

Triammine Complexes of Chromium(III). Synthesis and Characterization of the Two Isomeric Series

Peter Andersen,* Anders Døssing, Jørgen Glerup and Mette Rude

Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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It has been shown that *mer*-Cr(py)₃F₃ (py = pyridine), like *trans*-[Cr(py)₄F₂]⁺, is a convenient starting material for the synthesis of ammine and amine complexes of chromium(III).

Syntheses are described for the following triamminechromium(III) compounds: *fac*- and *mer*-Cr(NH₃)₃F₃, *fac*- and *mer*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃, *fac*-Cr(NH₃)₃(O₃SCF₃)₃, *fac*-Cr(NH₃)₃Cl₃ and *mer*-[Cr(NH₃)₃Cl₂(OH₂)₃]Cl · 2H₂O. *mer*-[Cr{NH(CH₂CH₂CH₂NH₂)₂}(OH₂)₃](ClO₄)₂F · H₂O was synthesized to demonstrate the generality of the procedure.

The compounds have been characterized by their UV/VIS and ESR spectra, and interconversion and isomerization reactions are discussed.

The six acid dissociation constants of the two isomeric [Cr(NH₃)₃(OH₂)₃]³⁺ ions have been determined and their magnitudes discussed in relation to those of other ammineaqua complexes of chromium(III).

Synthesis of the two isomeric series of triammine complexes of chromium(III) with facial or meridional configuration, respectively, of the ammonia ligands have primarily been based on either thermal decomposition of higher ammine complexes¹ or on treatment of Cr(NH₃)₃(O₂)₂ with strong acids such as perchloric acid or hydrochloric acid.² Garner and House have given a thorough review³ on ammine complexes of chromium(III), and references to the chemistry, including syntheses, of the triamines up to 1969 can be found there. The yields by these methods are, in our experience, moderate, and some of the products are mixtures of less well defined species. Most of the products belong to the meridional series. Since then Andersen *et al.*⁴ have isolated *fac*-Cr(NH₃)₃Cl₃ in moderate yields and from this *fac*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃. The trichloro complex was made by addition of hydrogen chloride to chromium(III) ammine solutions with a high content of oligomers. Oxidation of aqueous suspensions of Cr(NH₃)₃(CO)₃⁵ with chlorine have also given reasonable yields of the facial chromium(III) triammine.⁶

In connection with investigations of binuclear hydroxide-bridged complexes of chromium(III) triamines,^{4,7,8} the need for easy procedures with high yields led us to the syntheses described in the following. The procedures used are general in character and are based on the substitution properties of the inner complex Cr(py)₃F₃ first made by Costachescu⁹ by treating CrF₃ · aq¹⁰ with pyridine.

The substitution properties of Cr(py)₃F₃ are very similar to those of *trans*-[Cr(py)₄F₂]⁺ investigated by Glerup and

Schäffer.^{11–13} Thus we found that in Cr(py)₃F₃, pyridine can easily be replaced by ammonia or other amines without loss of fluoride from the coordination sphere, and subsequently the relatively basic fluoride ions can be replaced by other acido ligands or water with the aid of strong acids. Isomerization may or may not take place during these processes.

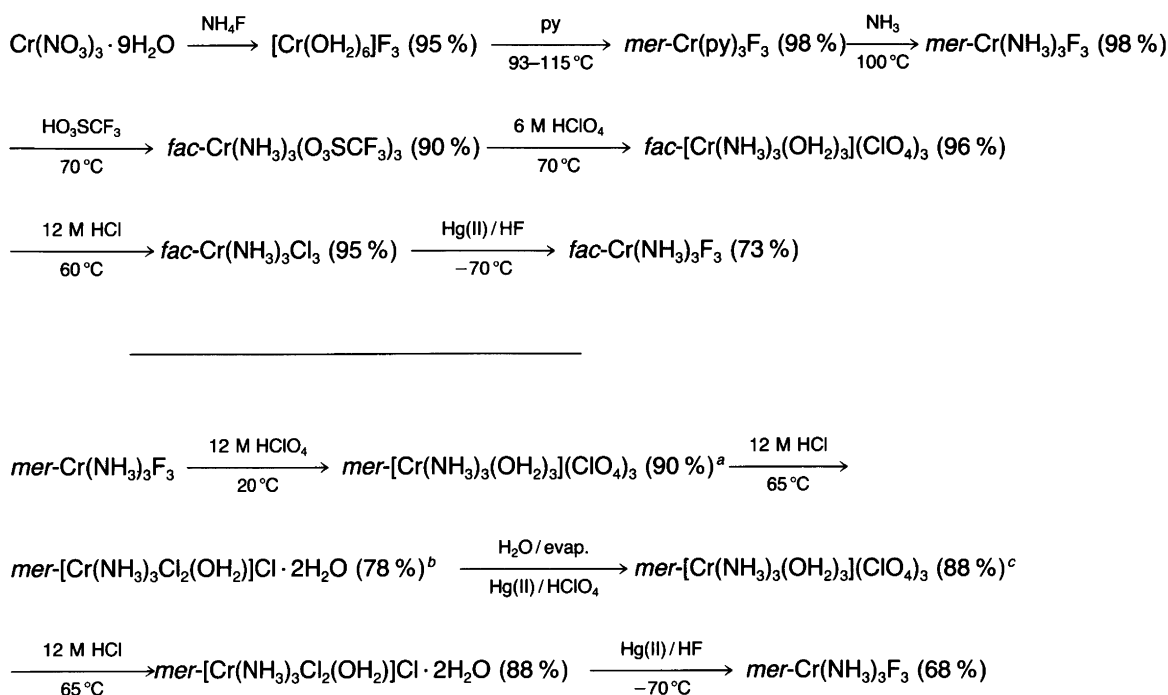
In the present work we emphasize the easy syntheses of some convenient salts of the meridional as well as of the facial triamminechromium(III) complexes in high yields and of high purity, and discuss some of their properties.

Results and discussion

The main reactions involved in the syntheses, given later in the experimental section, are outlined in Scheme 1. The scheme pays attention to the fact that it turned out to be difficult to remove small amounts of the facial isomer in *mer*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃ by crystallization methods. However, moderate treatment of such a mixture with concentrated hydrochloric acid (see below) produces easily separable salts of chloro complexes of the two isomeric triammine complexes. Data on chemical analyses and absorption spectra are given in the experimental section, and relevant frozen glass ESR spectra are given in Fig. 1.

Configurational assignment. The configuration of *fac*-[Cr(NH₃)₃(OH₂)₃]³⁺ has been determined from a variety of earlier observations. The ESR spectrum of this ion, the holohedrized symmetry of which is O_h, is almost identical to those of [Cr(OH₂)₆]³⁺ and [Cr(NH₃)₆]³⁺ with a characteristic relatively narrow transition as the main feature at a

* To whom correspondence should be addressed.



Scheme 1. The relevant reactions with yields relative to the preceding reactant given in parentheses. ^aContaining ca. 5% of the facial isomer. ^bContaining ca. 5% of the *fac*-Cr(NH₃)₃Cl₃. ^cWater extraction leaves ca. 5% of the insoluble *fac*-Cr(NH₃)₃Cl₃ on the filter.

field strength corresponding to $g=2$, as expected for chromium(III) with nearly isotropic surroundings. These ESR spectra differ from those of all other ammineaqua-chromium(III) complexes.^{4,14} Kinetic studies of this triamminetriaqua ion show three kinetically equivalent water ligands, contrary to the two types of water ligands in the meridional isomer.^{15,16} Condensation of the facial isomer to binuclear complexes with one, two or three hydroxo bridges, in which the facial configuration of the ammonia ligands has been demonstrated, e.g. by X-ray diffraction, is another piece of evidence.^{4,7,8} The configurational assignment and the visible spectrum of the present *mer*-[Cr(NH₃)₃(OH₂)₃]³⁺ are in correspondence with those of the triamminetriaqua complex obtained from Cr(NH₃)₃(O₂)₂.^{2,3}

The configurational assignment of the other complexes of Scheme 1 is based primarily on interconversions and is confirmed by ESR spectra. Thus the assignment of *mer*-Cr(NH₃)₃F₃ is based on the observation that hydrolysis of this compound with 70% perchloric acid at room temperature nearly quantitatively gives *mer*-[Cr(NH₃)₃(OH₂)₃]³⁺ (see later) and that treatment of *mer*-[Cr(NH₃)₃Cl₂(OH₂)]Cl · 2H₂O with hydrogen fluoride (−70°C) gives the original compound, while similar treatment of *fac*-Cr(NH₃)₃Cl₃ gives the other trifluoro isomer. Retention rather than conversion of the ammine configuration is expected under these circumstances (see later). Similar arguments have been used in the meridional/facial assignment of the other

ammine complexes of Scheme 1; the Hg(II)-assisted substitution of chloride by water in amminechlorochromium(III) complexes has in all known cases led to retention of the ammine configuration. The ESR spectra (Fig. 1) confirm in a unique way the configurational assignments obtained by the interconversion reactions. The ESR spectrum of *mer*-Cr(py)₃F₃ was simulated¹⁷ using the spin Hamiltonian of eqn. (1).

$$\mathcal{H} = g \beta \mathbf{H} \cdot \mathbf{S} + D [\text{S}_z^2 - \frac{1}{3} S(S+1)] + E (\text{S}_x^2 - \text{S}_y^2) \quad (1)$$

On this basis it was possible to decide the configuration also of the present Cr(py)₃F₃, which according to its ESR spectrum must be meridional. In this context it is worth mentioning that Cr(py)₃Cl₃ and Cr(py)₃Br₃ have also been characterized structurally,¹⁸ and, as for the trifluoro complex, only the meridional isomers are known. The optical spectra do not tell the configuration of these complexes in a correspondingly simple way. A relatively high value of ϵ and λ for the first (⁴A_{2g} → ⁴T_{2g} parentage) absorption band (see the experimental section) is, however, a common feature for the facial isomers when compared to the meridional ones.

The configuration of the two coordinated chloride ions in *mer*-[Cr(NH₃)₃Cl₂(OH₂)]Cl · 2H₂O is *trans*, as indicated by kinetic behaviour and spectral data.² A preliminary X-ray structure determination¹⁹ confirms this assignment as well as the meridional configuration of the ammonia ligands.

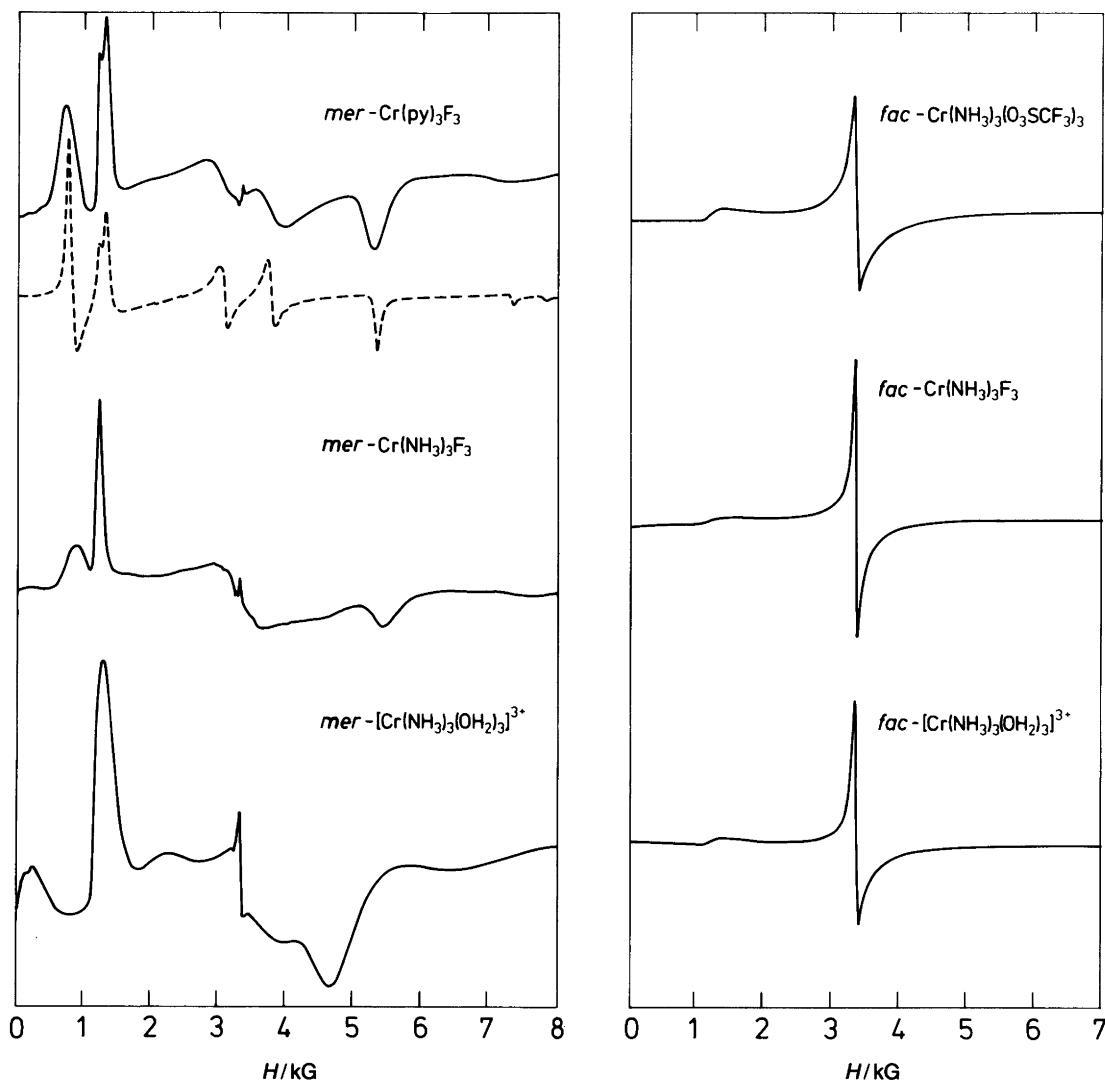


Fig. 1. First derivative ESR spectra at 9.38 GHz of frozen solutions (*N*-methylformamide or 1:1 water/glycerol glass at ca. -190°C) of some of the complexes from Scheme 1. The dashed curve is a simulated spectrum¹⁷ of *mer*-Cr(py)₃F₃ with the following parameters: $g = 1.98$, $D = 0.205\text{ cm}^{-1}$ and $E = 0.055\text{ cm}^{-1}$ [eqn. (1)]. The half-width of the Lorentzian curve used was 100 G. The small narrow transitions at 3.3 kG for the meridional isomers possibly originate from facial impurities. Deliberate addition of small amounts of the facial isomer to the samples of the meridional isomers showed that the relative amount of facial impurity is less than 0.1–0.3%.

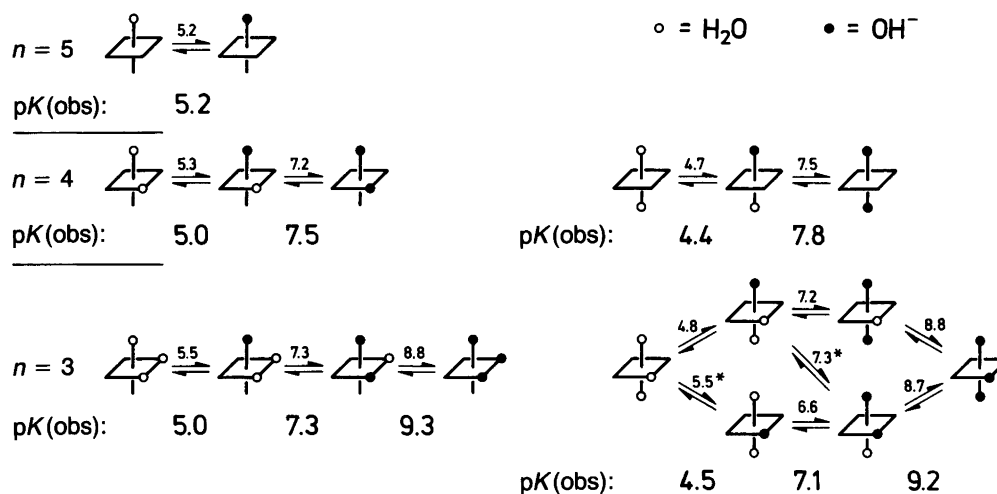
Isomerization. Complete conversion, or nearly so, from meridional to facial ammine configuration takes place without the loss of ammonia when *mer*-Cr(NH₃)₃F₃ is treated with anhydrous triflic acid at elevated temperature. The same conversion takes place when *mer*-Cr(NH₃)₃F₃ is treated with perchloric acid, but owing, probably, to lower solubility of the products in this medium the conversion here is far from complete even at elevated temperatures. A couple of days' treatment of *mer*-Cr(NH₃)₃F₃ with 70% perchloric acid at room temperature gives the triaquatriammine with only ca. 5% conversion, while the same treatment for a day at ca. 80°C results in 30–40% conversion to the facial triaquatriammine. Treatment of *mer*-Cr(NH₃)₃F₃ with concentrated hydrochloric acid results in less well defined mixtures of mainly meridional isomers where fluo-

ride has not been completely removed. The triaquatriammines, however, with concentrated hydrochloric acid give pure precipitates of chloro complexes with retention of the ammine configuration provided the treatment is moderate, i.e. less than $60\text{--}70^{\circ}\text{C}$ for less than 0.5–1 h.

It has been shown²⁰ that in acid media with a lower hydrogen ion concentration than in these concentrated acid media the facial/meridional isomerization is much slower than the substitution of ammonia with water.

All of these observations have been used in the procedures for the syntheses of the pure salts of the triammine complexes given in the experimental section.

Other aspects. Preliminary investigations show that *mer*-Cr(py)₃F₃ is also a convenient starting material for the



Scheme 2. Acid dissociation constants for $[\text{Cr}(\text{NH}_3)_n(\text{OH}_2)_{6-n}]^{3+}$ ($\text{p}K$ values at 25 °C in 1.0 M NaClO_4). The $\text{p}K$ values over the arrows are the statistically corrected values. For the meridional triammine two of these values (marked with *) have been assumed equal to the values of the facial isomer, the only difference in the configuration being the sequence of the four ligands *cis* to the reacting water ligand.

formation of triammine complexes of chromium(III) with amine ligands other than ammonia, e.g. tridentate amine ligands, and an example of such a synthesis is given in the experimental section for *mer*- $[\text{Cr}\{\text{NH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\}(\text{OH}_2)_3](\text{ClO}_4)_2\text{F}\cdot\text{H}_2\text{O}$.

The triaminetriaqua complexes of chromium(III) are excellent monomers for the study of the stepwise condensation to hydroxo-bridged dimers. The facial ammonia isomer reacts via the mono- and dihydroxo-bridged species to the fully condensed dimer, $[(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3]^{3+}$, and the four different dimers have been isolated and their interconversion studied as described elsewhere.^{4,7,8}

The acid dissociation constants of the two triaminetriaquachromium(III) isomers were determined in 1.0 M NaClO_4 at 25 °C where $\text{p}K_1$, $\text{p}K_2$ and $\text{p}K_3$ are 5.00(5), 7.27(6) and 9.28(9) for the facial isomer and 4.46(2), 7.12(3) and 9.21(5) for the meridional isomer, respectively. In Scheme 2 the statistically corrected $\text{p}K$ values of the aquapentaammine,²¹ the diaquatetraammines²² and the triaquatriammines are compared. In order to get the full scheme for the meridional isomer an assumption has been made for two of the values as explained in the scheme's caption. It is then seen that the $\text{p}K$ value for the *trans*-dihydroxo complex (meridional isomer) equals the corrected $\text{p}K_3$ value for the facial isomer (8.8) in accordance with this assumption. Successive deprotonation increases $\text{p}K$ by ca. 1.8 and 1.5 for the first two steps, respectively, with the same type of ligand *trans* to the reacting water ligand. The difference between the $\text{p}K_1$ values can be attributed mainly to the difference in σ -bond strength of the ligand *trans* to the reacting water ligand, as it has been done for octahedral amine complexes of rhodium(III) and other transition metals.²³ For these ammineaqua complexes of chromium(III) the acid strength of a water ligand is 4–5 times larger if it is situated *trans* to a water ligand than if it

is *trans* to ammonia. In addition there is a tendency to a small increase of the $\text{p}K_1$ values as the number of water ligands increases relative to the number (n) of ammonia ligands: With NH_3 *trans* to the reacting water ligand $\text{p}K_1$ increases from 5.2 to 5.5 when n decreases from 5 to 3; with H_2O *trans* to the reacting water ligand $\text{p}K_1$ increases from 4.7 to 5.1²⁴ when n decreases from 4 to 0. This may be connected to solvent effects which are probably partly responsible for the increase in acid strength observed when the ammonia ligands are exchanged by organic amine ligands. However, as the acidity of the water ligand depends on bond strengths (σ and π) and of the solvation for the acid complex as well as for the conjugate base, further data are required before it is possible in a more precise way to distinguish between the influence of the different factors on the relative magnitudes of the $\text{p}K$ values.

Experimental

Chemicals and chemical analysis. The chemicals were of reagent grade or of a similar or better quality. The synthesized compounds were analysed on a microscale for Cr, C, H, N and Cl.

Apparatus. Visible absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer with automatic disk data collection. The optical absorption data ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$, λ/nm) are given for compounds purified by reprecipitation, until the positions of the maxima and minima remained constant upon a further reprecipitation, and a deviation of less than 1% in molar absorptivity (ϵ) (for both maxima and minima) was found between the two products. pH measurements were made point by point with extrapolation, owing to loss of ammonia, as previously described.⁷ The ESR spectra were recorded with a Bruker

ESP 300 instrument on frozen glasses at 9.38 GHz with 100 kHz modulation frequency and 8 G modulation width.

Syntheses. Caution. In the following procedures handling of perchlorates and 70 % HClO₄ must be done with caution.²⁵ Syntheses on a larger scale than prescribed should be avoided or done with utmost care. Use plastic rods and avoid scraping and high (local) heat. Dilute mixtures of organic solvents and 70 % HClO₄ at once. Compounds precipitated from concentrated perchloric acid were washed with ice-cold 70 % HClO₄ and then with diethyl ether until they were free of acid, the suction flask half filled with water to secure fast dilution of the perchloric acid–diethyl ether mixture. Using this procedure we did not experience explosions.

1. *mer-Cr(py)₃F₃*. 400 g of Cr(NO₃)₃ · 9H₂O (1.0 mol) were dissolved in 200 ml water. The solution was filtered and cooled in ice. An ice-cold solution of 123 g of NH₄F (3.3 mol) in 150 ml water was then added slowly with stirring and cooling. The resultant grey–violet precipitate of [Cr(OH₂)₆]F₃ was filtered off, washed with ice-cold water and ethanol and air-dried. The crude product was then added to 1.5 l pyridine. The mixture was heated to boiling, and the pyridine–water azeotrope (b.p. 93 °C) was distilled off while stirring mechanically, until all water was removed (the temperature of the leaving vapours reached 115 °C). During the distillation pyridine was added (ca. 0.5 l). After being cooled in ice, the resultant violet crystals were filtered off, washed with acetone and diethyl ether and air-dried. Yield: 322 g (93 %). Found: Cr 14.82; C 51.86; H 4.30; N 12.25. Calc. for Cr(NC₅H₅)₃F₃: Cr 15.01; C 52.03; H 4.37; N 12.13. (ε, λ)_{max} (medium: 0.001 M HClO₄/1.0 M NaClO₄): (27.6, 553), (15.6, 377).

2. *mer-Cr(NH₃)₃F₃*. 322 g of *mer-Cr(py)₃F₃* (0.93 mol) were placed in a steel autoclave (1 l) and liquid ammonia was added to a total volume of 600 ml. The autoclave was closed and kept at 100 °C for 2 h. After being cooled, the mixture was filtered, washed with liquid ammonia, ethanol and diethyl ether, and the violet powder was dried in air. Yield: 146 g (98 %). The crude product was used directly for subsequent synthetic work. For recrystallization 10 g of the crude product were dissolved in 150 ml 0.01 M HClO₄ preheated to 60 °C. The solution was filtered and then kept at 5 °C for 3 h for crystallization. The product was filtered off, washed with ethanol and ether. After air-drying the yield was 2.5 g. Found: Cr 32.40; N 26.33; H 5.55. Calc. for Cr(NH₃)₃F₃: Cr 32.48; N 26.25; H 5.67. The absorption spectrum is identical with that of the product from synthesis 11.

3. *fac-Cr(NH₃)₃(O₃SCF₃)₃*. 10 g of crude *mer-Cr(NH₃)₃F₃* (0.063 mol) were added under vigorous stirring to 60 ml anhydrous triflic acid in small portions within 30 min. After the addition the flask was equipped with a CaCl₂ drying tube, and the mixture was stirred for 24 h at 65–70 °C. The

mixture was then cooled in ice and filtered. The resultant pink precipitate was washed with diethyl ether, until the washings were free of acid. (*Caution.* The reaction between diethyl ether and triflic acid is very exothermic.) After air-drying the yield was 31.0 g (90 %). For recrystallization 10 g of the crude product were dissolved in 100 ml acetone. The solution was filtered, and 250 ml diethyl ether were added within 5 min. The product was filtered off, washed with diethyl ether and air-dried. Yield: 7.8 g. Found: Cr 9.34; C 6.39; H 1.66; N 7.52. Calc. for Cr(NH₃)₃(O₃SCF₃)₃: Cr 9.45; C 6.55; H 1.65; N 7.64. (ε, λ)_{max} (medium: acetone): (6.1, 666), (107, 545), (30.3, 396) (extrapolated values due to hydrolysis with traces of water).

4. *fac-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃*. A mixture of 15.5 g of crude *fac-Cr(NH₃)₃(O₃SCF₃)₃* (0.028 mol) and 170 ml 6 M HClO₄ was stirred at 70 °C for 24 h in an uncovered beaker. The mixture was then cooled to room temperature, and the red, crystalline solid was filtered off and washed as described in the beginning of this section. After air-drying the yield was 12.3 g. For recrystallization the crude product was dissolved in 12 ml ice-cold 0.01 M HClO₄. The solution was filtered, 65 ml ice-cold 70 % HClO₄ were added dropwise with stirring, and the mixture was then kept at 0 °C for 30 min for crystallization. The resultant precipitate was filtered off and washed as described in the beginning of this section. After air-drying the yield was 12.0 g (93 %). Found: Cr 11.54; N 9.28; H 3.28; Cl 23.57. Calc. for [Cr(NH₃)₃(OH₂)₃](ClO₄)₃: Cr 11.42; N 9.23; H 3.32; Cl 23.35. (ε, λ)_{max} (medium: 0.1 M HClO₄/0.9 M NaClO₄): (37.1, 513), (22.7, 375).

5. *fac-[Cr(NH₃)₃(OH₂)(OH)₂](ClO₄)₃*. 10.0 g of *fac-Cr(NH₃)₃(OH₂)₃](ClO₄)₃* (0.022 mol) were stirred with 30 ml 1.5 M LiOH at 0 °C for ca. 10 min. The flaky, violet precipitate was then filtered off and washed thoroughly with ethanol to remove all LiClO₄. After a final washing with diethyl ether and air-drying the yield was 4.3 g (77 %). Found: Cr 20.33; N 16.39; H 5.15; Cl 14.12. Calc. for [Cr(NH₃)₃(OH₂)(OH)₂](ClO₄)₃: Cr 20.43; N 16.51; H 5.15; Cl 13.93.

6. *fac-Cr(NH₃)₃Cl₃*. 20.0 g of *fac-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃* (0.044 mol) and 32 ml 12 M HCl were mixed. The flask was closed and kept with stirring at 60–65 °C for 45 min. After cooling of the mixture in ice, the grey–blue precipitate was filtered off, washed once with 12 M HCl, twice with water and three times with ethanol. After air-drying the yield was 8.7 g (95 %). Found: Cr 24.75; N 20.01; H 4.22; Cl 50.63. Calc. for Cr(NH₃)₃Cl₃: Cr 24.83; N 20.06; H 4.33; Cl 50.78.

7. *fac-Cr(NH₃)₃Cl₃ from fac-Cr(NH₃)₃(O₃SCF₃)₃*. 10 g of crude *fac-Cr(NH₃)₃(O₃SCF₃)₃* (0.018 mol) and 200 ml 12 M HCl were mixed. The flask was closed and kept with stirring at 60–65 °C for 3 h. After cooling of the mixture in ice, the grey–blue precipitate was filtered off, washed once with 12 M HCl, twice with water and three times with acetone

(to remove traces of unreacted starting material). After air-drying the yield was 3 g (79%). Found: Cr 24.80; N 19.93; H 4.29; Cl 50.55.

8. *fac*-Cr(NH₃)₃F₃. 5.0 g of *fac*-Cr(NH₃)₃Cl₃ (0.024 mol) were added to 50 ml anhydrous hydrogen fluoride cooled to -70°C with dry ice. 12 g of mercury(II) acetate (0.038 mol) were then added to the mixture. The colour of the mixture changed rapidly from blue to violet. 50 ml methanol, precooled with dry ice, were then added to the solution, and the solution was filtered (Whatman No. 50) into 500 ml diethyl ether cooled with dry ice. The precipitated complex was filtered off and washed with diethyl ether and air dried. Yield: 2.8 g (73%). For recrystallization the crude product was dissolved in 140 ml 0.01 M HClO₄ preheated to 60°C. The solution was filtered, and then kept at 5°C for ca. 3 h for crystallization. The violet product was filtered off, washed with ethanol and diethyl ether and finally air-dried. Yield: 0.9 g. Found: Cr 32.41; N 26.09; H 5.66. Calc. for Cr(NH₃)₃F₃: Cr 32.48; N 26.25; H 5.67. (ε, λ)_{max} (medium: 0.001 M HClO₄/1.0 M NaClO₄): (4.2, 662), (40.4, 556), (15.8, 401).

9. *mer*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃. 10.0 g of crude *mer*-Cr(NH₃)₃F₃ (0.063 mol) were dissolved in 80 ml 70% HClO₄ in a beaker. The solution was stirred uncovered at room temperature for three days, during which a red solid precipitated. The mixture was cooled in ice to complete the crystallization, filtered, and the precipitate was washed as described in the beginning of this section. After air-drying the yield was 27 g of *mer*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃ containing a few percent of the facial isomer. Next, this mixture was reacted with 45 ml 12 M HCl. The flask was closed and stirred at 60–65°C for 45 min. The resultant violet mixture was cooled in ice for 30 min, then filtered and washed once with ice-cold 12 M HCl, three times with methanol and finally with diethyl ether. After air-drying the yield was 12.7 g of *mer*-[Cr(NH₃)₃Cl₂(OH₂)₂]Cl·2H₂O containing a little *fac*-Cr(NH₃)₃Cl₃. This mixture was extracted on the filter with small 40°C portions of 0.001 M HCl, until the extracts were colourless leaving ca. 0.5 g of the insoluble *fac*-Cr(NH₃)₃Cl₃ on the filter (see Isomerization section). The extract was concentrated to almost dryness on a rotary evaporator at 40°C. 23 ml ice-cold 3.5 M Hg(ClO₄)₂/0.5 M HClO₄ were added under cooling and stirring, which was continued at 0°C, until the dark colour of the chloro complex had disappeared. The mercury(II) chloride was filtered off and washed with 5 ml ice-cold water, which were added to the filtrate. Next, 110 ml 70% HClO₄, precooled to 0°C, were added to the filtrate dropwise under stirring and cooling. The red precipitate was filtered off and washed as described in the beginning of this section. After air-drying the yield was 18.5 g. For recrystallization the crude product was dissolved in 20 ml ice-cold 0.001 M HClO₄, the solution was filtered, and the complex was reprecipitated by adding 80 ml ice-cold 70% HClO₄ dropwise. The precipitate was filtered off and

washed as described in the beginning of this section. After air-drying the yield was 16.8 g (59%). Found: Cr 11.46; N 9.20; H 3.26; Cl 23.55. Calc. for [Cr(NH₃)₃(OH₂)₃](ClO₄)₃: Cr 11.42; N 9.23; H 3.32; Cl 23.35. (ε, λ)_{max} (medium: 0.1 M HClO₄/0.9 M NaClO₄): (25.9, 502), (26.8, 375).

10. *mer*-[Cr(NH₃)₃Cl₂(OH₂)₂]Cl·2H₂O. 16.8 g of *mer*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃ (0.037 mol) and 27 ml 12 M HCl were mixed. The flask was closed and kept with stirring at 60–65°C for 45 min. After the mixture had been cooled in ice the blue-violet precipitate was filtered off, washed once with ice-cold 12 M HCl, three times with methanol and finally with diethyl ether. After air-drying the yield was 8.5 g (88%). Found: Cr 19.49; N 16.01; H 5.61; Cl(total) 40.20; Cl(ionic) 13.31. Calc. for [Cr(NH₃)₃Cl₂(OH₂)₂]Cl·2H₂O: Cr 19.73; N 15.95; H 5.74; Cl(total) 40.37; Cl(ionic) 13.46. (ε, λ)_{max} (medium: 0.1 M HClO₄/0.9 M NaClO₄): (26.6, 596), (27.7, 408), (ε, λ)_{shoulder}: (16.6, 527).

11. *mer*-Cr(NH₃)₃F₃ from *mer*-[Cr(NH₃)₃Cl₂(OH₂)₂]Cl·2H₂O. The procedure is the same as that of synthesis 8. 6.3 g of *mer*-[Cr(NH₃)₃Cl₂(OH₂)₂]Cl·2H₂O (0.024 mol) and 12 g of mercury(II) acetate (0.038 mol) were used. Yield: 2.6 g (68%). The product was recrystallized as described in synthesis 2. Found: Cr 32.40; N 26.19; H 5.65. Calc. for Cr(NH₃)₃F₃: Cr 32.48; N 26.25; H 5.67. (ε, λ)_{max} (medium: 0.001 M HClO₄/1.0 M NaClO₄): (19.3, 546), (11.0, 389).

12. *mer*-[Cr{NH(CH₂CH₂CH₂NH₂)₂}(OH₂)₃](ClO₄)₂F·H₂O. 20 g of *mer*-Cr(py)₃F₃ (0.058 mol) and 7.6 g of bis(3-aminopropyl)amine (0.058 mol) were added to 75 ml 2-methoxyethanol. The solution was refluxed for 2 h and then concentrated to dryness on a rotary evaporator. The pink solid was transferred with diethyl ether to a filter and washed with diethyl ether. After air-drying the yield was 13.8 g of crude *mer*-Cr{NH(CH₂CH₂CH₂NH₂)₂}F₃. The crude product was added to 17 ml 70% HClO₄, and the mixture was kept at 40°C for 3 days, during which a red solid precipitated. The precipitate was filtered off and washed with diethyl ether as described in the beginning of this section. After air-drying the yield was 15.0 g (55%). For recrystallization the crude product was dissolved in 6 ml water preheated to 50°C (it is very soluble). The solution was filtered, and the complex was reprecipitated by adding ca. 2 ml 70% HClO₄ dropwise with stirring and cooling. To complete the crystallization the mixture was kept at 5°C for 4 h. The precipitate was filtered off and washed with diethyl ether as described in the beginning of this section. After air-drying the yield was 8.0 g. Found: Cr 10.80; C 15.22; H 4.96; N 8.87; Cl 15.12. Calc. for [Cr{NH(CH₂CH₂CH₂NH₂)₂}(OH₂)₃](ClO₄)₂F·H₂O: Cr 10.99; C 15.23; H 5.33; N 8.88; Cl 14.99. (ε, λ)_{max} (medium: 0.1 M HClO₄/0.9 M NaClO₄): (24.8, 505), (29.5, 376). The meridional assignment is based on the ESR spectrum, which is very similar to those of the other meridional complexes (see above). Fluoride must be present for the precipitation of the triqua complex. However, with two

equivalents of base a fluoride-free perchlorate of the dihydroxo complex is precipitated.

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