The Formation of $[Ru(NH_3)_5N_2]^{2+}$ from Ruthenium Trichloride and Ammonia

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THE report by Harrison and Taube[1] that $[Ru(NH_3)_5(H_2O)]^{2+}$ reacts in aqueous solution with gaseous nitrogen to form $[Ru(NH_3)_5N_2]^{2+}$ prompts us to report some of our observations in this field.

In an attempt to prepare pure $[Ru(NH_3)_6]Cl_2$ by the reduction of ruthenium trichloride in aqueous ammonia (0·880) with zinc dust,[2] we obtained a solid product having an infrared band at about 2120 cm.$^{-1}$. Allen and Senoff's $[Ru(NH_3)_5N_2]Cl_2$[3] has a band in exactly this region. We find that the intensity of the band in our product depends on the strength of the ammonia solution, the time of reaction, and the nature of pre-treatment of the ruthenium trichloride. The same product was produced in ND_3–D_2O in place of aqueous ammonia.

The presence of the nitrogen complex in our solid, which was mainly $[Ru(NH_3)_6]Cl_2$, was shown by its reaction with concentrated hydrochloric acid to give nitrogen and hydrogen. The latter is formed in the oxidation of $[Ru(NH_3)_6]^{2+}$ to ruthenium(III) products. Previous experiments have shown that 40% of the nitrogen ligand in $[Ru(NH_3)_5N_2]^{2+}$ is liberated as nitrogen gas under the conditions used, and the gas obtained from our product indicated the presence of 1—3% of the nitrogen complex in the isomorphous $[Ru(NH_3)_6]Cl_2$. The nitrogen ligand must come from the ammonia, because the 2120 cm.$^{-1}$ band is found in the spectrum of the complex even when it is produced *in vacuo*, or under argon with rigorous exclusion of atmospheric nitrogen.

During the reduction of ruthenium trichloride in aqueous ammonia by zinc the hydrogen evolved also contains nitrogen, and we surmised that in our reaction some such species as $[RuH_m(NH_3)_1]^{n+}$ or $[Ru(NH_3)_5(H_2O)]^{n+}$ was formed and picked up nitrogen gas produced from the ammonia. This suggested that the yield of $[Ru(NH_3)_5N_2]^{2+}$ would be increased at the expense of $[Ru(NH_3)_6]^{2+}$ by working in a more dilute ammonia solution, but dilution reduced the yield, and the greatest yields were obtained by carrying out the reduction in anhydrous ammonia at its boiling point. After evaporation of the ammonia a residue mixed with zinc was obtained, which gives mainly $[Ru(NH_3)_6]Cl_2$, contaminated with 10—15% of $[Ru(NH_3)_5N_2]Cl_2$, on treatment with water. No gas is evolved in the reduction stage and only hydrogen on the treatment with water. The yield is not increased if nitrogen is passed through the water at the hydrolysis stage, nor is it decreased if argon is passed through.

It appears therefore that in our reaction the nitrogen ligand is being produced by dehydrogenation of ammonia on the ruthenium ion. It is not obvious how ammonia can be converted to nitrogen under such strongly reducing conditions and it would indicate an extraordinary stability of the RuN_2 entity. This is emphasised by the remarkable ease with which $[Ru(NH_3)_5N_2]^{2+}$ is formed, as manifested by the great variety of reactions from which it may be obtained. Ammonia, hydrazine,[3,4] nitrogen gas,[1] and azide ion[4] have now all been used as a source of the nitrogen ligand. It is also remarkable that very few degradative reactions regenerate it as gaseous nitrogen in 100% yield, but usually in some substantially lesser amount.

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