The *trans*-Difluorotetramminechromium(III) Complex and Other Novel Compounds of the *trans*-Tetramminechromium(III) Series

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THE following would seem to be the first *trans*-tetramminechromium(III) compounds to be described. On the basis of the reaction between difluorotetrapyridinechromium(III) iodide[1,2] and liquid ammonia in an autoclave at 100° giving a mixture of *cis*- and *trans*-difluorotetramminechromium(III) iodide, we have prepared the pure *trans*-difluoro-complex and several other crystalline salts of the *trans*-tetrammine series.

trans-$[Cr(NH_3)_4F_2]I$ (slightly brownish red, *cis*-complex violet red) was isolated as the least soluble component of the above-*cis–trans*-iodide mixture by a recrystallisation from water (acidified with a few drops of HCl and at 70°) under addition of NaI. Reaction between *trans*-$[Cr(NH_3)_4F_2]ClO_4$ and 70% $HClO_4$ (1 hr., room temperature) gave $[Cr(NH_3)_4F(H_2O)](ClO_4)_2$ (slightly brownish red). With aqueous HBr (prepared by saturation at 1 atm. and −10°) at room temperature in an autoclave overnight $[Cr(NH_3)_4F_2]ClO_4$ gave *trans*-$[Cr(NH_3)_4Br_2]Br$ (green) which could be aquated to give *trans*-$[Cr(NH_3)_4Br(H_2O)]Br_2$ (olive green) and *trans*-$[Cr(NH_3)_4(H_2O)_2]Br_3$ (brick red). The diaquo-complex was isolated through the *trans*-$[Cr(NH_3)_4(OH)(H_2O)]Br_2$ (pink).

On analogous treatment, but with HCl, *trans*-$[Cr(NH_3)_4F_2]ClO_4$ gave a mixture of the dichloro- and the chloro-aquo-complexes. Slightly acidified water at 30° extracted the chloro-aqua-complex, which could then be isolated as *trans*-$[Cr(NH_3)_4Cl(H_2O)]Cl_2$ (reddish brown) by precipitation with concentrated HCl at 0°. The residue from the extraction was purified as *trans*-$[Cr(NH_3)_4Cl_2]Cl$ (greyish green) by rapid dissolution in water (30°) and reprecipitation with conc. HCl at 0°.

The configurations of the tetrammine complexes were unambiguously established by comparison of their ligand field spectra with those of the corresponding bis(ethylenediamine) complexes. No *trans–cis*-isomerisation reactions were observed.

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