Reaction of Penta-amminenitrosylruthenium with Hydroxide Ion: Formation of Penta-amminedinitrogenruthenium and *cis*-Tetra-amminehydroxonitrosyl-ruthenium

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Summary When $[Ru(NH_3)_5NO]^{3+}$ reacts with OH^-, $[Ru(NH_3)_5N_2]^{2+}$ and $[RuOH(NH_3)_4NO]^{2+}$ are obtained *via* the reaction: $[Ru(NH_3)_5NO]^{3+} + [RuNH_2(NH_3)_4NO]^{2+} \rightarrow [Ru(NH_3)_5N_2]^{2+} + [RuOH(NH_3)_4NO]^{2+}$, and the $[RuOH(NH_3)_4NO]^{2+}$ produced is largely the *cis*-isomer.

We have previously indicated that in aqueous alkaline solution $[Ru(NH_3)_5NO]^{3+}$ is in equilibrium with $[RuNH_2(NH_3)_4NO]^{2+}$ and $[Ru(NH_3)_5NO_2]^{+}$, but when such solutions are set aside some $[Ru(NH_3)_5N_2]^{2+}$ is produced also.[1] We speculated that this latter product is obtained by nucleophilic attack of NH_3 (liberated from one of the constituents of the equilibrium on substitution) on the co-ordinated nitrosyl of $[Ru(NH_3)_5NO]^{3+}$. We now present evidence that $[Ru(NH_3)_5NO]^{3+}$ and OH^- form $[Ru(NH_3)_5N_2]^{2+}$ and $[RuOH(NH_3)_4NO]^{2+}$ predominately by the reaction (1), and that the $[RuOH(NH_3)_4NO]^{2+}$ produced is the *cis*-isomer.

$$[Ru(NH_3)_5NO]^{3+} + [RuNH_2(NH_3)_4NO]^{2+} \rightarrow [Ru(NH_3)_5N_2]^{2+} + [RuOH(NH_3)_4NO]^{2+} + H^+ \qquad (1)$$

Optimum conditions for production of $[Ru(NH_3)_5N_2]^{2+}$ are when $[Ru(NH_3)_5NO]^{3+}$ is set aside in 0·1M aqueous NaOH at 5 °C for 6 days. Under these conditions the product solution is a mixture of the composition: $[Ru(NH_3)_5N_2]^{2+}$, 25%; *cis*-$[RuOH(NH_3)_4NO]^{2+}$, 20%; *trans*-$[RuOH(NH_3)_4NO]^{2+}$, 5%; unchanged starting material 50%.† $[Ru(NH_3)_5NO_2]^{+}$ is not a product. Because of the similarity of the chemical and physical properties of the constituents, we have been unable to effect a quantitative separation, and the percentage yields are therefore approximate. However, by fractional crystallization we have separated, purified, and identified *all* the constituents. Since the complexes listed above are the only products, and the reaction proceeds identically under air or argon, $[Ru(NH_3)_5N_2]^{2+}$ must be formed by one or both of two routes: (i) the above-mentioned attack of liberated NH_3 on $[Ru(NH_3)_5NO]^{3+}$;[2] (ii) a similar attack by the co-ordinated NH_2^- of $[RuNH_2(NH_3)_4NO]^{2+}$. The yield of $[Ru(NH_3)_5N_2]^{2+}$ was essentially identical in solutions of aqueous NH_3 or NaOH having the same OH^- concentration, and also varied with OH^- concentration rather than with NH_3 concentration indicating (ii) as the predominant route. This was confirmed by the reaction of $[Ru(^{15}NH_3)_5{}^{14}NO]^{3+}$ (0·03M) with aqueous $^{14}NH_3$ (10M). Even under these conditions, which strongly favour direct attack by NH_3, the $[Ru(NH_3)_5N_2]^{2+}$ produced contained *ca.* 50% $^{14}N^{15}N$ and 50% $^{14}N^{14}N$ {determined by mass-spectrometric analysis of the gas evolved on heating the precipitated $[Ru(NH_3)_5N_2]Br_2$ *in vacuo*}. Under conditions where there is no added NH_3 it is unlikely that direct attack by NH_3 (if any is liberated from the complex) occurs.

Under our conditions there is some *cis*- to *trans*-isomerization of $[RuOH(NH_3)_4NO]^{2+}$, but no *trans*- to *cis*-isomerization.[3] Hence the *cis*-$[RuOH(NH_3)_4NO]^{2+}$ must result because (a) the attacking $[RuNH_2(NH_3)_4NO]^{2+}$ has the *cis*-configuration; or (b) there is a stereochemical rearrangement involving a 5-co-ordinate species such as $[Ru(NH_3)_4NO]^{3+}$ produced during attack by a *trans*-amido complex. Though both possibilities are unprecedented in this area, (a) is somewhat favoured over (b) because under our conditions substitution isomerisation is very slow.

We thank the National Research Council of Canada and the University of New Brunswick Research Fund for financial support, Johnson, Matthey and Mallory, Montreal, for the loan of ruthenium, and the Canadian International Development Agency for a Commonwealth Scholarship (to E.M.R.K.).

(*Received*, 6*th November* 1974; *Com.* 1357.)

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† The products were identified by their chemical and physical properties, which are all known from the literature.

[1] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

[2] Formation of N_2 by attack of NH_3 on co-ordinated NO occurs with $[IrX_5NO]^-$ (X = Cl, Br); F. Bottomley, S. G. Clarkson, and S. B. Tong, *J.C.S. Dalton*, in the press. For a related reaction see W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084. It has been shown that $[Ru(NH_3)_5NO]^{3+}$ is readily attacked by nucleophiles; see ref. 1 and F. Bottomley and J. R. Crawford, *J. Amer. Chem. Soc.*, 1972, **94**, 9092.

[3] S. Pell and J. N. Armor, *Inorg. Chem.*, 1973, **12**, 873. These workers note there is almost complete *cis*- to *trans*-isomerisation of $[RuOH(NH_3)_4NO]^{2+}$ in warm alkaline solutions, an observation confirmed by us. However, at 5 °C this isomerisation proceeds only very slowly.