

## Formation of the Molecular Nitrogen Complex Cation of Pentammineruthenium(II) from Nitrous Oxide

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**Summary** Molecular nitrogen complexes of pentammine-ruthenium(II) have been prepared by reducing chloropentammineruthenium(III) in the presence of nitrous oxide.

THE reaction of  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{X}$  (I) with nitrogen and with  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  has been reported.<sup>1,2</sup> It has been shown<sup>2</sup> that the co-ordinated nitrogen in  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  is as reactive as free nitrogen towards (I). Benzonitrile has also been shown to react with (I).<sup>3</sup> These reports prompted an investigation of the reaction between nitrous oxide and  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{X}$ , as  $\text{N}_2\text{O}$  contains the grouping  $\text{N}\equiv\text{N}$ - which can be expected to have ligand properties analogous to those of co-ordinated nitrogen and organonitrilic compounds.

On reducing 0.01 M solutions of  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  with amalgamated zinc under nitrous oxide the following results were obtained:

*Formation of molecular nitrogen complexes from nitrous oxide at room temperature*

Reaction	Time (hr.)	% Yield of† $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$	% Yield of† $[\text{Ru}(\text{NH}_3)_5]_2\text{N}_2^{4+}$
$\text{N}_2$ (1 atmos.)	3	16.5	20.6
	6	21.1	31.1
$\text{N}_2\text{O}$ (0.065 atmos.)	3	21.5	19.0
	18	35.0	35.5
$\text{N}_2\text{O}$ (1 atmos.)	1	81.4	7.4
	3	82.7	9.1

† Expressed as [moles product/moles  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ ]  $\times$  100%.

The yields were estimated from the reported extinction coefficients<sup>2</sup> at 221 nm. and 262 nm. The products of the reaction were identified by the i.r. and u.v. spectra of the precipitated tetrafluoroborate salts. Oxidation of the reaction solution with cerium(IV) sulphate led to a 99% recovery of the amount of nitrogen calculated from the spectroscopic measurements.

The presence of excess of reducing agent is necessary for the reaction to proceed to completion. When the reduced solution was exposed to  $\text{N}_2\text{O}$  (1 atm.) in the absence of amalgamated zinc the final yields after three hours were:  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+} = 17.4\%$  and  $[\text{Ru}(\text{NH}_3)_5]_2\text{N}_2^{4+} = 11.5\%$ .

Recent reports that nitrous oxide is reduced to molecular nitrogen by transition metals<sup>4</sup> prompted the investigation of the gas above the reaction mixture; analysis by mass spectrometry showed that it contained nitrous oxide, hydrogen and insignificant amounts of molecular nitrogen. The formation of the nitrogen complexes is faster under nitrous oxide than under nitrogen at the same pressure (Table); higher ratios of mononuclear to binuclear nitrogen complex are formed with nitrous oxide (Table). The above evidence suggests that nitrous oxide reacts directly with the reduced ruthenium species to form an intermediate which is subsequently reduced by the amalgamated zinc [or by  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{X}$ ] to form  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ . The formation of the binuclear complex can be explained by the known reaction<sup>1,2</sup> between the mononuclear complex and  $\text{Ru}^{\text{II}}, (\text{NH}_3)_5\text{X}$ .

No spectroscopic evidence was obtained for the existence of a nitrous oxide complex in solution. However, in the

cerium(IV) sulphate oxidation of the reaction mixture the nitrogen which was evolved was found to contain about 5% of nitrous oxide. This suggests that a small amount of a nitrous oxide complex may be present in the reaction mixture.

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<sup>4</sup> R. G. S. Banks, R. J. Henderson, and J. M. Pratt, *J. Chem. Soc. (A)*, 1968, 2886.