Simple Syntheses of *trans*-Tetramminechromium(III) Complexes by Cleavages of a Binuclear Complex

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IN a recent Communication, Glerup and Schäffer[1] reported syntheses of a number of *trans*-diacidotetramminechromium(III) compounds, entry to the *trans*-series having been achieved by the reaction of difluorotetrapyridine chromium(III) iodide with liquid ammonia in an autoclave at 100°. We report that the synthesis of most of the compounds described by Glerup and Schäffer may be achieved without resort to such drastic conditions. Our syntheses are based on the acid cleavage of the ion,[2]

$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$ (I) in which the chloro-ligand is located *trans* to the hydroxo-bridge.

The chloride of (I) (40 g.), prepared according to the method of Linhard and Weige,[2] was added as a fine powder to 70% $HClO_4$ (125 ml.) and stirred to allow the escape of HCl. The mixture was diluted with water (600 ml.) and heated at 60° with stirring until the solids had dissolved (*ca.* 30 min.). The solution was cooled, and 70% $HClO_4$ was added to precipitate $[(NH_3)_5CrOH_2](ClO_4)_3$, which was removed by filtration. The addition of an equal volume of 12 M-HCl to the filtrate gave *trans*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$, in good yield.

When the powdered chloride of (I) (10 g.) was stirred with 20 ml. of 70% $HClO_4$ and 10 ml. of 12 M-HCl in a stoppered flask at 25° for 3 hr., and the resulting solid was extracted with 1 M-$HClO_4$ on a filter until the filtrate was clear, the green solid (4·5 g.) which remained was *trans*-$[Cr(NH_3)_4Cl_2]ClO_4$. Exactly analogous treatment of the corresponding bromide with a 2:1 mixture of 70% $HClO_4$ and 47% HBr gave green *trans*-$[Cr(NH_3)_4BrCl]ClO_4$.

From *trans*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$, *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ was prepared, by stirring the former (10 g.) with 50 ml. of 1 M-NaOH for 5 min. and then adding 100 ml. of 70% $HClO_4$ to the ice-cold solution; *trans*-$[Cr(NH_3)_4(OH_2)_2]Br_3$ was prepared by dissolving *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ in methanol and adding concentrated HBr. By heating *trans*-$[Cr(NH_3)_4(OH_2)_2]Br_3$ (dry, 4 hr. at 80°), *trans*-$[Cr(NH_3)_4(OH_2)Br]Br_2$ was obtained; it was purified by recrystallization from water with concentrated HBr.

Heating *trans*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$ and *trans*-$[Cr(NH_3)_4(OH_2)Cl]Br_2$, respectively, *in vacuo*, also gives *trans*-$[Cr(NH_3)_4Cl_2]Cl$ and *trans*-$[Cr(NH_3)_4BrCl]Br$.

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[1] J. Glerup and C. E. Schäffer, *Chem. Comm.*, 1968, 38.

[2] M. Linhard and M. Weigel, *Z. anorg. Chem.*, 1959, **299**, 15.