Nitrous Oxide Complexes: the Isolation of Pentammine(dinitrogen oxide)ruthenium(II) Tetrafluoroborate

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Summary The product of the reaction between aquopentammineruthenium(II) and nitrous oxide has been isolated and formulated as $[Ru(NH_3)_5N_2O](BF_4)_2,H_2O$ on the basis of i.r. and u.v. spectra and elemental analysis.

THE reaction between nitrous oxide and $[Ru(NH_3)_5H_2O]^{2+}$ to give $[Ru(NH_3)_5N_2]^{2+}$ has been reported.[1,2] Taube[2] has presented spectral evidence for the existence of $[Ru(NH_3)_5N_2O]^{2+}$ in equilibrium with N_2O in aqueous solution.

We now report a pale yellow solid was prepared in good yields by exposing solutions of $[Ru(NH_3)_5H_2O]^{2+}$ (2×10^{-2} M) to high pressures (30—40 atm.) of oxygen-free nitrous oxide in the presence of sodium fluoroborate. The compound which is diamagnetic and microcrystalline (truncated cubes) is stable in dry air and in high vacuum at room temperature for periods of 2—3 days and for longer periods in the dark at $-6°$. The compound has been formulated as $[Ru(NH_3)_5N_2O](BF_4)_2,H_2O$ on the basis of elemental analysis carried out three days after its preparation (found N = 22·2, F = 36·8, and H = 4·02%; calc. N = 23·2, F = 36·0, and H = 4·06%). Analyses carried out after longer periods give low N and high F values, consistent with a slow loss of N_2O.

The presence of nitrous oxide in the compound was confirmed by oxidising the complex in solution and recovering the evolved gas which was shown to be nitrous oxide by mass spectrometry. Yields varied depending on the nature of the oxidiser used (*viz.* O_2, Fe^{3+}, Ce^{4+}) and values of 73—77% were obtained when using ceric sulphate.

Further evidence for the formulation has been obtained from i.r. and u.v. spectral studies. The i.r. spectrum of the solid in the range 4000—500 cm^{-1} reveals a medium absorption at 2275 cm^{-1} and a very strong absorption at 1210 cm^{-1}. These two bands have been assigned to the ν_3 and ν_1 stretching vibrations of N_2O with a shift of $+51$ cm^{-1} for ν_3 and -76 cm^{-1} for ν_1 compared to the spectrum of gaseous N_2O.[3] Shifts in the same directions, but of smaller magnitudes, have been reported for the ν_3 and ν_1 bands of N_2O adsorbed on evaporated alkali-metal halide films.[4] There are also two ill-defined bands in the region 500—250 cm^{-1}. It is not as yet possible to decide whether these bands are due to the bending mode of the N_2O molecule [ν_2 in $N_2O(g)$ 589 cm^{-1}][3] or due to metal–ligand vibrations. The spectra also show the fluoroborate bands, and the ammine vibrations expected for a Ru^{II} ammine complex; bands at 3615, 3525, and a shoulder at 1700 cm^{-1} were assigned to lattice water.[5] In some preparations a weak band at 2144 cm^{-1} was observed; this was assigned to the ν_{N-N} of $[Ru(NH_3)_5N_2](BF_4)_2$, present as an impurity.

In agreement with the equilibrium and kinetic data reported by Taube[2] the complex was found to be decomposed rapidly in water. Initial u.v. spectra (after *ca.* 200 sec.) showed an absorbtion band at 237·5 nm (lit.[2] 238) and an extinction which indicated that approximately 50% of the complex had decomposed at the time of recording the spectrum.

Spectra taken in solutions in which argon was bubbled through to displace the nitrous oxide showed quantitative conversion into $[Ru(NH_3)_5(H_2O)]^{2+}$ (λ_{max} 268 nm, ϵ 520; *lit.*[6] λ_{max} 267 nm, ϵ *ca.* 530). Oxidation of an aqueous solution with Fe^{3+} gave a quantitative conversion into

$[Ru(NH_3)_5OH]^{2+}$ (λ_{max} 297 nm, ϵ 2145; *lit.*[7] λ_{max} 297 nm, ϵ 2145).

Thermal decomposition of the solid at 135° in high vacuum gave N_2, N_2O, and H_2O as gaseous products. The solid residue contained $[Ru(NH_3)_5N_2](BF_4)_2$ which was identified by i.r. and u.v. spectra. It also contained "ruthenium red"[8] identified by the visible spectra in neutral and in acid solutions. This is in agreement with the oxidising action of the nitrous oxide complex in solution reported previously.[1]

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