Preparation of Chromium(III) Complexes with Two Fluorine Atoms and Four Nitrogen Atoms as Ligators. *trans*-Difluorotetrakis(pyridine)chromium(III) Salts as Initial Materials

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A general procedure for preparing complexes analogous to the difluorotetramminechromium(III) ion, but containing aliphatic amines or heterocycles with ligating nitrogen atoms, has been described. Prescriptions have been given for the preparations of the initial materials, which are salts of the *trans*-difluorotetrakis(pyridine) chromium(III) ion.

The following new or fairly new compounds have been obtained: *trans*-Difluoro complexes with methylamine, ethylamine, propylamine, allylamine, ethylenediamine (en), trimethylenediamine (tn),(+,−) and (−)propylenediamine (pn), (−)*trans*-1,2-cyclohexanediamine (−chxn), 1,4,8,11-tetraazaundecane (entnen), and 1,5,8,12-tetraazadodecane (tnentn), *cis*-difluoro complexes with tris(2-aminoethyl)-amine (tren), 1,4,7,10-tetraazadecane (trien), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen). The new aliphatic tetramine 1,5,8,12-tetraazadodecane has been prepared.

I n the chemical literature there has been a lack of systematic approaches to the preparation of chromium(III) ammine and amine complexes.

The formation of ammine and amine complexes has in aqueous solution a strong competition from the hydroxide ion which, in addition to forming mononuclear species, also tends to form bridged structures.[1]

One way of avoiding [2,3] or partially avoiding [4,5] the hydroxide ion competition problem has been to start from the chromium(II) system. In this way the reactions forming the chromium(III) complexes become kinetically controlled by the oxidation process and several products can be obtained depending on the conditions.[3] By the presence of charcoal one can even approach equilibrium within the chromium(III) system.[1]

Another way of overcoming the hydroxide difficulties has been to work under more or less anhydrous conditions. Thus anhydrous chromium(III) chloride reacts with liquid ammonia to form mainly chloropentamminechromium(III) chloride,[6] slightly contaminated with hexammine chloride. Through catalysis [7],[8] from the strong nucleophile, the amide ion, the hexammine may be formed almost exclusively. Analogously trichlorotris(pyridine)chromium-(III) reacts with ethylenediamine hydrate [9] to give the tris(ethylenediamine)-chromium(III) chloride. An even better method for the preparation of tris-(diamine)chromium(III) complexes is one [10] based upon the use of a dimethyl-sulphoxide medium from which the water has been distilled off.

In the present paper a general method has been described for synthesizing chromium(III) complexes in which two of the ligating atoms are fluorine and the remaining four are nitrogen belonging to amines or to heterocyclic aromatic ligands. The principle here is that fluoride is so strongly bound to chromium(III) that there is hardly any competition from the other ligands. The method has been used earlier to form the corresponding ammine complexes.[11],[12] The difluoro complexes have the advantage that the basic fluoride ion, through the action of strong acids, can be replaced by other ligands, [11]–[16] *e.g.* chloride, bromide, and water. These reactions will be described in forthcoming publications from this laboratory together with a discussion of the absorption spectra, and in some cases the circular dichroism spectra, of the complexes obtained.

The initial material here is a salt of the difluorotetrakis(pyridine)chromium(III) cation, described by Costachescu.[17] It has recently been shown that this complex possesses the *trans*-configuration.[18]

<div align="center">RESULTS</div>

Initial materials. *trans*-Difluorotetrakis(pyridine)chromium(III) nitrate was synthesized from a concentrated aqueous solution containing chromium-(III) and fluoride in a stoichiometric ratio. This solution is approximately an equilibrium solution with respect to fluoride complexation and the main chromium(III) species is $[Cr(H_2O)_4F_2]^+$. Chromium(III) nitrate was used for preparing this solution and excess nitrate, whose presence would give rise to two moles of pyridinium nitrate per mole of chromium, was conveniently removed by adding the fluoride as hydrofluoric acid and reducing with formaldehyde

$$2 \ Cr^{3+} + 3 \ CH_2O + 4 \ HF + 4 \ NO_3^- = 2 \ CrF_2^+ + 3 \ CO_2 + 4 \ NO + 5 \ H_2O$$
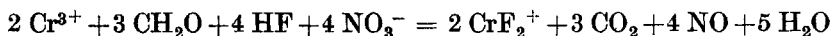
By addition of pyridine to these fluoride complexes no basic precipitates are formed and the pyridine may gradually be made to replace water in the coordination sphere by azeotropically removing the water from the solution.

The *trans*-difluorotetrakis(pyridine)chromium(III) nitrate obtained has peculiar solubility characteristics. It is quite soluble in water as well as in chloroform, but almost insoluble in acetone. It can easily be transformed into other salts of the same cation, and in the present paper the perchlorate, the iodide, and the bromide have been described. The perchlorate is soluble in acetone insoluble in chloroform and very little soluble in cold water. However, it can be recrystallized from hot water. The iodide is little soluble in

water, soluble in acetone and very soluble in chloroform. The bromide has solubility properties as the nitrate.

The preparative reactions. The *trans*-difluorotetrakis(pyridine)chromium(III) ion reacts at about 120°C with a series of amines and with 2,2'-bipyridine and 1,10-phenanthroline. In all cases the two fluorine ions remain bound to the chromium while the four pyridine molecules become substituted by the reacting ligands. However, in some cases the resulting compounds turned out to have the fluorides in the *cis* position, in other cases in the *trans* position.

For the high boiling amines the reaction can be performed directly in the boiling amine, but since this for merely physical reasons requires a great excess of amine, a suitable solvent was hunted for. 2-Methoxyethanol (b.p. 124°C) was found suitable. With this solvent the perchlorate of the difluoro-tetrakis(pyridine)chromium(III) ion was used. This salt is soluble in the hot 2-methoxyethanol, which has the additional advantages that the reactions take place reasonably fast at the solvent's boiling point and that the solvent reacts neither with the amines, nor with the heterocyclic ligands.

Apparently *trans*-difluoro complexes are formed by these reactions unless the particular nitrogen donor provides steric reasons for stabilizing the *cis*-complex relative to the *trans*.

With bidentate ligands, *trans*-complexes are formed with all the ordinary diamines, ethylenediamine, propylenediamine, trimethylenediamine, and *trans*-1,2-cyclohexanediamine, while the bidentate heterocyclic [13,19] ligands, *e.g.* bipyridine, form *cis*-complexes. Here two hydrogen atoms in α-position, one from each ligand, make up a steric hindrance for a *trans*-complex to be formed.[13]

With the quadridentate amines one of the *trans*-isomers[20] is formed with 1,4,8,11-tetraazaundecane (entnen) and the *trans*-isomer also with 1,5,8,12-tetraazadodecane (tnentn). Both these ligands contain at least one six-membered ring.*

However, with 1,4,7,10-tetraazadecane (trien) where only five-membered chelate rings are formed, the reaction has been found to give one of the *cis*-isomers.[22,23] A steric strain argument [21] has been put forward to explain a similar *cis*-stabilization within the cobalt(III) series. Finally, the quadridentate amine tris(2-aminoethyl)amine (tren), which could not possibly form a *trans*-complex, does form a *cis*-complex quite smoothly.

With the aliphatic primary monamines, methylamine, ethylamine, propylamine, and allylamine *trans*-complexes were in all cases formed.

EXPERIMENTAL

Materials. Ethylenediamine, trimethylenediamine, propylenediamine, methylamine, ethylamine, propylamine, and allylamine were purchased from Fluka. Methylamine and ethylamine had the description "purum", all the other amines "purissimum". Propylamine and allylamine were dried over molecular sieves (Merck 3 Å) for several days before use.

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* A short systematic nomenclature, in accordance with recent literature,[20,21] has been used here. The quadridentate ligands can be thought of as forming a number of chelate rings either of ethylenediamine type or of trimethylenediamine type, and the abbreviations have been chosen accordingly. For example, 1,5,8,12-tetraazadodecane (= 4,7-diazadecane-1,10-diamine = N,N'-bis(3-aminopropyl)ethylenediamine) has been called tnentn.

(−)Propylenediamine was isolated as (−)pnH₂{(+)Htart}₂ (H₂tart=tartaric acid) from racemic propylenediamine using a basket-centrifuge as earlier described.[24]

(−)Cyclohexanediamine was isolated as (−)chxnH₂(+)tart from *cis-trans*-cyclo-hexanediamine (Fluka, *practicum*) by direct precipitation. 1,10-Phenanthroline, mono-hydrate was purchased from B.D.H., 2,2′-bipyridine from Riedel-de Haën. Both chemi-cals were of analytical grade. 1,4,7,10-Tetraazadecane and tris(2-aminoethyl)amine were obtained [25] from the technical product, triethylenetetramine, from Union Carbide. The separation has been described below. All other chemicals were of reagent grade and were used without further purification.

Spectra. Absorption spectra in the 300−650 mμ region, recorded using a Cary Model 14 spectrophotometer, were used as characterization of the compounds. Data for maxima, minima, and shoulders have been given below as (ε,λ), the molar extinction coefficient ε in liter/mol·cm, the wavelength λ in mμ.

Preparations

1. trans-*Difluorotetrakis(pyridine)chromium(III) nitrate*, trans-[Crpy₄F₂]NO₃. 400 g (1 mol) chromium(III) nitrate enneahydrate was heated on the steam bath with 89 ml 40 % hydrofluoric acid (2 mol) in a polyethylene beaker. 70 ml 40 % formalin (0.9 mol) was slowly added and a violent foam formation (NO₂, NO, CO₂) was observed. During this reaction two thirds of the nitrate was reduced. The solution was now evaporated to a porridge consistency. It was found useful to remove as much water as possible, but dangerous to evaporate to dryness, since this resulted in the formation of an in-soluble green precipitate which did not react properly with pyridine. The mass was washed into a 2 l flask using 500 ml pyridine for the washing. The mixture was then heated to the boiling point and another 500 ml pyridine was added. Under stirring the water was now essentially distilled off with the pyridine. When the temperature of the leaving vapours had reached 105°C (azeotrope 43 % water, b.p. 93°C; pyridine, b.p. 115°C), the distillation was discontinued and after cooling to 0°C 325 g of violet-red crystals were isolated with a basket centrifuge and washed with acetone. Another crop of 50 g was obtained from the mother liquor after further distillation. Total yield of crude product 80 %. After recrystallization from water with a temperature range from 60°C to 0°C it was analysed. (Found: Cr 10.97; F 7.98. Calc. for [CrC₂₀H₂₀N₄F₂]NO₃, 0.5 H₂O: Cr 10.89; F 7.96).

2. trans-*Difluorotetrakis(pyridine)chromium(III) perchlorate*, trans-[Crpy₄F₂]ClO₄. 47 g (0.1 mol) crude [Crpy₄F₂]NO₃ was dissolved in 90 ml water at 60°C and a solution of 18 g sodium perchlorate (0.15 mol) in 25 ml water was gradually added. After cooling to room temperature the perchlorate was centrifuged off and washed with cold water. The crystals crumble in the laboratory air (ca. 60 % humidity) and thereby change the colour from violet-red to more violet. Yield of dried substance 46 g (91 % based upon nitrate). Recrystallization as in preparation 1. (Found: Cr 10.27; F 7.51. Calc. for [CrC₂₀H₂₀N₄F₂]ClO₄: Cr 10.28; F 7.51).

This perchlorate was heated to 100°C in an oven before used as an initial material for the preparations described below.

3. trans-*Difluorotetrakis(pyridine)chromium(III) iodide*, trans-[Crpy₄F₂]I. This com-pound was prepared in a way identical to that of the perchlorate except that 24 g potas-sium iodide (0.15 mol) in 40 ml water was used here. After cooling to 0°C the violet-red crystals were centrifuged off and washed with a small quantity of ice-cold water. Yield 48 g (90 %). Recrystallization as in preparation 1. (Found: Cr 9.67; F 7.09; I 23.55. Calc. for [CrC₂₀H₂₀N₄F₂]I: Cr 9.75; F 7.13; I 23.80). Like the perchlorate, this iodide was dried before being used as an initial material.

4. trans-*Difluorotetrakis(pyridine)chromium(III) bromide*, trans-[Crpy₄F₂]Br,2H₂O. 150 g (0.32 mol) crude trans-[Crpy₄F₂]NO₃ was dissolved in 550 ml water at 50°C and a hot solution of 50 g sodium bromide dissolved in 50 ml water was gradually added in such a way that the temperature remained about 50°C during the mixing. After a slow cooling, finally in ice, the crystals were filtered off and washed with a little ice-cold water and a large quantity of acetone. Yield 140 g (84 %). Recrystallization as in preparation 1. (Found: Cr 10.01; F 7.35; Br 15.15. Calc. for [CrC₂₀H₂₀N₄F₂]Br,2H₂O: Cr 9.95; F 7.27;

Br 15.30). Like the perchlorate, this bromide was dried before being used as an initial material.

5. trans-*Difluorobis (ethylenediamine)chromium(III) perchlorate*, trans-[Cren$_2$F$_2$]ClO$_4$. A mixture of 10.1 g trans-[Crpy$_4$F$_2$]ClO$_4$ (20 mmol) and 2.46 g ethylenediamine (44 mmol) in 80 ml 2-methoxyethanol was boiled under reflux. From the solution, whose colour gradually changed from bluish violet to red, the complex precipitated. After boiling for 45 min, the precipitation was almost quantitative, and after cooling, the pink fine crystals were filtered off and washed with 96 % ethanol. Yield of apparently pure first product was 6.0 g (95 % based upon chromium). The product was recrystallized from 0.1 M perchloric acid by dissolving it on the filter in the dilute perchloric acid preheated to 90°. Bright red needle-shaped crystals separated on cooling to 0°C. Yield 4.0 g (65 %) after washing with 96 % ethanol. (Found: C 15.47; H 5.14; N 18.31; Cl 11.57; Cr 16.80; F 12.26. Calc. for [Cr(C$_4$H$_{16}$N$_4$)F$_2$]ClO$_4$: C 15.52; H 5.20; N 18.09; Cl 11.45; Cr 16.79; F 12.27). $(\varepsilon,\lambda)_{shoulder}$: (16.5, 530), $(\varepsilon,\lambda)_{max}$: (21.0, 465); (13.2, 397); (14.4, 351). $(\varepsilon,\lambda)_{min}$: (11.1, 375); (0.6, 283). Medium: water.

The chloride and the iodide of this complex have earlier been described in the literature.[14,26] The chloride was first [26] thought to be [Cren$_2$(OH)F]Cl and was described [14] as such. Later it was shown that Dahme's compound was actually trans-[Cren$_2$F$_2$]Cl and the genuine trans-[Cren$_2$FOH]ClO$_4$ was isolated.[12]

A series of diamine complexes were prepared analogously.

6. trans-*Difluorobis(trimethylenediamine)chromium(III) perchlorate*, trans-[Crtn$_2$F$_2$]-ClO$_4$. Initial materials: 10.1 g trans-[Crpy$_4$F$_2$]ClO$_4$ (20 mmol), 3.3 g trimethylenediamine (44 mmol), 80 ml 2-methoxyethanol. The first product (6 g), which was bluish red was recrystallized from 0.1 M perchloric acid as in preparation 5. Yield 3.0 g of bright red needle-shaped crystals (44 % based upon chromium). (Found: C 21.26; H 6.5; N 16.37; Cl 10.66; Cr 15.36; F 11.15. Calc. for [Cr(C$_6$H$_{20}$N$_4$)F$_2$]ClO$_4$: C 21.34; H 6.0; N 16.61; Cl 10.51; Cr 15.39; F 11.28). $(\varepsilon,\lambda)_{max}$: (16.8, 538); (20.7, 468); (16.5, 398); (16.3, 360). $(\varepsilon,\lambda)_{min}$: (15.8, 512); (14.5, 423); (15.4, 377); (1.2, 293). Medium: water. From the mother liquor further 2.0 g (30 %) pure compound could be precipitated by adding ethanol and ether. This portion was characterized by its absorption spectrum. This cation has undoubtedly been had by Vaughn,[15] who prepared derivatives of it.

The following complexes are believed to be new.

7. trans-*Difluorobis (propylenediamine)chromium(III) perchlorate*, trans-[Cr($\pm$)pn$_2$F$_2$]ClO$_4$,H$_2$O. Initial materials: 10.1 g trans-[Crpy$_4$F$_2$]ClO$_4$ (20 mmol), 3.3 g propylenediamine, 80 ml 2-methoxyethanol. The reaction mixture was here homogeneous and was evaporated to dryness at reduced pressure at 80°C and washed with acetone. The first product was pink. It was recrystallized from 0.01 M perchloric acid as in preparation 5. Yield 3.0 g of light red, fine needle-shaped crystals (44 % based upon chomium). (Found: C 20.11; H 6.24; N 15.92; Cl 10.23; Cr 14.55; F 10.63. Calc. for [CrC$_6$H$_{20}$N$_4$F$_2$]ClO$_4$, H$_2$O: C 20.26; H 6.23; N 15.75; Cl 9.97; Cr 14.62; F 10.68). $(\varepsilon,\lambda)_{shoulder}$: (17.0, 530). $(\varepsilon,\lambda)_{max}$: (23.1, 467); (13.9, 400); (15.2, 351). $(\varepsilon,\lambda)_{min}$: (12.4, 375); (1.4, 288). Medium: water.

8. $(+)_D$ trans-*Difluorobis{(−)propylenediamine}chromium*(III) *perchlorate*, $(+)_D$ trans-[Cr{(−)pn}$_2$F$_2$]ClO$_4$,H$_2$O. Exactly as preparation 7 except for the use of (−)propylenediamine. (Found: C 20.22; H 6.15; N 15.50; Cl 10.05). Visible absorption spectrum as the racemic compound. $(\varepsilon_l-\varepsilon_r, \lambda)_{extremum}$: (0.39, 532); (−0.15, 452). $([M],\lambda)$: (712, 589); (777, 578); (446, 546); (87, 434); (535, 364); (847, 313). ([M] in deg/m·M).

9. trans-*Difluorobis[(−)trans-1,2-cyclohexanediamine]chromium(III) perchlorate*, trans-[Cr(−chxn)$_2$F$_2$]ClO$_4$,H$_2$O. Initial materials: 22 g (−)cyclohexanediamine (210 mmol), 50 g trans-[Crpy$_4$F$_2$]ClO$_4$ (100 mmol), 100 ml 2-methoxyethanol. The first product was a pink powder. Yield 37 g (90 % based upon chromium). 5 g was recrystallized from water, in which it is almost insoluble when cold. Yield 4 g. This product was shown by thermogravimetry to be a monohydrate. The thermobalance has been described previously.[10] 9.08 mg was heated 5°C min^{-1} in air (35 % relative humidity, 25°) under static atmosphere conditions. A constant weight was observed up to 120°C. 0.37 mg was lost between 120° and 220°C, followed by weight constancy up to 280°C. (Found: Cr 11.96; C 33.2; H 6.83; N 13.0; F 8.73; Cl 8.19. Calc. for [Cr(C$_{12}$H$_{28}$N$_4$)F$_2$]ClO$_4$,H$_2$O: Cr 11.94; C 33.08; H 6.93; N 12.9; F 8.72; Cl 8.14). $(\varepsilon,\lambda)_{max}$: (18.1, 354); (17.3, 397); (26.9, 467). $(\varepsilon,\lambda)_{shoulder}$: (19.5, 530). $(\varepsilon,\lambda)_{min}$: (2.3, 285); (16.3, 375); (17.1, 412). Medium: water.

10. *1,4,7,10-Tetraazadecane (trien) and tris(2-aminoethyl)amine (tren)*. A brown technical product of "triethylenetetramine" was distilled over potassium hydroxide at 11 torr. The fraction between 154.0 and 156.5°C was collected as a faintly yellow liquid. Yield 85 %. From a solution of 905 ml of the distilled product ($\varrho = 0.976$ g/ml) in 1800 ml ethanol tren trihydrochloride was precipitated [15] by slowly adding 1810 ml of a solution of equal volumes of 12 M hydrochloric acid and ethanol. The white crystalline product was filtered at 1°C and washed with ethanol and ether. Yield 103.5 g tren trihydrochloride. (Found: C 28.3; H 8.3; N 22.2; Cl 41.7. Calc. for $C_6H_{21}N_4Cl_3$: C 28.2; H 8.2; N 21.9; Cl 41.6). The yield corresponds to 6.7% tren in the distilled product. The crude trien ("triethylenetetramine") gave a similar yield of tren trihydrochloride but the following separation of trien tetrahydrochloride then resulted in a product containing a red-brown impurity. To the filtrate further 680 ml of the hydrochloric acid solution was added. Precipitation of trien tetrahydrochloride started after addition of 200 ml. The white fluffy product was washed with ethanol and ether. Yield 803 g. Further addition of hydrochloric acid solution gave a product containing a red impurity which could not be removed later on. (Found: C 24.6; H 7.6; N 19.2; Cl 48.6. Calc. for $C_6H_{22}N_4Cl_4$: C 24.6; H 7.6; N 19.2; Cl 48.6). The amines were prepared by boiling 0.5 moles of the hydrochlorides for 30 min in 300 ml ethanol containing 1.2 moles of sodium hydroxide per mole chloride. Sodium chloride was removed by filtration and most of the ethanol distilled off at atmospheric pressure. Tren was distilled at 9.0 torr. B.p. 137.0—137.5°C. Yield 96 %. Trien at 20 torr. B.p. 156—158°C. Yield 80 %.

11. *cis-Difluoro{tris(2-aminoethyl)amine}chromium(III) perchlorate*, cis-[Cr{N(CH$_2$—CH$_2$—NH$_2$)$_3$}F$_2$]ClO$_4$. Initial materials: 5.2 g tren (36 mmol), 18 g trans-[Crpy$_2$F$_2$]ClO$_4$ (36 mmol), 18 ml 2-methoxyethanol. The first product was a red violet oil which crystallized after a few minutes by stirring with a glass spatula. After cooling in ice the product was filtered and washed with ethanol and ether. Yield 11.0 g corresponding to 87 %. 5 g of the crude product was dissolved at 60°C in 3.5 ml 0.2 M perchloric acid which was subsequently almost saturated with sodium perchlorate. After 2 days at 0°C the precipitation seemed to be complete. After washing with ice water, in which the product is very soluble, the yield was 1.7 g of red violet crystals. (Found: Cr 15.56; C 21.30; H 5.41; N 16.07; F 11.35; Cl 10.39. Calc. for [Cr(C$_6$H$_{18}$N$_4$)F$_2$]ClO$_4$: Cr 15.51; C 21.47; H 5.40; N 16.70; F 11.33; Cl 10.56). $(\varepsilon,\lambda)_{max}$: (56.8, 378); (116.5, 528). $(\varepsilon,\lambda)_{min}$: (19.9, 310); (32.5, 438). Medium: water.

12. *cis-Difluoro(1,4,7,10-tetraazadecane)chromium(III) perchlorate*, cis-[Cr{H$_2$N—(CH$_2$)$_2$—NH—(CH$_2$)$_2$—NH—(CH$_2$)$_2$—NH$_2$}F$_2$]ClO$_4$. Initial materials: 5.0 g trien (34 mmol), 17 g trans-[Crpy$_4$F$_2$]ClO$_4$ (34 mmol). Yield 9.0 g red violet product, corresponding to 74 %. The very water soluble product was recrystallized as in preparation 11. Yield 2.0 g of red violet crystals. (Found: Cr 15.48; C 21.8; H 5.6; N 16.5; F 11.34; Cl 10.57. Calc. for [Cr(C$_6$H$_{18}$N$_4$)F$_2$]ClO$_4$: Cr 15.51; C 21.47; H 5.4; N 16.7; F 11.33; Cl 10.56). $(\varepsilon,\lambda)_{max}$: (56.2, 374); (120.6, 523). $(\varepsilon,\lambda)_{min}$: (19.2, 315); (27.8, 432). Medium: water.

13. *trans-Difluoro(1,4,8,11-tetraazaundecane)chromium(III) perchlorate*, trans-[Cr{H$_2$N—(CH$_2$)$_2$—NH—(CH$_2$)$_3$—NH—(CH$_2$)$_2$—NH$_2$}F$_2$]ClO$_4$. 1,4,8,11-tetraazaundecane (entnen) was prepared according to Van Alphen.[27] B.p.$_{12}$: 158—163°C. From 13.5 g of entnen (84 mmol) and 40 g trans-[Crpy$_4$F$_2$]ClO$_4$ (84 mmol) in 100 ml 2-methoxyethanol was obtained 21 g corresponding to 72 %. The product was recrystallized from water as bright red crystals. (Found: Cr 14.84; C 24.1; H 5.7; N 15.7; F 10.85; Cl 10.3. Calc. for [Cr(C$_7$H$_{20}$N$_4$)F$_2$]ClO$_4$: Cr 14.88; C 24.1; H 5.8; N 16.0; F 10.87; Cl 10.2). $(\varepsilon,\lambda)_{max}$: (16.2, 348); (22.5, 453); (16.0, 522). $(\varepsilon,\lambda)_{shoulder}$: (14.9, 395); (18.5, 425). $(\varepsilon,\lambda)_{min}$: (1.9, 285); (13.8, 372); (15.5, 503). Medium: water.

14. *trans-Difluoro(1,5,8,12-tetraazadodecane)chromium(III) perchlorate*, trans-[Cr{H$_2$N—(CH$_2$)$_3$—NH—(CH$_2$)$_2$—NH—(CH$_2$)$_3$—NH$_2$}F$_2$]ClO$_4$. 1,5,8,12-tetraazadodecane (tnentn) is believed to be a new compound. It was prepared in a way equivalent to that of entnen from 1.2 moles of 1,2-dibromoethane and 4.6 moles of 1,3-propanediamine. B.p.$_{10}$: 163—165°C. Yield 40 g, corresponding to 12 % calc. from 1,2-dibromoethane. (Found: C 55.3; H 12.6; N 31.9. Calc. for $C_8H_{22}N_4$: C 55.1; H 12.7; N 32.2) From 12 g tnentn (67 mmol) and 34 g trans-[Crpy$_4$F$_2$]ClO$_4$ (67 mmol) in 50 ml 2-methoxyethanol was obtained 22 g of the *trans*-complex, corresponding to 90 %. The product was recrystallized from water as bright red crystals. (Found: Cr 14.30; C 26.5; H 6.05; N 15.6; F 10.44; Cl 9.84. Calc. for [Cr(C$_8$H$_{22}$N$_4$)F$_2$]ClO$_4$: Cr 14.30; C 26.4; H 6.10; N 15.4; F 10.45;

Cl 9.76). $(\varepsilon,\lambda)_{max}$: (23.3, 354); (37.2, 460). $(\varepsilon,\lambda)_{shoulder}$: (17.4, 530); (24.2, 427). $(\varepsilon,\lambda)_{plateau}$ (17.3, 390—400). $(\varepsilon,\lambda)_{min}$: (1.8, 290). Medium: water.

15. trans-*Difluorotetrakis(methylamine)chromium(III) iodide*, trans-[Cr(H$_2$NCH$_3$)$_4$F$_2$]I. 12.5 g trans-[Crpy$_4$F$_2$]I (22.5 mmol) was heated overnight in an autoclave at 100° with 22 ml methylamine (500 mmol, $d = 0.70$ g/ml). The excess amine was removed by decantation and pumping. The violet, sticky solid that remained was triturated with acetone until a reddish powder (the first product) was obtained. This was washed with small portions of methanol and extracted on the filter with 35 ml of hot 0.01 M hydrochloric acid (70°C) to which a little ascorbic acid had been added. After the addition of 12 g sodium iodide the filtrate was cooled to precipitate brickred crystals which were washed with water and methanol. The product (6.5 g) was recrystallized from 35 ml of hot water (70°C) yielding 3.8 g (50 %) of glistening, flaky, red crystals which were washed as above. (Found: Cr 14.95; F 10.95; C 13.8; N 16.2. Calc. for [Cr(H$_2$NCH$_3$)$_4$F$_2$]I,0.3H$_2$O: Cr 14.98; F 10.94; C 13.8; N 16.2). More than half of the water could be removed over phosphorus pentoxide at 90°C. For the above compound and for the following the hydrogen analyses failed to come out reproducibly. $(\varepsilon,\lambda)_{max}$: (22.4, 494.5); (14.5, 408); (16.3, 356.5). $(\varepsilon,\lambda)_{shoulder}$: (19.0, 555). $(\varepsilon,\lambda)_{min}$: (12.4, 438); (12.2, 382). Medium: 0.1 M hydrochloric acid.

The addition of sodium iodide to the filtrate from the recrystallization gave an extra yield of 1.8 g (23 %).

A series of monoamine complexes were prepared analogously.

16. trans-*Difluorotetrakis(ethylamine)chromium(III) iodide*, trans-[Cr(H$_2$NC$_2$H$_5$)$_4$F$_2$]I. Initial materials: 12 g trans-[Crpy$_4$F$_2$]I (22.5 mmol), 20 ml ethylamine (300 mmol, $d = 0.68$ g/ml). The first product was extracted in portions with 60 ml of water (preheated to 70°C and with acids added as in preparation 15). To the hot solution 25 g of sodium iodide was added and on cooling small, pink crystals appeared. They were washed with ice-water and acetone. The product (2.4 g) was dissolved in 30 ml water at 70°C, 10 g sodium iodide was added and the crystals that came out were washed as above. Yield 1.5 g (17 %). (Found: Cr 12.96; F 9.49; C 24.1; N 14.2. Calc. for [Cr(H$_2$NC$_2$H$_5$)$_4$F$_2$]I: Cr 13.09; F 9.56; C 24.2; N 14.1). $(\varepsilon,\lambda)_{max}$: (22.4, 494.5); (14.5, 408); (16.3, 356.5). $(\varepsilon,\lambda)_{shoulder}$: (19.0, 555). $(\varepsilon,\lambda)_{min}$: (12.4, 438); (12.2, 382). Medium: 0.1 M hydrochloric acid.

17. trans-*Difluorotetrakis(propylamine)chromium(III) iodide*, trans-[Cr(H$_2$NC$_3$H$_7$)$_4$F$_2$]I. Initial materials: 6 g trans-[Crpy$_4$F$_2$]Br (12.3 mmol), 15 ml propylamine (183 mmol, $d = 0.72$ g/ml). The reddish first product was extracted with 130 ml of hot water (70°C and containing acids as in preparation 15) in portions, and the addition of sodium iodide gave a pink precipitate (3.2 g), which was washed with ice-water and acetone. The compound was recrystallized by dissolving it in 120 ml water at 70°C, adding 10 g of sodium iodide and cooling. Washing as above. Yield 2.4 g (43 %). (Found: Cr 11.58; F 8.43; C 31.6; N 12.3; H 8.07. Calc. for [Cr(H$_2$NC$_3$H$_7$)$_4$F$_2$]I: Cr 11.47; F 8.38; C 31.8; N 12.4; H 8.02). $(\varepsilon,\lambda)_{max}$: (26.1, 502); (16.1, 413); (17.5, 356). $(\varepsilon,\lambda)_{shoulder}$: (23.7, 555). $(\varepsilon,\lambda)_{min}$: (13.7, 440); (12.1, 383). Medium: 0.1 M hydrochloric acid.

18. trans-*Difluorotetrakis(allylamine)chromium(III) iodide*, trans-[Cr(H$_2$NC$_3$H$_5$)$_4$F$_2$]I. Initial materials: 6 g trans-[Crpy$_4$F$_2$]Br (12.3 mmol), 15 ml allylamine (220 mmol, $d = 0.76$ g/ml). The red first product was extracted with 100 ml of hot water (70°C and containing hydrochloric acid and ascorbic acid) in portions. After the addition of 20 g of sodium iodide the desired compound crystallized on cooling to 0°C. Washing with ice-water and acetone. Yield 3.6 g. The product was recrystallized from 100 ml of hot water by slow cooling from 70° to 0°C. Glistening, violet-red crystals. Washing as above. Yield 2.4 g (44 %). (Found: Cr 11.73; F 8.51; C 31.7; N 12.4; H 6.53. Calc. for [Cr(H$_2$NC$_3$H$_5$)$_4$F$_2$]I: Cr 11.68; F 8.53; C 32.4; N 12.6; H 6.3). $(\varepsilon,\lambda)_{max}$: (27.3, 509); (16.0, 415); (18.3, 353). $(\varepsilon,\lambda)_{shoulder}$: (24.8, 555). $(\varepsilon,\lambda)_{min}$: (13.3, 444); (10.9, 382). Medium: 0.1 M hydrochloric acid.

19. cis-*Difluorobis(1,10-phenanthroline)chromium(III) perchlorate*, cis-[Crphen$_2$F$_2$]ClO$_4$, H$_2$O. The procedure here was that of preparation 5. Initial materials: 1.0 g trans-[Crpy$_4$F$_2$]ClO$_4$ (2 mmol), 0.90 g phen,H$_2$O (4.4 mmol), 9 ml 2-methoxyethanol. The first product, which was violet-red, was recrystallized from 0.01 M perchloric acid with a temperature range from 90° to 0°C. 0.88 g (76 %) of large dark violet-red crystals, which were washed with 96 % ethanol. (Found: Cr 9.14; F 6.69; C 50.7; H 3.21; Cl 6.20. Calc.

for $[Cr(C_{12}H_8N_2)_2F_2]ClO_4,H_2O$: Cr 9.16; F 6.68; C 50.7; H 3.19; Cl 6.25). $(\varepsilon,\lambda)_{max}$: (46.5, 522). $(\varepsilon,\lambda)_{min}$: (16.6, 455). $(\varepsilon,\lambda)_{shoulder}$: (69.2, 420). Medium: water.

The nitrogen analyses by the Dumas method failed for unknown reasons to give reproducible results for this compound.

20. cis-*Difluorobis(2,2'-bipyridine)chromium(III) perchlorate*, cis-[Crbipy$_2$F$_2$]ClO$_4$. The procedure here was that of preparation 5. Initial materials: 1.5 g *trans*-[Crpy$_4$F$_2$]ClO$_4$ (8 mmol), 0.9 g bipy (6 mmol), 17 ml 2-methoxyethanol. The first product, which was violet-red, was recrystallized as in preparation 19 and gave 1.1 g (70 %) of large dark violet-red crystals. (Found: Cr 10.36; F 7.58; C 47.8; H 3.29; N 11.0; Cl 7.1. Calc. for $[Cr(C_{10}H_8N_2)F_2]ClO_4$: Cr 10.37; F 7.58; C 47.8; H 3.21; N 11.2; Cl 7.1). $(\varepsilon,\lambda)_{max}$: (48.6, 519); (57.3, 443); (144, 415). $(\varepsilon,\lambda)_{min}$: (22.0, 461); (53.6, 438); (139, 409). Medium: water.

REFERENCES

1. Schäffer, C. E. and Andersen, P. In Jezowska-Trzebiatowska, B. *Theory and Structure of Complex Compounds*, Pergamon, London 1964, p. 571.
2. Berman, D., Bokerman, G. and Parry, R. W. *Inorg. Syn.* **10** (1967) 35.
3. Schäffer, C. E. In Kirschner, S. *Advan. Chem. Coordination Compounds*, Macmillan, New York 1961, p. 628.
4. Jørgensen, S. M. *J. prakt. Chem.* [2] **25** (1882) 321.
5. Linhard, M. and Weigel, M. *Z. anorg. Chem.* **299** (1959) 15.
6. Christensen, O. T. *Z. anorg. Chem.* **4** (1893) 227.
7. Rollinson, C. L. and Bailar, Jr., J. C. *J. Am. Chem. Soc.* **65** (1943) 250.
8. Oppegard, A. L. and Bailar, J. C. *Inorg. Syn.* **3** (1950) 153.
9. Pfeiffer, P. *Z. anorg. Chem.* **24** (1900) 279.
10. Pedersen, E. *J. Sci. Instr. (Journal of Physics E)* Ser. 2, **1** (1968) 1013.
11. Glerup, J. and Schäffer, C. E. *Chem. Commun.* **1968** 38.
12. Glerup, J. and Schäffer, C. E. *Acta Chem. Scand. To be published.*
13. Josephsen, J. and Schäffer, C. E. *Acta Chem. Scand. To be published.*
14. Vaughn, J. W., Stvan, O. J. and Magnuson, V. E. *Inorg. Chem.* **7** (1968) 736.
15. Vaughn, J. W. *Inorg. Nucl. Chem. Letters* **4** (1968) 183.
16. Fee, W. W., MacHarrowfield, J. N. and Jackson, W. G. *Australian J. Chem.* **22** (1969).
17. Costachescu, N. *Ann. Sci. Univ. Jassy* **7** (1912) 87.
18. Glerup, J. and Schäffer, C. E. *Acta Chem. Scand. To be published.*
19. Andersen, P., Josephsen, J., Waind-Nord, G., Schäffer, C. E. and Tranter, R. L. *Chem. Commun.* **1969** 408.
20. Hamilton, H. G. and Alexander, M. Dale. *J. Am. Chem. Soc.* **89** (1967) 5065.
21. Bosnich, B., Gillard, R. D., McKenzie, E. D. and Webb, G. A. *J. Chem. Soc.* A **1966** 1331.
22. Sargeson, A. M. and Searle, G. H. *Inorg. Chem.* **6** (1967) 787.
23. Buckingham, D. A., Marzilli, P. A. and Sargeson, A. M. *Inorg. Chem.* **6** (1967) 1032.
24. Andersen, P., Galsbøl, F. and Harnung, S. E. *Acta Chem. Scand.* **23** (1969) 3027.
25. Jørgensen, C. K. *Absorption Spectra of Complexes of Heavy Metals Final Technical Report*, European Research Office, U.S. Department of the Army, Frankfurt am Main, Contract No. DA-91-508-EUC-247 (1958), p. 13.
26. Dahme, W. *Dissertation. Bergakademie Clausthal*, (1957), p. 36.
27. van Alphen, J. *Rec. Trav. Chim.* **56** (1937) 343.

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