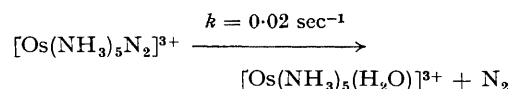
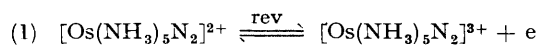


Dinitrogen Complexes of Osmium(III) and Ruthenium(III) Ammines

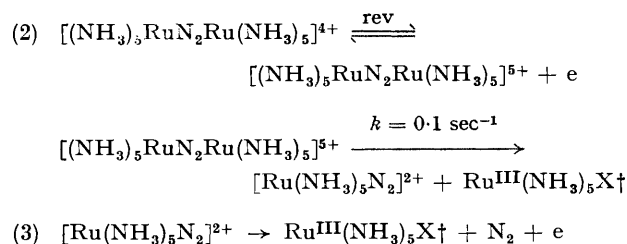
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Summary Electrochemical oxidation of known dinitrogen complexes in aqueous solution has been shown to produce transient $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ and $[(\text{NH}_3)_5\text{RuN}_2\text{Ru}(\text{NH}_3)_5]^{5+}$ species with decomposition rate constants of 0.02 sec^{-1} and 0.10 sec^{-1} , respectively; no $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{3+}$ was detected.

We have been studying the electrochemistry of the dinitrogen complexes of Os^{II} and Ru^{II} and our results are consistent with the following:



† X = SO_4^{2-} or HSO_4^- in sulphate electrolyte.



The starting materials were prepared according to published procedures.¹ All potentials reported are relative to a saturated calomel reference. The work was carried out at 25.0° .

For $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$, controlled-potential oxidation in a $0.08 \text{ M-MeSO}_3\text{H}$ electrolyte on Pt at $+0.32 \text{ v}$ consumed 1.0 faraday per mole and gave a solution with a u.v.

spectrum² consistent with that of $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. Cyclic voltammetry on the $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ was carried out in a $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ electrolyte (pH 1.1, $\mu = 0.31$) at a Pt disc electrode. The forward scan gave an anodic peak ($E_p = +0.315$ v) and the reverse scan a cathodic peak ($E_p = +0.255$ v). The voltammograms were entirely consistent with the requirements for a reversible one-electron charge-transfer followed by a break up of the product.^{3,4} Decomposition of the $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ was observed only at slow scan rates: the ratio of peak currents, $(i.p.)_c/(i.p.)_a$, was significantly less than 1. The rate constant for the decomposition was determined from the voltammograms³ using scan rates of 10, 20, and 50 mv sec^{-1} and switching potentials of $+0.375$ to $+0.475$ v. The results were also confirmed by double-potential step chronoamperometry⁵ using pulses of 2.5 to 10 sec duration. A rate constant for the decomposition of $2 \times 10^{-2} \text{ sec}^{-1}$ was consistently obtained.

Controlled-potential oxidation of the dimeric $[(\text{NH}_3)_5\text{-RuN}_2\text{Ru}(\text{NH}_3)_5]^{4+}$ in a $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ electrolyte (pH 2.3, $\mu = 0.30$) on Pt at $+0.50$ v consumed 1.0 faraday per mole. The products were $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ and $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}$ in a 1:1 mole ratio as determined by the u.v. spectrum and polarography, respectively.⁶ Cyclic voltammetry in a $0.28 \text{ M-H}_2\text{SO}_4$ electrolyte at a Pt disc electrode gave an anodic peak ($E_p = +0.495$ v) on the forward scan and a cathodic peak ($E_p = +0.435$ v) on a reverse scan. The

criteria used before were again consistent with a reversible one-electron charge-transfer followed by break up of the product. The rate constant for the decomposition was a consistent $1 \times 10^{-1} \text{ sec}^{-1}$ (scan rates 10 to 200 mv sec^{-1} for switching potential of $+0.600$ v; 5 sec pulses).

Controlled-potential oxidation of the $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ in the $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ electrolyte (pH 2.3, $\mu = 0.30$) on Pt at $+0.72$ v consumed 1.0 faraday per mole and gave a solution with the u.v. spectrum⁶ characteristic of $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}$. However, in this case, cyclic voltammetry did not give evidence for the formation of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{3+}$ even at scan rates up to 100 v sec^{-1} . Rather, the forward scan on a graphite electrode gave an anodic peak ($E_p = +0.81$ v) while the reverse scan gave a well displaced cathodic peak ($E_p = -0.33$ v at 100 mv sec^{-1}). This latter peak is characteristic of $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}$ in the sulphate electrolyte.

The existence of N_2 complexes of Os^{III} was first suggested by Chatt *et al.*⁷ While we have not prepared a solid complex, our results substantiate their findings. The fact that we are unable to detect a monomeric $\text{Ru}^{\text{III}}\text{-N}_2$ complex may be attributed to a lack of stabilizing π back bonding. However the dimeric $\text{Ru}^{\text{III}}\text{-N}_2\text{-Ru}^{\text{II}}$ complex is relatively stable, presumably due to the π back bonding from Ru^{II} .

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¹ A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595; D. F. Harrison, E. Weissberger, and H. Taube, *Science*, 1968, **159**, 320; A. D. Allen, and J. R. Stevens, *Chem. Comm.*, 1967, 1147.

² H. Taube, personal communication.

³ R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

⁴ P. A. Malachuk, *Analyt. Chem.*, 1969, **41**, 1493.

⁵ W. M. Schwarz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.

⁶ I. J. Itzkovitch and J. A. Page, *Canad. J. Chem.*, 1968, **46**, 2743.

⁷ J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, and J. R. Sanders, *Chem. Comm.*, 1970, 90.