Formation of Penta-ammine(dinitrogen)- and *cis*-Tetra-amminehydroxonitrosyl-ruthenium from Penta-amminenitrosylruthenium and Hydroxide Ion

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When $[Ru(NH_3)_5(NO)]^{3+}$ is set aside in 0.1M aqueous NaOH for 7 d, $[Ru(NH_3)_5(N_2)]^{2+}$ (25%), *cis*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ (11%), and *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ (8%) are formed. Evidence is presented that the reactions (i) and (ii) are occurring. The $[Ru(OH)(NH_3)_4(NO)]^{2+}$ formed is the *cis*-isomer.

$$[Ru(NH_3)_5(NO)]^{3+} + OH^- \rightleftharpoons [Ru(NH_2)(NH_3)_4(NO)]^{2+} \quad \text{(i)}$$

$$[Ru(NH_3)_5(NO)]^{3+} + [Ru(NH_2)(NH_3)_4(NO)]^{2+} \longrightarrow [(H_3N)_5Ru\{N(O)NH_2\}Ru(NH_3)_4(NO)]^{5+} \longrightarrow [Ru(NH_3)_5(N_2)]^{2+} + [Ru(OH)(NH_3)_4(NO)]^{2+} \quad \text{(ii)}$$

In a previous paper [1] we reported that in aqueous alkaline solutions $[Ru(NH_3)_5(NO)]^{3+}$ is in equilibrium with $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ and $[Ru(NH_3)_5(NO_2)]^{+}$. We also indicated that such solutions gave $[Ru(NH_3)_5(N_2)]^{2+}$ when set aside, and speculated that this product was obtained by nucleophilic attack of NH_3 (liberated by OH^- substitution of NH_3 in one of the constituents of the equilibrium) at the co-ordinated NO of residual $[Ru(NH_3)_5(NO)]^{3+}$. Although $[Ru(NH_3)_5(NO)]^{3+}$ is readily susceptible to nucleophilic attack,[1-3] the yields of $[Ru(NH_3)_5(N_2)]^{2+}$ {*ca.* 25% of the initial $[Ru(NH_3)_5(NO)]^{3+}$} indicated a remarkably efficient reaction, which required further investigation. The results presented here show that $[Ru(NH_3)_5(N_2)]^{2+}$ is formed predominantly by the remarkable reaction (1). A brief report of this work has been given.[4]

$$[Ru(NH_3)_5(NO)]^{3+} + [Ru(NH_2)(NH_3)_4(NO)]^{2+} + OH^- \longrightarrow [Ru(NH_3)_5(N_2)]^{2+} + cis\text{-}[Ru(OH)(NH_3)_4(NO)]^{2+} + H_2O \quad (1)$$

RESULTS

When aqueous alkaline solutions of $[Ru(NH_3)_5(NO)]^{3+}$ were set aside at 5 °C for 7 d $[Ru(NH_3)_5(N_2)]^{2+}$ was formed $\leqslant 33\%$ yield. The yield was investigated as a function of the concentrations of $[Ru(NH_3)_5(NO)]^{3+}$ and OH^-, time, and temperature. Some $[Ru(NH_3)_5(N_2)]^{2+}$ was formed under all conditions providing $[OH^-]$ 10^{-2}—5 mol dm^{-3}. At higher $[OH^-]$ there was increasing interference by $[Ru(NH_3)_5(NO_2)]^{+}$ and a decreased yield of $[Ru(NH_3)_5(N_2)]^{2+}$; hence 0.1 mol dm^{-3} NaOH was generally used. Over the range 1×10^{-2}—7.5×10^{-2} mol dm^{-3} of $[Ru(NH_3)_5(NO)]^{3+}$ the relative yield of $[Ru(NH_3)_5(N_2)]^{2+}$ did not change markedly. When KBr or KI was added to a solution of $[Ru(NH_3)_5(NO)]^{3+}$ in aqueous NaOH immediately after mixing, the products were $[Ru(NH_3)_5(NO)]^{3+}$ and $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ respectively. These were the only products, at 5 °C, up to a period of 1 h, when $[Ru(NH_3)_5(N_2)]^{2+}$ was first detectable. The yield of $[Ru(NH_3)_5(N_2)]^{2+}$ at this temperature continued to increase for 5—7 d, after which time some decomposition occurred. The reaction proceeded more rapidly at room temperature, but then both *cis–trans* isomerisation of $[Ru(OH)(NH_3)_4(NO)]^{2+}$ and direct substitution, forming (as the observed product) *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$, were quite rapid.[1,5] Hence the usual conditions adopted were 5 °C and 5—7 d. The reaction proceeded identically under argon or air.

When the reaction was quenched by addition of HBr,

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

[2] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 200.

[3] F. Bottomley and J. R. Crawford, *J. Amer. Chem. Soc.*, 1972, **94**, 9092.

[4] F. Bottomley, S. G. Clarkson, and E. M. R. Kiremire, *J.C.S. Chem. Comm.*, 1975, 91.

[5] S. Pell and J. N. Armor, *Inorg. Chem.*, 1973, **12**, 873.

$[Ru(NH_3)_5(N_2)]Br_2$ and unchanged $[Ru(NH_3)_5(NO)]Br_3{\cdot}OH_2$ were precipitated. These were readily separated by fractional crystallization from mildly alkaline solution. Evaporation of the mother liquor after removal of the $[Ru(NH_3)_5(N_2)]Br_2$–$[Ru(NH_3)_5(NO)]Br_3{\cdot}OH_2$ mixture gave $[Ru(OH)(NH_3)_4(NO)]Br_2$, whose physical properties (i.r., u.v.) indicated a mixture of *cis* and *trans* isomers. These could not be separated, but were converted into *cis*- and *trans*-$[RuCl(NH_3)_4(NO)]Cl_2$ on heating under reflux in aqueous HCl. Fractional crystallization (several times) served to separate and purify the isomers of $[RuCl(NH_3)_4(NO)]Cl_2$. Under the experimental conditions the product yields {mean of seven determinations, based on the initial $[Ru(NH_3)_5(NO)]Cl_3{\cdot}OH_2$} were: $[Ru(NH_3)_5(N_2)]^{2+}$, 26%; *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$, 8%; *cis*-$[RuCl(NH_3)_4(NO)]^{2+}$, 11%; and unchanged $[Ru(NH_3)_5(NO)]^{3+}$, 14%. The only other product ever detected was $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$, observed when the reaction was quenched by adding KBr or KI.

When aqueous NH_3 was used as the source of OH^- the $[Ru(NH_3)_5(N_2)]^{2+}$ yield was negligible, except at a NH_3 concentration of 10 mol dm^{-3} {*i.e.* a solution of $[Ru(NH_3)_5(NO)]^{3+}$ in NH_3 (*d* 0.880)} where $[OH^-] = ca.\ 10^{-2}$ mol dm^{-3}. The complex $[Ru(^{15}NH_3)_5(^{14}NO)]^{3+}$ (0.03 mol dm^{-3}) was incubated with $^{14}NH_3$ (10 mol dm^{-3}) for 6 d at 5 °C and the product was precipitated with NaBr. The gas evolved on heating the product *in vacuo* was shown to be *ca.* 50% $^{29}N_2$ and 50% $^{28}N_2$ by mass spectrometry. The i.r. spectrum of the product exhibited bands attributable to $[Ru(NH_3)_5(^{28}N_2)]Br_2$ and $[Ru(NH_3)_5(^{29}N_2)]Br_2$.[6] The salt $[Ru(NH_3)_5(NO)]I_3$ was converted essentially quantitatively into $[Ru(NH_3)_5(N_2)]I_2$ on treatment with anhydrous NH_3 in a sealed tube at 10 °C for 8 d.

Several attempts at following the OH^- and NH_3 reactions kinetically were abortive. All the reactants and products absorb strongly in the u.v. region (<250 nm), and have weak and overlapping bands in the visible region; hence the electronic spectrum was unusable. The 2 123 cm^{-1} band of $[Ru(NH_3)_5(N_2)]^{2+}$ in the i.r. spectrum [7] was too weak, at least in aqueous alkaline solution, for accurate monitoring of the reaction. Fractional crystallization, while successful in separating all the products, could not do so quantitatively. An attempt to follow the reaction in liquid NH_3 was frustrated because there was evidence of a new species, possibly $[Ru(NH_2)_2(NH_3)_3(NO)]^+$.

The observations of Pell and Armor [5] on the isomerization of $[RuX(NH_3)_4(NO)]^{2+}$, which are clearly important for the present work, were checked and extended. In summary the results were: (*i*) neither *cis*- nor *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$ isomerized detectably (u.v., i.r.) when heated under reflux in aqueous HCl (6 mol dm^{-3}) for 6 h; (*ii*) *cis*- and *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ underwent substitution of OH^- by Cl^- on heating under reflux in dilute HCl without detectable isomerization; (*iii*) *cis*-$[RuCl(NH_3)_4(NO)]^{2+}$ was converted completely (u.v., i.r.) into *cis*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ within 3 min in 0.1 mol dm^{-3} NaOH at 5 °C; (*iv*) conversion of *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$ into *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ in 0.1 mol dm^{-3} NaOH at 5 °C was slower than for the *cis* isomer and appeared to be complete in *ca.* 12 h; (*v*) *cis*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ was 10% isomerized to the *trans* isomer after 7 d in 0.1 mol dm^{-3} NaOH at 5 °C and 30% isomerized after 23 d (*ca.* 15% isomerization was found after 6 h at room temperature); (*vi*) *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ was not detectably isomerized after 7 d in 0.1 or 0.5 mol dm^{-3} NaOH at 5 °C nor even after 4 d in 0.5 mol dm^{-3} NaOH at room temperature; and (*vii*) there was no substitution of Cl^- for NH_3 when $[Ru(NH_3)_5(NO)]^{3+}$ was heated under reflux in HCl.

We have previously used the reaction of ammineiodonitrosyls of osmium with liquid NH_3 to produce $[Os(NH_3)_5(NO)]^{3+}$,[8] and found no evidence of $[Os(NH_3)_5(N_2)]^{2+}$.[9] Neither was any $[Os(NH_3)_5(N_2)]^{2+}$ observed when $[Os(NH_3)_5(NO)]^{3+}$ was set aside at room temperature or at 5 °C in 0.1 mol dm^{-3} NaOH for 7 d.

DISCUSSION

Since $[Ru(NH_3)_5(N_2)]^{2+}$ was formed from $[Ru(NH_3)_5(NO)]^{3+}$ and OH^- under an argon atmosphere, the co-ordinated N_2 must arise from a reaction involving the only source of nitrogen available, the starting complex. Since $[Ru(NH_3)_5(N_2)]^{2+}$ was the sole N_2-containing product, intramolecular reaction of $[Ru(NH_3)_5(NO)]^{3+}$, $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$, or $[Ru(NH_3)_5(NO_2)]^{+}$ is impossible and the lack of $[Ru(NH_3)_5(N_2)]^{2+}$ formation at high $[OH^-]$, where the solution contains essentially only $[Ru(NH_3)_5(NO_2)]^+$,[1] indicates that this complex is not involved in the reaction. The most reasonable reaction is one involving nucleophilic attack of a nitrogen-containing species at co-ordinated NO. Precedents for this exist in the formation of N_2 and $[IrX_5(NH_3)]^{2-}$ from $[IrX_5(NO)]^-$ and NH_3,[10] and of $[RuCl(bipy)_2(N_2Ar)]^{2+}$ from $[RuCl(bipy)_2(NO)]^{2+}$ and $ArNH_2$ (bipy = 2,2′-bipyridyl).[11] Two questions then arise. What is the Ru–NO species attacked, and what is the nitrogen-containing species? We have shown that $[Ru(NH_3)_5(NO)]^{3+}$ is readily attacked by nucleophiles,[1-3] but neither *cis*- nor *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ is attacked,[1,12] and we have also shown that complexes with ν(NO) at < 1 886 cm^{-1}, such as $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ [ν(NO) at 1 885 cm^{-1}], $[Os(NH_3)_5(NO)]^{3+}$ (1 885), and $[Os(NH_2)(NH_3)_3(NO)]^{2+}$ (1 785), do not behave as electrophiles.[13] Hence the Ru–NO species must be $[Ru(NH_3)_5(NO)]^{3+}$. Only two nitrogen-containing species, NH_3 and the co-ordinated NH_2^- of $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$, are possible nucleophiles. The former can arise from loss of NH_3 from one of the complexes in solution when $[Ru(NH_3)_5(NO)]^{3+}$ and NaOH are the reactants. The experiments with added NH_3 indicate that such attack by free NH_3 may occur, but it is very inefficient, and when no added NH_3 is available is very unlikely; formation of $[Ru(NH_3)_5(^{29}N_2)]^{2+}$ from $[Ru(^{15}NH_3)_5(^{14}NO)]^{3+}$ in 10 mol dm^{-3} $^{14}NH_3$ provides convincing evidence of this. Hence the attacking nucleophile must be $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$.

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[7] J. Chatt, G. J. Leigh, and N. Thankarajan, *J.C.S. Dalton*, 1972, 3168.

[8] F. Bottomley and S. B. Tong, *J.C.S. Dalton*, 1973, 217.

[9] A. D. Allen and J. R. Stevens, *Chem. Comm.*, 1967, 1147.

[10] F. Bottomley, S. G. Clarkson, and S. B. Tong, *J.C.S. Dalton*, 1974, 2344.

[11] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.

[12] F. Bottomley, S. G. Clarkson, and M. Mangat, unpublished work.

[13] F. Bottomley, W. V. F. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919.

Because of its ease of isolation the observed yield of $[\mathrm{Ru(NH_3)_5(N_2)}]^{2+}$ (26%) is believed to accurately represent its actual production. Conversely, because it was not possible to estimate the yield of $[\mathrm{Ru(OH)(NH_3)_4(NO)}]^{2+}$ except after its conversion into the difficult to isolate $[\mathrm{RuCl(NH_3)_4(NO)}]^{2+}$, it is likely that the $[\mathrm{Ru(OH)(NH_3)_4(NO)}]^{2+}$ production is greater than the observed yield (19%). Hence the observed yields are in agreement, within experimental error, with the proposed reaction which requires that the yield of $[\mathrm{Ru(NH_3)_5(N_2)}]^{2+}$ equals that of $[\mathrm{Ru(OH)(NH_3)_4(NO)}]^{2+}$.

Under the reaction and work-up conditions *cis–trans* but not *trans–cis* isomerization occurs. Three routes to the *cis* product are available: (*i*) attack of preformed *cis*-$[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ on $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ with retention of stereochemistry during reaction; (*ii*) initial attack by *trans*-$[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ with stereochemical rearrangement during reaction; and (*iii*) direct substitution of $\mathrm{OH^-}$ for $\mathrm{NH_3}$ in $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$. The observed *trans* product may be produced by a similar three reactions or by *cis–trans* isomerization subsequent to reaction. It is to be noted that the independent isomerization experiments indicate all of the *trans* isomer could be produced by *cis–trans* isomerization. Route (*iii*) may be discounted for both isomers, except as a minor path, because it does not account for $[\mathrm{Ru(NH_3)_5(N_2)}]^{2+}$ production. Though both routes (*i*) and (*ii*) are without precedent in this area, we are unable to determine rigorously whether the *cis* product is formed by stereochemical rearrangement [route (*ii*)] or reaction of preformed *cis*-$[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ without stereochemical rearrangement [route (*i*)]. Some points may, however, be made. First, molecular models indicate that steric hindrance to formation of the intermediate $[\mathrm{(H_3N)_5Ru\{N(O)NH_2\}Ru(NH_3)_4(NO)}]^{5+}$ is much greater if the attacking $[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ is the *trans* rather than the *cis* isomer. Secondly, in general the ruthenium nitrosyls investigated here react predominantly with retention of configuration,[5] and where isomerization does occur it is *cis–trans*, not *trans–cis* as required by route (*ii*). Thirdly, our previous conclusion that $[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ is the *trans* isomer was based on the lowering of ν(NO) (to 1 837 cm^{-1}) compared to $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ (1 917 cm^{-1}).[1] It has since been shown that *cis*-$[\mathrm{Ru(OH)(NH_3)_4(NO)}][\mathrm{ClO_4}]_2$ [ν(NO) at 1 861 cm^{-1}] has a low ν(NO);[5] hence we can no longer assert that $[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$ is the *trans* isomer.* In summary, the $[\mathrm{Ru(NH_3)_5(N_2)}]^{2+}$-forming reaction is best represented by equation (2).

$$[\mathrm{Ru(NH_3)_5(NO)}]^{3+} + cis\text{-}[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+} + \mathrm{OH^-} \longrightarrow [\mathrm{Ru(NH_3)_5(N_2)}]^{2+} + cis\text{-}[\mathrm{Ru(OH)(NH_3)_4(NO)}]^{2+} + \mathrm{H_2O} \quad (2)$$

EXPERIMENTAL

Ruthenium trichloride hydrate (Johnson, Matthey, and Mallory, Montreal) was used as received. All other chemicals were reagent grade. The salts $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{X_3{\cdot}OH_2}$ (X = Cl or Br),[14] $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{X_2}$ (X = Cl or Br),[15] *cis*-$[\mathrm{RuCl(NH_3)_4(NO)}]\mathrm{Cl_2}$,[5] *cis*-$[\mathrm{Ru(OH)(NH_3)_4(NO)}]\mathrm{Cl_2}$,[5] *trans*-$[\mathrm{RuCl(NH_3)_4(NO)}]\mathrm{Cl_2}$,[16] *trans*-$[\mathrm{Ru(OH)(NH_3)_4(NO)}]\mathrm{Cl_2}$,[16,17] and $[\mathrm{Os(NH_3)_5(NO)}]\mathrm{I_3{\cdot}OH_2}$ [8] were prepared by the literature methods.

Reaction between Penta-amminenitrosylruthenium and Hydroxide Ion.—In a typical experiment $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Cl_3{\cdot}OH_2}$ (0.03 g) in aqueous NaOH (0.1 mol dm^{-3}, 2 cm^3) was set aside at 5 °C for 7 d. Some precipitated $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Cl_2}$ was then removed by filtration and cold HBr (48%) added dropwise to the resulting filtrate until precipitation of the yellow product was complete. The product was filtered off and the filtrate saved (see below). The product was washed with ethanol and diethyl ether and air dried. Its i.r. spectrum showed absorption bands in the 2 100 and 1 900 cm^{-1} regions, as well as bands assignable to $\mathrm{NH_3}$ vibrations, indicating a mixture of $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Br_2}$ and $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Br_3{\cdot}OH_2}$. The mixture was dissolved in aqueous NaOH (0.5 mol dm^{-3}) and reprecipitated with KBr. Two repetitions of this procedure gave pure pale-yellow $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Br_2}$ (0.009 g); total yield of $[\mathrm{Ru(NH_3)_5(N_2)}]^{2+}$, 27%. Acidification (ice-cold) with HBr (48%) of the two filtrates from the recrystallization gave $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Br_3{\cdot}OH_2}$ (0.007 g, 16%). The $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Br_2}$ was converted metathetically into $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Cl_2}$ with HCl and was washed with EtOH and $\mathrm{Et_2O}$ and dried *in vacuo* over $\mathrm{P_2O_5}$ (Found: H, 5.3; Cl, 24.9; N, 34.3. Calc. for $\mathrm{H_{15}Cl_2N_7Ru}$: H, 5.3; Cl, 24.9; N, 34.4%), ν($\mathrm{N_2}$) at 2 104vs cm^{-1} (lit.,[15] 2 105), and $\lambda_{\text{max.}}$ 221 nm (ε 1.6×10^4 dm^3 mol^{-1} cm^{-1}) [lit.,[18] 221 (1.8×10^4)].

The filtrate after initial removal of the $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Br_2}$–$[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Br_3}$ mixture (see above) was evaporated to dryness in a stream of air at room temperature. The resulting yellow solid was recrystallized by dissolving in water and reprecipitating with KBr (yield 0.007 g, 20%). The i.r. spectrum of the solid after recrystallization from water showed a very strong broad absorption centered at 1 850 cm^{-1} in the ν(NO) region; *cis*- and *trans*-$[\mathrm{Ru(OH)(NH_3)_4(NO)}]\mathrm{Br_2}$ absorb at 1861 and 1 845 cm^{-1} [5] (Found: H,3.5; Br, 42.3; N, 18.7. Calc. for $\mathrm{H_{13}Br_2N_5O_2Ru}$: H, 3.5; Br, 42.5; N, 18.6%).

The $[\mathrm{Ru(OH)(NH_3)_4(NO)}]\mathrm{Br_2}$ (0.10 g, obtained by combining the products of several reactions) was heated under reflux in aqueous HCl (0.2 mol dm^{-3}, 30 cm^3). After *ca.* 2 h a purple-orange precipitate had appeared. This was filtered off and the filtrate heated under reflux for a further 2 h, after which time a yellow precipitate had appeared. Spectral analysis indicated the purple-orange precipitate was mainly *cis*- and the yellow mainly *trans*-$[\mathrm{RuCl(NH_3)_4(NO)}]\mathrm{Cl_2}$. The two isomers were purified by repeated (up to 3 times) recrystallization from hot aqueous HCl (0.02 mol dm^{-3}), with final washing with dilute HCl, EtOH, and $\mathrm{Et_2O}$, and drying *in vacuo*: *cis*-$[\mathrm{RuCl(NH_3)_4(NO)}]\mathrm{Cl_2}$,

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* Recently (J. Mastone and J. Armor, *J. Inorg. Nuclear Chem.*, 1975, **37**, 473) it has been found that exchange of $\mathrm{NH_3}$ protons with solvent $\mathrm{H_2O}$ is faster for the *trans*- than for the *cis*-$\mathrm{NH_3}$ of $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$. This does not give the equilibrium position for formation of $[\mathrm{Ru(NH_2)(NH_3)_4(NO)}]^{2+}$, which may be present largely as the *cis* isomer; alternatively, of the two isomers only the *cis* reacts with $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ for steric reasons.

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[18] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 6170.

0.017 g (11%), ν(NO) at 1 933vs and 1 899vs cm^{-1} (lit.,[5] 1 933 and 1 899 cm^{-1}), $\lambda_{max.}$ 335 (142) and 490 nm (ε 17 dm^3 mol^{-1} cm^{-1}) [A sample prepared by the method of Pell and Armor[5] had $\lambda_{max.}$ 335 (136) and 490 nm (ε 16 dm^3 mol^{-1} cm^{-1}). Pell and Armor[5] quote $\lambda_{max.}$ 345 (126) and 480 nm (ε 19 dm^3 mol^{-1} cm^{-1}). The reason for the $\lambda_{max.}$ discrepancy is not clear, though the bands are very broad.] (Found: H, 4.1; Cl, 34.6; N, 22.7. Calc. for $H_{12}Cl_3N_5ORu$: H, 3.9; Cl, 34.9; N, 22.9%); *trans*-$[RuCl(NH_3)_4(NO)]Cl_2$, 0.014 g (9%), ν(NO) at 1 885vs and 1 871(sh) cm^{-1} [a sample prepared by the literature method[16,17] had ν(NO) at 1 884 and 1 870 cm^{-1}], $\lambda_{max.}$ 247 (4 206), 315 (97), and 450 nm (ε 17 dm^3 mol^{-1} cm^{-1}) [lit.,[5,16] $\lambda_{max.}$ 245 (4 300), 315 (90), and 453 nm (ε 17 dm^3 mol^{-1} cm^{-1})] (Found: H, 3.8; Cl, 35.0; N, 23.0 Calc. for $H_{12}Cl_3N_5ORu$: H, 3.9; Cl, 34.9; N, 22.9%).

I.r. spectra were measured (as Nujol mulls) on a Perkin-Elmer 457 instrument, electronic spectra (aqueous solutions) on a Perkin-Elmer–Hitachi EPS-3T. Microanalyses were by A. Bernhardt, West Germany.

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