Model Reactions for Nitrogen Fixation. Photo-induced Formation and *X*-Ray Crystal Structure of $[\mathrm{Os_2(NH_3)_8(MeCN)_2(N_2)}]^{5+}$ from $[\mathrm{Os^{VI}(NH_3)_4N}]^{3+}$

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UV-VIS irradiation of an acetonitrile solution of $[\mathrm{Os^{VI}(NH_3)_4N}](\mathrm{CF_3SO_3})_3$ and organic donors under degassed conditions gave $[\mathrm{Os_2(NH_3)_8(MeCN)_2(N_2)}]^{5+}$; the *X*-ray crystal structure of the μ-dinitrogen complex has been determined and the Os–N(N$_2$) distances found to be 1.873(9) and 1.893(9) Å.

The search for an inorganic system which cleaves the N≡N bond under mild conditions is an important area. In their elegant work on osmium ammine complexes, Taube and co-workers[1] proposed reaction (1) for the formation of molecular nitrogen from metal–nitrido complexes. This scheme is based on the isolation of a μ-dinitrogen complex from the oxidation of $[\mathrm{Os^{II}(NH_3)_5CO}]^{2+}$.[1b] The oxidation of $[\mathrm{Os^{II}\,(NH_3)_5(CO)}]^{2+}$ by $\mathrm{S_2O_8}^{2-}$ was suggested to give the $[\mathrm{Os^{V}(NH_3)_4(CO)(N)}]^{2+}$ intermediate, which then dimerised rapidly to give $[\mathrm{Os_2(NH_3)_8(CO)_2(N_2)}]^{4+}$.[1b] However, the observation of direct coupling of nitrogen atoms of metal–nitrido compounds has not been reported. We describe here the formation and *X*-ray crystal structure of a μ-dinitrogen complex through photo-redox reactions of $[\mathrm{Os^{VI}(NH_3)_4N}]^{3+}$ with organic donors.

$$\mathrm{M{\equiv}N + N{\equiv}M \rightarrow [M{\equiv}N \cdots N{\equiv}M] \rightarrow M{-}N{\equiv}N{-}M} \quad (1)$$

Excitation of an acetonitrile solution of $[\mathrm{Os^{VI}(NH_3)_4N}]^{3+}$ at 300—350 nm has been reported previously to give an emission at 545 nm, which comes from the $\mathrm{E_g(^3E_g)}$ state, the spin–orbit sublevel of the $(d_{xy})^1(d_\pi{}^*)^1$ $[d_\pi{}^* = d_{xz}, d_{yz}]$ excited state.[2] Importantly, the lifetime (τ) of the emission depends strongly on the concentration of the osmium complex. A linear Stern–Volmer plot of 1/τ *vs.* [Os] has been found, giving τ_0 (lifetime at infinite dilution) and k_{self} (self-quenching rate constant) values of 1.56 μs and $2.3 \times 10^8\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ respectively. We attribute the self-quenching reaction to the interaction of the two Os≡N moieties (reaction 2).

$$[\mathrm{Os^{VI}{\equiv}N}]^* + [\mathrm{N{\equiv}Os^{VI}}] \rightarrow [\mathrm{Os{\equiv}N \cdots N{\equiv}Os}] \rightarrow 2[\mathrm{Os^{VI}{\equiv}N}] \quad (2)$$

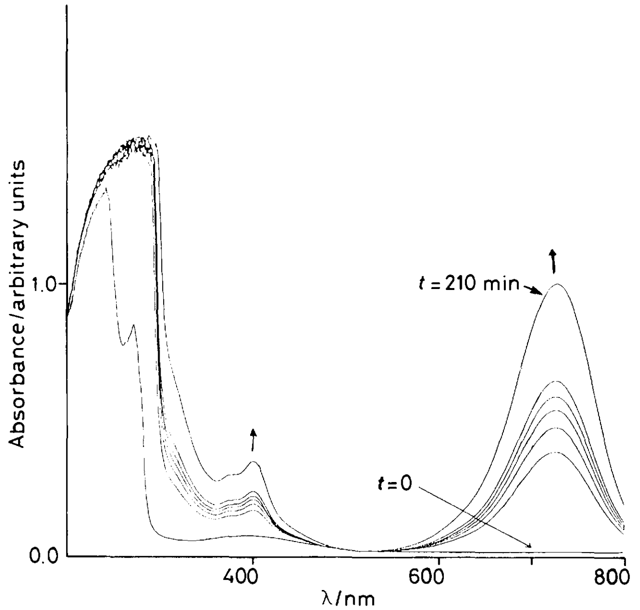

Figure 1. UV-VIS spectral trace for the photoreaction between $[\mathrm{Os^{VI}(NH_3)_4N}](\mathrm{CF_3SO_3})_3$ (~10^{-3} M) and hexamethylbenzene (~10^{-3} M) in degassed acetonitrile. Excitation: λ > 300 nm.

Attempts to investigate the mechanism of self-quenching by flash photolysis were unsuccessful. No detectable transient signal was observed after flashing a degassed acetonitrile solution of $[\mathrm{Os^{VI}(NH_3)_4N}]^{3+}$ (excitation: 355 nm output of a DCR-3 Nd-YAG laser). Furthermore, steady-state photolysis of the osmium complex at 300—400 nm in acetonitrile did not lead to a net reaction.

In the presence of an electron donor, the result of steady-state photolysis was completely different. Figure 1 shows the spectral trace for the photoreaction upon irradiation (λ > 300 nm) of a degassed acetonitrile solution of $[\mathrm{Os^{VI}(NH_3)_4N}](\mathrm{CF_3SO_3})_3$ (~10^{-3} M) and hexamethylbenzene (10^{-3} M). A new osmium complex which absorbs strongly at 720 and 400 nm was formed gradually. The photoreaction could be driven to completion by prolonged photolysis (over 3 h) and the product was isolated by precipitation with diethyl ether. Recrystallisation of the crude osmium product in HCl–HClO$_4$ solution afforded a green crystalline solid (yield > 70%), whose structure has been determined by *X*-ray crystallography† to be $[\mathrm{(MeCN)(NH_3)_4Os{-}N{\equiv}N{-}Os(NH_3)_4(MeCN)}]\,\mathrm{Cl_3(ClO_4)_2}$ (**1**).

Figure 2 shows the ORTEP drawing of the $[\mathrm{Os_2(N_2)(NH_3)_8(MeCN)_2}]^{5+}$ cation with atom numbering. To our knowledge, this is the first *X*-ray structure of a μ-dinitrogen diosmium(II,III) complex. The co-ordination geometries of the two osmium atoms are very similar, suggesting that the complex cation is valence delocalized. This is in good agreement with previous ESCA data which indicated that the analogous $[\mathrm{Os_2(N_2)(NH_3)_8Cl_2}]^{3+}$ ion is a delocalized Class III mixed-valence species.[3] Each osmium atom is surrounded by four NH$_3$, one MeCN, and one N$_2$ ligands. The N$_2$ and MeCN ligands are *trans* to each other. As expected, the Os–N≡C–Me and Os–N≡N–Os groups are essentially linear. An important structural feature of the $[\mathrm{Os_2(N_2)(NH_3)_8(MeCN)_2}]^{5+}$ cation is the Os–N distances. The measured Os–N(N$_2$) distances of

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† *Crystal data* for (**1**): $\mathrm{C_4H_{30}Os_2N_{12}Cl_5O_8}$, M = 932.02, monoclinic, space group $P2_1/n$, a = 8.429(1), b = 8.164(1), c = 20.905(1) Å, β = 100.38(1)°, U = 1415(1) Å^3, Z = 2, D_c = 2.187 g cm^{-3}, μ(Mo-K_α) = 95.1 cm^{-1}, F(000) = 884, no. of parameters (p) 143, no. of data measured 7057, no. of independent data 3307, no. of observed data with $F_o > 3\sigma F_o$ (n) 2821, R = 0.035, R_w = 0.059. The maximum and minimum residues in the final ΔF synthesis were 1.81 and −1.92 eÅ^{-3} in the neighbourhood of the perchlorate ions. Diffraction data were collected on an Enraf-Nonius CAD4 diffractomer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 296 K to $2\theta_{\max}$ = 54°. Intensity data were corrected for Lorentz, polarization, and absorption effects. The empirical absorption correction was based on a ψ scan with transmission factors 0.800—0.999. Calculations were carried out on a Microvax II computer using the Enraf-Nonius SDP package. The Os atoms were located from Patterson syntheses and all the other non-hydrogen atoms from subsequent Fourier maps. Refinement was by full-matrix least-squares: oxygen atoms isotropically, other non-hydrogen atoms anisotropically, and hydrogen atoms were omitted. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

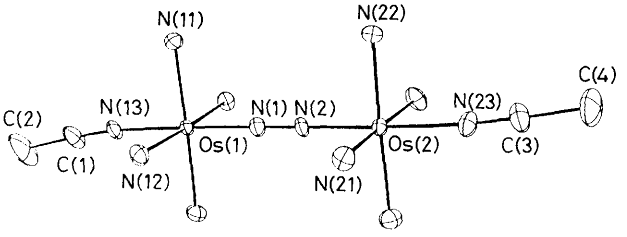

Figure 2. ORTEP drawing of the $[Os_2(N_2)(NH_3)_8(MeCN)_2]^{5+}$ ion of (**1**) showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 30% probability level. Bond distances (Å): Os(1)–N(1) 1.873(9), Os(1)–N(11) 2.124(6), Os(1)–N(12) 2.123(7), Os(1)–N(13) 2.010(9), Os(2)–N(2) 1.893(9), Os(2)–N(21) 2.124(6), Os(2)–N(22) 2.139(6), Os(2)–N(23) 2.02(1), N(1)–N(2) 1.14(1), N(13)–C(1) 1.14(1), N(23)–C(3) 1.12(2), C(1)–C(2) 1.45(3), C(3)–C(4) 1.49(3). Bond angles (°): N(1)–Os(1)–N(11) 90.6(2), N(1)–Os(1)–N(12) 91.9(2), N(1)–Os(1)–N(13) 178.6(4), N(11)–Os(1)–N(12) 92.0(2), N(11)–Os(1)–N(13) 90.4(2), N(12)–Os(1)–N(13) 87.1(2), N(2)–Os(2)–N(21) 91.4(2), N(2)–Os(2)–N(22) 91.5(2), N(2)–Os(2)–N(23) 177.9(3), N(21)–Os(2)–N(22) 92.7(2), N(21)–Os(2)–N(23) 90.1(3), N(22)–Os(2)–N(23) 87.1(3), Os(1)–N(1)–N(2) 178.9(7), Os(2)–N(2)–N(1) 179.6(9), Os(1)–N(13)–C(1) 171.9(7), Os(2)N(23)–C(3) 174.3(9), N(13)–C(1)–C(2) 175(2), N(23)–C(3)–C(4) 179(1).

1.873(9) and 1.893(9) Å are clearly much shorter than that expected for a pure σ bond. They are, however, comparable to the Os–N(N_2) distance of 1.842(13) Å in $[Os^{II}(NH_3)_5N_2]^{2+}$,[4] suggesting the presence of π-back bonding effects in the diosmium(II,III) systems. The measured N≡N distance of 1.14(1) Å is longer than that observed for gaseous nitrogen [1.0976(2) Å].[5] Interestingly, the measured Os–N(MeCN) distances of 2.010(9) and 2.02(1) Å are even longer than that for the Os–N(N_2) distances. The Os–N(NH_3) distances are normal.

Complex (**1**) is very stable in fluid solution for several days. Its optical spectrum, featuring an intense absorption at 720 nm, is characteristic of the μ-dinitrogen diosmium(II,III) complexes reported by Taube and co-workers.[1] The IR spectrum of (**1**) shows no ν(N_2) stretch, in accordance with the *X*-ray structural result that the co-ordination geometries of the two osmium atoms are not grossly different.

Complex (**1**) can also be formed with other organic donors (D), such as 1,4-dimethoxybenzene and 1,2,3-trimethylbenzene. UV-VIS excitation of $[Os^{VI}(NH_3)_4N]^{3+}$ would give the $E_g(^3E_g)$ excited state, which is a powerful oxidant with $E° >$ 2.0 V *vs.* normal hydrogen electrode (NHE).[2] In fact, reductive quenching of the $E_g(^3E_g)$ state by D has been found (reaction 3). The quenching rate constants (k_q) determined by

$$[Os^{VI}{\equiv}N]^* + D \rightarrow Os^{V}{\equiv}N + D^+ \qquad (3)$$

the equation $\tau_0/\tau = 1 + k_q\tau_0[D]$ are 7.49×10^7 and 0.40×10^7 $mol^{-1}\ dm^3\ cm^{-1}$ for hexamethylbenzene and 1,2,3-trimethylbenzene, respectively. The relative quantum yield (steady-state photolysis experiments) for the formation of (**1**) from hexamethylbenzene is 0.31, which is substantially higher than the value of 0.025 from 1,2,3-trimethylbenzene under the same reaction conditions. It is evidence that the quantum yields decrease with the quenching rate constants. The result suggests that formation of $Os^{V}{\equiv}N$ species through reductive quenching occurs prior to the formation of the μ-dinitrogen complex (**1**) (Scheme 1).

$$\begin{aligned}
&[Os^{VI}{\equiv}N] \xrightarrow{h\nu} [Os^{VI}{\equiv}N]^* \\
&[Os^{VI}{\equiv}N]^* + D \longrightarrow D^+ + [Os^{V}{\equiv}N] \\
&[Os^{VI}{\equiv}N] + [Os^{V}{\equiv}N] \rightarrow [Os^{II}\text{–}N{\equiv}N\text{–}Os^{III})
\end{aligned}$$

Scheme 1

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