Reactions of Nitrosylpenta-ammineruthenium(II) with Hydroxylamine, Hydrazine, and Ammonia

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Summary Nitrosylpenta-ammineruthenium(II) reacts with hydroxylamine, hydrazine, or ammonia to form (dinitrogen oxide)penta-ammineruthenium(II) and in the last two cases, dinitrogenpenta-ammineruthenium(II).

REACTIONS of nitrosylruthenium(II) complexes have attracted attention recently.[1-3] We report the reactions of hydroxylamine, hydrazine, and ammonia with nitrosylpenta-ammineruthenium(II).

$[Ru^{II}(NH_3)_5NO]X_3$ (X = Cl, I) reacted rapidly with hydroxylamine at room temperature to form $[Ru^{II}(NH_3)_5N_2O]X_2$.† The diamagnetic products have similar properties to those reported for $[Ru^{II}(NH_3)_5N_2O]BF_4$.[4] The gas evolved on oxidizing the iodide salt with cerium(IV) was shown to be N_2O by mass spectrometry, and on heating this salt *in vacuo* N_2O, N_2, and H_2O were evolved. The i.r. spectra showed a very strong band at 1175 cm^{-1} (I^- salt) or 1150 cm^{-1} (Cl^-) (the ν_1 band of N_2O) and a weak band at 2250 cm^{-1} (I^-) or 2240 cm^{-1} (Cl^-) (the ν_3 band of N_2O). Similar shifts in the position of i.r. bands with the counter-anion have been reported for $[Ru^{II}(NH_3)_5N_2]X_2$.[5] The iodide salt is very much more stable than the chloride or, as reported, the tetrafluoroborate.[4]

$[Ru^{II}(NH_3)_5NO]Cl_3)$ and excess of hydrazine hydrate at room temperature rapidly yielded $[Ru^{II}(NH_3)_5N_2]X_2$ (X = Cl, I), unlike $[Ru^{II}(das)_2ClNO]Cl_2$ which gave $[Ru^{II}(das)_2(N_3)Cl]^1$ (das = *o*-phenylenebisdimethylarsine). At − 23 °C immediate (10 s) addition of NH_4Cl, KBr, or KI yielded a mixture of $[Ru^{II}(NH_3)_5N_2O]X_2$ and $[Ru^{II}(NH_3)_5N_2]X_2$ (X = Cl, Br, I).‡ The diamagnetic mixed salt showed a band at 2105 (Cl^- salt), 2118 (Br^-), or 2129 cm^{-1} (I^-), assigned to ν_{N-N},[5] in addition to the bands due to N_2O described above (Br^- salt, ν_1 bands of N_2O, 1160 cm^{-1} and the ν_3 band of N_2O, 2260 cm^{-1}). No band assignable to co-ordinated NO was observed. The mixture evolved N_2O, N_2, and H_2O but no NO_2 on heating *in vacuo*.

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† Satisfactory elemental analyses were obtained for these salts.

‡ Elemental analyses are consistent with this formulation.

The same mixed salt was obtained at temperatures down to −40 °C.

With a longer reaction time (*ca.* 3 min) at −23 °C a brick red (Cl^-) or purple (I^-) salt was precipitated, which turned pale yellow when set aside. The i.r. spectra of the salts showed bands at 2020 cm^{-1} in addition to those described above. The electronic absorption spectrum showed a band at 460 nm ($\epsilon > 1000$) which decreased with time. These properties indicated the presence of $[Ru^{III}(NH_3)_5N_3]X_2$.[5]

The major product of the reaction of $[Ru^{II}(NH_3)_5NO]X_3$ (X = Cl, I) with ammonia was $[Ru^{II}(NH_3)_4(OH)NO]X_2$.[6] However, partial conversion into $[Ru^{II}(NH_3)_5N_2O]I_2$ or $[Ru^{II}(NH_3)_5N_2]I_2$ or a mixture of these also occurred, depending on the conditions. $[Ru^{II}(NH_3)_5NO]X_3$ was not converted into $[Ru^{II}(NH_3)_5NO_2]X$ by either ammonia or sodium hydroxide, in contrast to $[Ru^{II}(bipy)_2(NO)X]^{2+}$.[2]

The formation of $[Ru^{II}(NH_3)_5N_2O]^{2+}$ from $[Ru^{II}(NH_3)_5NO]^{3+}$ and any of the three reactants is presumed to take place *via* nucleophilic attack of hydroxylamine, hydrazine or ammonia at the nitrosyl-N atom in a manner analogous to that for carbonyl complexes.[7] $[Ru^{II}(NH_3)_5N_2O]^{2+}$ is known[2] to decompose in solution to $[Ru^{III}(NH_3)_5OH]^{2+}$, which is reduced by hydrazine under the conditions described here.[8] It seems likely that this reaction is the predominant source of $[Ru^{II}(NH_3)_5N_2]^{2+}$ in the reaction of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydrazine. $[Ru^{III}(NH_3)_5N_3]^{2+}$ may be formed by further nucleophilic attack of N_2H_4 on $[Ru^{II}(NH_3)_5N_2O]^{2+}$, followed by oxidation,[9] and this is under investigation.

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