The Reduction of Nitrogen Complexes

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THE nitrogen complexes of transition metals have generally been hailed as possible models for nitrogenase with nitrogen on the active site. To complete the model it is necessary to reduce the nitrogen to ammonia. We have attempted the reduction of $[CoH(N_2)(PPh_3)_3]$,[1] $[IrClN_2(PPh_3)_2]$,[2] $[Ru(NH_3)_5(N_2)]^{2+}$,[3] and $[Os(NH_3)_5(N_2)]^{2+}$[4] with various reagents, but no reduction to ammonia has yet been found.

It has already been reported by Allen and his co-workers[3,5] that the nitrogen molecule in $[Ru(NH_3)_5(N_2)]^{2+}$ is reduced to give a 50% yield of ammonia by alkaline $NaBH_4$, a result which appeared to be substantiated when we repeated their experiments. However, Borod'ko and his co-workers[6] failed to find any $^{15}NH_3$ after attempted $NaBH_4$ reduction of $[Ru(NH_3)_5(^{15}N_2)]^{2+}$. Using Harrison and Taube's preparation[7] of $[Ru(NH_3)$-$(N_2)]^{2+}$ from 91·5% enriched $^{15}N_2$ we obtained the mixed product $[Ru(NH_3)_5(^{15}N_2)][BF_4]_2$ + $[Ru(NH_3)_6][BF_4]_2$ with a 17·85% enrichment of the total nitrogen in the mixture. This mixture showed a $^{15}N{\equiv}^{15}N$ stretching band at 2080 ± 5 cm.$^{-1}$ and no bands due to $^{14}N{\equiv}^{15}N$ or $^{14}N{\equiv}^{14}N$ in the infrared spectrum. On treating the mixture with alkaline borohydride we found no ^{15}N enrichment of the ammonia recovered. It is thus certain that N_2 in $[Ru(NH_3)_5(N_2)]^{2+}$, like that in the other nitrogen complexes, is not reduced to ammonia by $NaBH_4$.

We have therefore sought the cause of the discrepancy between these findings and previous reports of reduction, and conclude that the nitrogen complexes $[Ru(NH_3)_5(N_2)]X_2$ (X = mono-anion) prepared by Allen and Senoff's method[3] from ruthenium trichloride and hydrazine contain up to 50% of $[Ru(NH_3)_5(N_2H_4)]X_2$, or a similar substance. It is the reduction of the hydrazine which produces the ammonia. Our evidence is:

(1) Analytical figures for hydrogen are always high (see ref. 5).

(2) Hydrazine can be detected in aqueous solutions of the supposed pure salts of $[Ru(NH_3)_5(N_2)]^{2+}$.

(3) The infrared spectrum shows bands at **945** and **1145** cm.$^{-1}$ consistent with a hydrazine complex impurity.

(4) We find that mercuric chloride reacts with $[Ru(NH_3)_6]^{2+}$ and similarly with $[Ru(NH_3)_5$-$(N_2H_4)]^{2+}$, but not with $[Ru(NH_3)_5(N_2)]^{2+}$. By treating the product of Allen and Senoff's preparation with mercuric chloride we have been able to remove all the impurity and so obtained the pure nitrogen complex $[Ru(NH_3)_5(N_2)]Cl_2$. This gives only 5 mol. of ammonia on treatment with alkaline borohydride and recovery of the ammonia.

It still remains to find a reductant for the nitrogen complexes before they can be considered models for nitrogenase.

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