Evidence of a Binuclear Nitrous Oxide Complex of Ruthenium

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Summary A binuclear nitrous oxide complex, [Ru-$(NH_3)_5)_2N_2O](BF_4)_4$, has been isolated from the reaction between aquopenta-ammineruthenium(II) and N_2O (at 1 atm.).

SOME properties of $Ru(NH_3)_5N_2O^{2+}$ in solution have been described, as have observations on the reduction of the co-ordinated oxide.[1,2] Concurrent with continued work on on reduction,[3] we have attempted to prepare a solid containing the nitrous oxide complex. Though these experiments have not been satisfactory in all respects, they do point to an interesting difference between the material we have obtained and that reported recently by Diamantis and Sparrow.[4] The evidence we have obtained suggests that our solid contains a binuclear complex of nitrous oxide; Diamantis and Sparrow interpret their evidence in favour of a mononuclear complex. In reporting a composition differing from theirs we are not challenging their findings or conclusions. The conditions of preparation are sufficiently different (Diamantis and Sparrow used N_2O at 30—40 atm.) to allow for solids of differing composition in the two cases.

A solution $2\cdot3 \times 10^{-2}$M in $Ru(NH_3)_5Cl^{2+}$ and $0\cdot010$M in HCl was reduced by Zn(Hg) or H_2 on Pt. The solution was

then transferred by syringe to a two-necked flask which had previously been purged with oxygen-free N_2O. A saturated solution of either NaBr or $NaBF_4$ was added until the volume increased by 80%. Within a matter of minutes a precipitate began to form which, in the case of the bromide salt, was brown, and in the case of the tetrafluoroborate salt, was yellow. Similar behaviour was observed when the precipitation was done under N_2O at 5 atm., but little or no precipitate forms when N_2O is replaced by Ar.

The precipitates were collected by filtration inside a plastic glove-bag under N_2O, dried by suction and washed with diethyl ether. The i.r. spectra taken on KBr pellets revealed new bands at 2110 (weak to medium, Br^- salt), 2105 (BF_4^-) and 1160 (strong, Br^-), 1155 (BF_4^-)† in addition to bands at 3450 (shl), 3290, 1625, 1290 (shl), 1275, 790 cm^{-1} characteristic of NH_3 and H_2O on ruthenium. The spectra were scanned to 416 cm^{-1}, but no strong absorptions were observed below 700 cm^{-1}. Similar spectra were obtained with Nujol mulls.

Analyses for N_2O were performed by adding degassed water to a round-bottom flask, sealed with a heavy rubber septum and containing a weighed amount of the solid, and the gas released was subjected to chromatographic analysis. The gas chromatograph (columns: 6 ft. Porapak Q in series with 6 ft. of molecular sieve, 5A) was calibrated by injecting a known amount of N_2O (using a gas-tight syringe) into a similar flask, with the same volume of water as before. By varying the conditions of preparation such as [Ru^{II}] and the time of contact with N_2O, the yield of N_2O varied from extremes of 43% to 59% of that expected for a $Ru : N_2O$ ratio of 1·00; the yield of N_2O usually being in the range 51 ± 3% (6 expts.). When the decomposition of the bromide salt was carried out in the presence of Fe^{III} in large excess, the amount of N_2O thereby released was unaltered, and no N_2 was observed.‡ However, when an excess of Cr^{2+} solution was added to the solid, no N_2O appeared. When Fe^{III} in large excess was added to the resulting solution, N_2 was formed in an amount equivalent to the N_2O shown by the analysis described above. Other experiments[1,3] have demonstrated that Cr^{2+} reacts rapidly with co-ordinated N_2O but very slowly with free N_2O.

When the solid is added to air-saturated water, initial absorption is produced at 238 nm, which decays within 2 min to produce a band at 298 nm, characteristic of $Ru(NH_3)_5OH^{2+}$. The BF_4^- salt also showed an additional absorption at 221 nm. Attributing this to $Ru(NH_3)_5N_2^{2+}$, the impurity would account for < 10% of the material.

The solids were analysed for Ru^{II}, taking advantage of the strong charge-transfer absorption which develops in the presence of isonicotinamide.[5] These analyses showed that in the bromide salt only 61—73% of the ruthenium is in the 2+ state. When a concentrated NaBr solution is added to the dissolved solid under an Ar atmosphere, the absorption characteristic of Ru^{III} develops, and 25% of the

ruthenium is thereby accounted for. On adding Zn(Hg) to reduce Ru^{III} to Ru^{II}, 97% of the ruthenium expected was found in the 2+ state. For the BF_4^- salt, the iso-nicotinamide method of analysis revealed 83—97% of the ruthenium in the 2+ state [Ru^{II} in the form $Ru(NH_3)_5N_2^{2+}$ does not respond to isonicotinamide under our experimental conditions]. The Ru^{III} appearing in the bromide salt may be a result of exposure to air. The solid becomes dis-coloured in air over a period of a few hours. In addition, we found that when the BF_4^- salt was exposed to air for 5 h, an increase of ca. 10% in the Ru^{III} level was registered.

The observations cited, particularly for the BF_4^- salt, where contamination by Ru^{III} is not severe, point to the conclusion that the solid approaches the composition $2Ru^{II}$ for each N_2O. If the Ru^{III} content of the Br^- salt is attributed to its sensitivity to air, or to an internal redox process, the conclusion follows that in this case also the solid first precipitated contains 2Ru for each N_2O. More decisive, perhaps, than this evidence are the results of the microanalyses§ which repeatedly showed less than 7N for each Ru.

Diamantis and Sparrow's[4] preparations also showed low analyses for N, and it is possible that their solid contains an admixture of the solid we have prepared. The i.r. data (bands at 2275 and 1210 cm^{-1} for the BF_4^- salt) do indicate that the major part of the N_2O in their material is in a different state of combination from ours (bands at 2105 and 1160 cm^{-1}).

Preliminary experiments were performed on the thermal stability of the complexes. A small amount of the bromide salt was added to a round-bottom flask and sealed with a heavy septum cap and with wax. The flask was heated in an oil bath for 3 h at 115°. During this period no N_2O was observed. However, on cooling the flask and adding water, a large yield of N_2O was obtained. The BF_4^- salt is dis-coloured at this temperature, but still behaves in the same manner as the Br^- salt.

The kinetic analysis of the system of $Ru(NH_3)_5OH_2^{2+}$–N_2O in solution[1] is compatible only with $Ru(NH_3)_5N_2O^{2+}$ being the dominant form of the complex in solution. Equilibrium between this form and [$Ru(NH_3)_5N_2ORu(NH_3)_5$]$^{4+}$ at the ruthenium levels used is expected to be established rapidly,[6] and if the salts of the binuclear complex are much less soluble than of the mononuclear, there is no difficulty in understanding the present work in relation to the earlier.

Though the possibility that we are observing co-precipita-tion rather than binuclear complex formation is rendered remote by the fact that two different anions show similar behaviour, it is by no means eliminated. Crystal structure work will be undertaken.

† BF_4^- absorbs strongly in the region, making difficult the assignment of the position of the band due to co-ordinated N_2O.
‡ There is a large uncertainty in detecting a 10% gaseous yield of N_2 from a mixture of 10% [$Ru(NH_3)_5N_2$]Br_2 and 90% of the binuclear N_2O complex by weight.
§ For the BF_4^- salt at 1 atm. of N_2O: Found: Ru, 25·5; N, 21·1; H, 4·5; B, 5·8; F, 37·5. Calc. for [$Ru(NH_3)_5N_2O$](BF_4)$_2$: Ru, 25·0; N, 24·3; H, 3·7; B, 5·35; F, 37·9. Calc. for [{$Ru(NH_3)_5$}$_2$$N_2O$]($BF_4$)$_4$: Ru, 26·5; N, 22·0; H, 4·0; B, 5·65; F, 39·8.

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