectrum of *trans*-chlorofluorotetraamminechromium(III) perchlorate. Figure 2 shows the spectra of the latter salt in water and in dimethylformamide. That no substitution reaction has taken place was proved by recovery of the original compound from the dimethylformamide solution. The pronounced difference in the two spectra can be rationalized by invoking hydrogen bond formation. In aqueous solution a hydrogen bond can be formed between the two strongly electronegative atoms, the fluorine of the coordination sphere and the oxygen of the water molecule, while in dimethylformamide the oxygen atom is replaced by the much less electronegative carbon atom. This rationale is supported by the fact that dimethyl sulfoxide produces approximately the same effect as dimethylformamide, while monomethylformamide and formamide, which allow F–H–N bonds, give spectra which are roughly intermediate between those of water and dimethylformamide. Further, a similar spectral dependence on solvent has been observed by us for several other fluoride-containing chromium(III) complexes, while complexes lacking fluoride, but containing chloride, exhibit these solvent effects to an order-of-magnitude lesser extent than do those complexes containing fluoride. For the spectra in water and in dimethylformamide there are the hydrogen-bonding possibilities Cl–H–O and Cl–H–C, respectively, none of which would be expected to be important and whose difference therefore would not be so either. It is concluded that the solvent effects observed are associated with varying extents of hydrogen bond formation, but the particular variations found in the spectra are not understood.

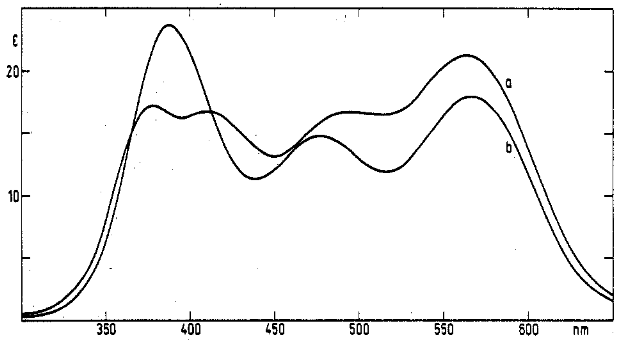

Figure 2. Absorption spectra of *trans*-[Cr(NH$_3$)$_4$ClF]ClO$_4$ in dimethylformamide (a) and in water (b).

Experimental Section

Materials. *trans*-Difluorotetrakis(pyridine)chromium(III) iodide was prepared as described previously.[12] Most other chemicals used were of analytical grade, purchased from Merck Darmstadt.

Spectra. Absorption spectra in the 800–220-nm region were recorded using a Cary Model 14 spectrophotometer. All the compounds prepared were characterized in this way and some data have been collected together in Table I.

Analyses. The chromium analyses were performed using a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Ammonia and halogens were determined using standard procedures.

Washing and Drying of Samples. In all of the following recipes the complexes have been washed with ethanol and air-dried, unless otherwise stated.

Dangers. The mechanical handling of the perchlorates represents a potential danger because of the reducing character of the coordinated ammonia. Also the washing with alcohol should be done with caution. However, we have never experienced any explosions with the present compounds.

Preparations. 1. ***trans*-[Cr(NH$_3$)$_4$F$_2$]I.** *trans*-[Cr(py)$_4$F$_2$]I (100 g) was dried at 100 °C for 1 h. The dried product was placed in a steel autoclave (volume 260 ml) and liquid ammonia was added to give a total volume of ca. 200 ml (but no more to be sure of avoiding a hydrostatic pressure). The autoclave was heated in an oven at 100 °C for 2 h (the pressure is ca. 60 atm). After cooling, the precipitate was filtered off on a sintered-glass funnel, washed with liquid ammonia (500 ml) to remove the cis complex, and then washed with ethanol; yield 39 g. The product was dissolved in hydrochloric acid (ca. 150 ml, 0.01 M) preheated to 70 °C and was recrystallized by adding potassium iodide (20 g) before cooling; yield 34.4 g of brick red crystals.

2. ***trans*-[Cr(NH$_3$)$_4$F$_2$]ClO$_4$.** The iodide (34.4 g) was dissolved in perchloric acid (ca. 150 ml, 0.01 M) preheated to 70 °C and was recrystallized by addition of concentrated perchloric acid (30 ml). Ethanol (200 ml) was then added gradually to the cooled solution over a period of 10 min. The resulting precipitate was filtered off and washed with ethanol. The product was then recrystallized by dissolving in perchloric acid (150 ml, 0.01 M) preheated to 70 °C and precipitating by addition of concentrated perchloric acid (10 ml); yield 30.6 g of dark red crystals. Anal. Calcd for [Cr(NH$_3$)$_4$F$_2$]ClO$_4$: Cr, 20.20; N, 21.75; F, 14.76. Found: Cr, 20.18; N, 21.67; F, 14.78.

3. ***cis*-[Cr(NH$_3$)$_4$F$_2$]I.** The ammonia solution from preparation 1 was evaporated to dryness with an electric fan and the product was washed with ethanol; yield 13 g of violet-red crystals. The complex was dissolved in hydrochloric acid (80 ml, 0.01 M) preheated to 70

Table I.

trans-$[Cr(NH_3)_4F_2]ClO_4$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{sh}$:[a] (13.8, 535) $(\epsilon, \lambda)_{max}$: (14.9, 492); (10.9, 405); (11.1, 358); (4.0, 243) $(\epsilon, \lambda)_{min}$: (9.0, 437); (9.5, 380); (0.1, 285); (2.4, 223)
cis-$[Cr(NH_3)_4F_2]ClO_4$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{max}$: (42.1, 526); (18.1, 380); (7.3, 237) $(\epsilon, \lambda)_{min}$: (7.2, 437); (0.2, 290); (7.0, 227)
trans-$[Cr(NH_3)_4F(H_2O)](ClO_4)_2\cdot{}^1/_2H_2O$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{max}$: (20.6, 529); (25.9, 378); (9.1, 243) $(\epsilon, \lambda)_{sh}$: (18.8, 480) $(\epsilon, \lambda)_{min}$: (11.9, 432); (0.1, 290); (8.4, 224)
trans-$[Cr(NH_3)_4Br_2]Br\cdot H_2O$ in 10^{-2} M HCl	$(\epsilon, \lambda)_{max}$: (34.1, 617); (17.1, 467); (30.6, 395) $(\epsilon, \lambda)_{min}$: (7.5, 530); (16.8, 457); (11.9, 350)
trans-$[Cr(NH_3)_4Br(H_2O)]Br_2$ in 10^{-2} M HCl	$(\epsilon, \lambda)_{max}$: (21.9, 572); (19.3, 467); (39.1, 386) $(\epsilon, \lambda)_{min}$: (12.0, 510); (15.2, 440); (6.2, 328)
trans-$[Cr(NH_3)_4Cl_2]Cl\cdot H_2O$ in 10^{-2} M HCl	$(\epsilon, \lambda)_{max}$: (24.3, 591); (15.0, 474); (29.6, 399) $(\epsilon, \lambda)_{min}$: (7.4, 525); (13.5, 445); (0.3, 305)
trans-$[Cr(NH_3)_4Cl(H_2O)]Cl_2$ in 10^{-2} M HCl	$(\epsilon, \lambda)_{max}$: (18.2, 560); (16.8, 467); (38.7, 384) $(\epsilon, \lambda)_{min}$: (12.9, 510); (13.1, 436); (0.2, 290)
trans-$[Cr(NH_3)_4ClF]ClO_4$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{max}$: (18.0, 566); (14.8, 477); (23.7, 388) $(\epsilon, \lambda)_{min}$: (12.0, 516); (11.3, 436); (0.3, 300)
trans-$[Cr(NH_3)_4BrF]ClO_4$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{max}$: (21.7, 575); (17.8, 464); (32.5, 388) $(\epsilon, \lambda)_{sh}$: (15.4, 480) $(\epsilon, \lambda)_{min}$: (11.8, 513); (13.7, 439); (4.4, 325)
trans-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ in 10^{-2} M $HClO_4$	$(\epsilon, \lambda)_{sh}$: (18.6, 520) $(\epsilon, \lambda)_{max}$: (21.4, 470); (31.4, 368) $(\epsilon, \lambda)_{min}$: (11.7, 416); (0.2, 285)
trans-$[Cr(NH_3)_4(H_2O)(OH)](ClO_4)_2$ in water	$(\epsilon, \lambda)_{sh}$: (25.1, 550); (19.5, 354) $(\epsilon, \lambda)_{max}$: (30.6, 514); (42.5, 404) $(\epsilon, \lambda)_{min}$: (21.7, 458); (0.7, 290)
trans-$[Cr(NH_3)_4(OH)_2]^+$ in 2 × 10^{-2} M NaOH	$(\epsilon, \lambda)_{max}$: (26.2, 535); (29.7, 407); (11.5, 338) $(\epsilon, \lambda)_{min}$: (14.4, 459); (8.3, 359); (1.7, 285)
trans-$[Cr(NH_3)_4F(OH)]^+$ in 5 × 10^{-2} M NaOH	$(\epsilon, \lambda)_{max}$: (23.4, 523); (15.9, 453); (26.6, 412); (11.0, 348) $(\epsilon, \lambda)_{min}$: (15.2, 460); (15.7, 450); (9.8, 362); (0.4, 280)
trans-$[Cr(NH_3)_4BrF]ClO_4$ in dimethylformamide	$(\epsilon, \lambda)_{max}$: (26.4, 576); (20.8, 467); (36.0, 388) $(\epsilon, \lambda)_{sh}$: (17.3, 485) $(\epsilon, \lambda)_{min}$: (14.6, 512); (17.3, 447); (4.6, 327)
trans-$[Cr(NH_3)_4ClF]ClO_4$ in dimethylformamide	$(\epsilon, \lambda)_{max}$: (21.3, 563); (16.7, 495); (16.8, 412); (17.2, 378) $(\epsilon, \lambda)_{min}$: (16.5, 513); (13.2, 450); (16.2, 395); (0.6, 300)

[a] sh = shoulder; ϵ in M^{-1} cm^{-1}; λ in nm.

°C and was recrystallized by addition of sodium iodide (5 g) before cooling; yield 11.5 g. Anal. Calcd for $[Cr(NH_3)_4F_2]I$: Cr, 18.24; N, 19.66; I, 44.52. Found: Cr, 18.23; N, 19.53; I, 44.50.

4. *cis*-**$[Cr(NH_3)_4F_2]ClO_4\cdot 0.25H_2O$.** The iodide salt from preparation 3 (11.5 g) was dissolved in perchloric acid (60 ml, 0.01 M) at 70 °C. Concentrated perchloric acid (10 ml) was added and then ethanol (50 ml); yield 10 g. The product was recrystallized by the same procedure except that no ethanol was added; yield 9 g of violet-red needles. Anal. Calcd for $[Cr(NH_3)_4F_2]ClO_4\cdot 0.25H_2O$: Cr, 19.85; N, 21.38; F, 14.50. Found: Cr, 19.81; N, 21.27; F, 14.32.

5. *trans*-**$[Cr(NH_3)_4F_2]ClO_4$ from** *trans*-**$[Cr(NH_3)_4Br_2]Br\cdot H_2O$.** *trans*-$[Cr(NH_3)_4Br_2]Br\cdot H_2O$ (5 g, 13.2 mmol) (see preparation 8) was dissolved in anhydrous hydrogen fluoride (50 ml) cooled to −70 °C with dry ice. To the green solution was added mercury(II) acetate (6.5 g, 20.4 mmol). The color changed rapidly from green to red. To the solution was then added methanol (50 ml) precooled with dry ice, and the solution was filtered (Whatman No. 50) into ether (500 ml) cooled with dry ice. The precipitated complex was filtered off, dissolved in perchloric acid (30 ml, 0.01 M) preheated to 60 °C, and recrystallized by the addition of concentrated perchloric acid (5 ml); yield 3.0 g (88%). The absorption spectrum is identical with that of the product from preparation 2.

6. *cis*-**$[Cr(NH_3)_4F_2]ClO_4$ from** *cis*-**$[Cr(NH_3)_4ClH_2O]Cl_2$.** The procedure is the same as that of preparation 5. *cis*-$[Cr(NH_3)_4ClH_2O]Cl_2$ (5 g) and mercury(II) acetate (10 g) were used. The complex was precipitated with ether and recrystallized by dissolving in perchloric acid (30 ml, 0.01 M) preheated to 50 °C and precipitating by the addition of concentrated perchloric acid (5 ml); yield 4.7 g (89%). The absorption spectrum is identical with that of the product from preparation 4.

7. *trans*-**$[Cr(NH_3)_4FH_2O](ClO_4)_2\cdot 0.5H_2O$.** *trans*-$[Cr(NH_3)_4F_2]ClO_4$ (4 g) was ground in a mortar with concentrated perchloric acid (10 ml) and left for 1 h (*caution*). The complex dissolved and after some time a precipitate began to form. When a porridge consistency was obtained, the mixture was cooled to −15 °C and the product was filtered off and washed with ether. [To prevent explosions the suction flask was half filled with water and the ether–perchloric acid mixture was immediately sucked into the water.] The crude product was then dissolved in perchloric acid (0.01 M) preheated to 60 °C (it is very soluble) and precipitated by the addition of concentrated perchloric acid and cooling. The product was washed with a little ice-cold water. After two such recrystallizations large red crystals were obtained; yield 2.5 g (44%). Anal. Calcd for $[Cr(NH_3)_4FH_2O](ClO_4)_2\cdot 0.5H_2O$: Cr, 14.24; N, 15.35; F, 5.21. Found: Cr, 14.18; N, 15.39; F, 5.18.

8. *trans*-**$[Cr(NH_3)_4Br_2]Br\cdot H_2O$.** *trans*-$[Cr(NH_3)_4F_2]ClO_4$ (5 g) was dissolved in hydrobromic acid (25 ml, 48%) in a round-bottom flask. The solution was saturated at −10 °C with hydrogen bromide gas. The flask was then fitted with a tight stopper and the solution stirred magnetically at room temperature for 20 h. The precipitated green product was isolated by filtration and washed with ethanol; yield 6.7 g (91%). For recrystallization, the crude product (3 g) was dissolved in hydrobromic acid (150 ml, 0.01 M) at 25 °C. To the solution was then added hydrobromic acid (30 ml, 48%) with cooling; yield 2.3 g of green crystals. Anal. Calcd for $[Cr(NH_3)_4Br_2]Br\cdot H_2O$: Cr, 13.75; N, 14.84; Br, 63.44. Found: Cr, 13.71; N, 14.87; Br, 63.63.

Hydrogen bromide gas was passed through the filtrate from the recrystallization and *trans*-$[Cr(NH_3)_4BrH_2O]Br_2$ (0.4 g) was precipitated.

9. *trans*-**$[Cr(NH_3)_4BrH_2O]Br_2$.** *trans*-$[Cr(NH_3)_4Br_2]Br\cdot H_2O$ (3.7 g) was heated in hydrobromic acid (40 ml, 0.01 M) at 60 °C until the green solution became brown (2–3 min). The solution was then filtered and cooled, and ice-cold hydrobromic acid (20 ml, 48%) was added slowly; yield 2.8 g (75%). The crystals were grayish in artificial light and olive green in daylight. Anal. Calcd for $[Cr(NH_3)_4BrH_2O]Br_2$: Cr, 13.75; N, 14.84; Br, 63.44. Found: Cr, 13.75; N, 14.96; Br, 63.38.

10. *trans*-**$[Cr(NH_3)_4Cl_2]Cl\cdot H_2O$ and** *trans*-**$[Cr(NH_3)_4ClH_2O]Cl_2$.** *trans*-$[Cr(NH_3)_4F_2]ClO_4$ (5 g) was added to concentrated hydrochloric acid (25 ml) and the slurry was then saturated at −10 °C with hydrogen chloride gas. The mixture was left under pressure with magnetic stirring for 20 h at room temperature. The product was gray in artificial light and green in daylight; yield 4.6 g of a mixture of *trans*-$[Cr(NH_3)_4Cl_2]Cl\cdot H_2O$ and *trans*-$[Cr(NH_3)_4ClH_2O]Cl_2$.

11. *trans*-**$[Cr(NH_3)_4ClH_2O]Cl_2$.** The crude product from preparation 10 was extracted on a sintered-glass funnel with hydrochloric acid (0.01 M) at 30 °C, giving a brownish red solution. When the filtered extract became green, the extraction was stopped. The volume of the extract was increased by 50% by addition of ice-cold concentrated hydrochloric acid, and precipitation began immediately; yield 1.6 g. For recrystallization the product was dissolved in hydrochloric acid (0.01 M) at 50 °C and the solution was filtered and cooled. A half-volume of ice-cold hydrochloric acid was then added dropwise with stirring; yield 1.4 g of brownish red crystals. Anal. Calcd for $[Cr(NH_3)_4ClH_2O]Cl_2$: Cr, 21.25; N, 22.94; Cl, 43.50. Found: Cr, 21.26; N, 23.01; Cl, 43.39.

12. *trans*-**$[Cr(NH_3)_4Cl_2]Cl\cdot H_2O$.** The green residue from the extraction in preparation 11 was dissolved in hydrochloric acid (0.01 M) at 30 °C and the complex was precipitated from the filtered solution by cooling and addition of a half-volume of ice-cold concentrated hydrochloric acid; yield 2.3 g. The product was recrystallized by repeating the procedure but with slow addition of the concentrated hydrochloric acid; yield 2.2 g of green crystals. Anal. Calcd for $[Cr(NH_3)_4Cl_2]Cl \cdot H_2O$: Cr, 21.25; N, 22.94; Cl, 43.50. Found: Cr, 21.29; N, 23.02; Cl, 43.46.

13. ***trans*-$[Cr(NH_3)_4(H_2O)(OH)](ClO_4)_2$.** *trans*-$[Cr(NH_3)_4Br_2]Br \cdot H_2O$ (8.3 g) was dissolved in perchloric acid (20 ml, 0.01 M) at 80 °C. The dibromo complex thereby aquates within 10 min giving a red solution of the diaqua complex. A saturated solution of sodium perchlorate (20 ml) was added to the solution and on cooling and slow addition of pyridine (3 ml) crystallization began; yield 6 g. The product was dissolved in water (80 ml) preheated to 50 °C and recrystallized by addition of saturated sodium perchlorate solution (5 ml); yield 4.9 g of shiny pinkish red crystals. Anal. Calcd for $[Cr(NH_3)_4(H_2O)(OH)](ClO_4)_2$: Cr, 14.70; N, 15.82. Found: Cr, 14.64; N, 15.86.

14. ***trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$.** *trans*-$[Cr(NH_3)_4(H_2O)(OH)](ClO_4)_2$ (3 g) was dissolved in the minimum volume of 1 M perchloric acid preheated to 70 °C. Concentrated perchloric acid (5 ml) was added and the solution was left in a vacuum desiccator over concentrated sulfuric acid for ca. 24 h, giving large crystals of the diaqua complex. The complex was filtered off and washed with ether (it is soluble in ethanol); yield 3.7 g. Anal. Calcd for $[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$: Cr, 11.45; N, 12.32. Found: Cr, 11.40; N, 12.30.

15. ***trans*-$[Cr(NH_3)_4ClF]ClO_4 \cdot H_2O$.** *trans*-$[Cr(NH_3)_4Cl_2]Cl \cdot H_2O$ (5 g, 20.4 mmol) was added to anhydrous hydrogen fluoride (40 ml) cooled to −70 °C with dry ice. To the solution was added mercury(II) acetate (6.5 g, 20.4 mmol) in small portions, whereupon the color changed from green to brown-red. Precooled methanol (50 ml) was then added slowly and the solution was filtered into ether (500 ml) cooled with dry ice. The precipitate was filtered off and dissolved in water (ca. 40 ml), and the complex was reprecipitated by the addition of concentrated perchloric acid (5 ml). The product was recrystallized by dissolving it in perchloric acid (60 ml, 0.01 M) preheated to 60 °C and slowly adding concentrated perchloric acid (5 ml) to the filtered, cooled solution; yield 2.5 g (65%) of brownish crystals. Anal. Calcd for $[Cr(NH_3)_4FCl]ClO_4 \cdot H_2O$: Cr, 17.81; N, 19.19; F, 6.51; Cl, 24.28. Found: Cr, 17.73; N, 19.22; F, 6.48; Cl, 24.56.

16. ***trans*-$[Cr(NH_3)_4BrF]ClO_4 \cdot 2.5H_2O$.** Crude *trans*-$[Cr(NH_3)_4Br_2]Br \cdot H_2O$ (5 g) was dissolved in nitric acid (150 ml, 0.01 M) at 25 °C. By addition of concentrated nitric acid (20 ml), *trans*-$[Cr(NH_3)_4Br_2]NO_3$ (3.5 g) was precipitated. This complex was added in small portions to anhydrous hydrogen fluoride (40 ml) precooled with dry ice to −70 °C. The complex dissolved immediately giving a green solution which in a few minutes became grayish brown and precipitated a red solid (apparently a glass containing N_2O_4 and Br_2). After 10 min concentrated perchloric acid (5 ml) was added to the solution, whereupon the complex precipitated. The mixture was added to ether (400 ml) precooled with dry ice, and the precipitate was filtered off and washed with ether. The complex was recrystallized by dissolving it in perchloric acid (20 ml, 0.01 M) and precipitating by the addition of concentrated perchloric acid (2 ml) and saturated sodium perchlorate solution (10 ml); yield 1.5 g. Another crop (0.5 g) was obtained by addition of ethanol (30 ml) to the filtrate and cooling at −15 °C. Anal. Calcd for $[Cr(NH_3)_4BrF]ClO_4 \cdot H_2O$: Cr, 14.30; N, 15.41; Br, 21.98. Found: Cr, 14.44; N, 15.37; Br, 21.72.

Registry No. *trans*-$[Cr(NH_3)_4F_2]I$, 18770-18-8; *trans*-$[Cr(NH_3)_4F_2]ClO_4$, 40029-16-1; *cis*-$[Cr(NH_3)_4F_2]I$, 58864-85-0; *cis*-$[Cr(NH_3)_4F_2]ClO_4$, 58864-87-2; *trans*-$[Cr(NH_3)_4F(H_2O)](ClO_4)_2$, 18737-48-9; *trans*-$[Cr(NH_3)_4Br_2]Br$, 18737-49-0; *trans*-$[Cr(NH_3)_4Br(H_2O)]Br_2$, 18737-50-3; *trans*-$[Cr(NH_3)_4Cl_2]Cl$, 18770-19-9; *trans*-$[Cr(NH_3)_4Cl(H_2O)]Cl_2$, 18737-53-6; *trans*-$[Cr(NH_3)_4(H_2O)(OH)](ClO_4)_2$, 58816-88-9; *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$, 21034-95-7; *trans*-$[Cr(NH_3)_4ClF]ClO_4$, 40029-18-3; *trans*-$[Cr(NH_3)_4BrF]ClO_4$, 58816-89-0; *trans*-$[Cr(NH_3)_4(OH)_2]^+$, 51266-65-0; *trans*-$[Cr(NH_3)_4F(OH)]^+$, 58816-90-3; *trans*-$[Cr(py)_4F_2]I$, 27731-46-0; *cis*-$[Cr(NH_3)_4Cl(H_2O)]Cl_2$, 58816-91-4.

References and Notes

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