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N_2 Activation

Photolysis of Aqueous $[(NH_3)_5Os(\mu\text{-}N_2)Os(NH_3)_5]^{5+}$: Cleavage of Dinitrogen by an Intramolecular Photoredox Reaction**

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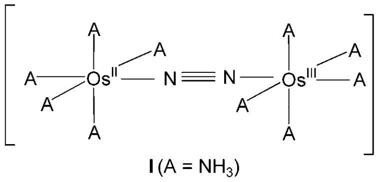
The lack of reactivity of dinitrogen which complicates its chemical conversion has been a challenge to chemists for many decades.[1,2] This difficulty is based on the extreme stability of the nitrogen–nitrogen triple bond. The huge energy difference between HOMO and LUMO (23 eV) makes N_2 rather redox inert. Moreover, the conversion of N_2 into simple species, such as ammonia or nitride, requires the transfer of six electrons. Such multi-electron transfer processes are generally associated with large activation barriers. Nevertheless, the reduction of N_2 to NH_3 occurs in nature through the utilization of the enzyme nitrogenase as catalyst. This conversion also takes place in the Haber–Bosch process, however, extreme conditions are required. Accordingly, it is of considerable interest to accomplish this reaction at ambient conditions. In principle, catalysis can be replaced by a photochemical procedure. The activation energy is then supplied by light. In favorable cases the photoactivation is selective and avoids interfering processes. Moreover, light may not only provide the activation energy but also the energy for an endothermic reaction which does not occur in catalysis at lower temperatures.

In this context, it should be emphasized that some photochemical studies of binuclear N_2-bridged complexes have been reported before.[3,4] However, in these cases N_2 is present in a reduced form containing a N=N double bond instead of a triple bond. This feature considerably facilitates the splitting of the N_2 ligand and may even take place thermally.[4] In contrast, the reductive splitting of the N≡N triple bond in a molecular complex is certainly much more difficult to achieve (see below), and has not yet been accomplished, neither thermally nor photochemically.

Accordingly, we decided to examine a binuclear complex with a bridging N_2 ligand which largely preserves its integrity as a free dinitrogen molecule. For this purpose, we selected the cation $[(NH_3)_5Os^{II}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{5+}$ [5,6] (**I**).



I (A = NH_3)

This complex offers several attractive features. It is easily accessible and rather stable in aqueous solution in the absence of light. Owing to the intense color of **I** its disappearance can be precisely monitored. Although it is a mixed-valence system with considerable electronic delocalization between both metal centers, the triple bond of free N_2 is also present in the coordinated state as indicated by vibrational spectroscopy. Finally, the splitting of N_2 in the complex can be anticipated to proceed by a simple intramolecular redox reaction which produces only one excess electron that can lead to complications [Eq. (1)].

$$[(NH_3)_5Os^{II}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{5+} \rightarrow 2\,[Os^{VI}(NH_3)_4N]^{3+} + 2\,NH_3 + 1\,e^- \quad (1)$$

The expected photoproduct $[Os(NH_3)_4N]^{3+}$ is also quite stable and well characterized.[7–9] In this context, it should be stressed that the reverse reaction has been observed as photochemical[8,9] and thermal[10,11] process. It is clearly easy to couple two nitride complexes containing the $Os^{VI}\equiv N|$ moiety to give a binuclear N_2 complex owing to the extreme stability of the resulting N≡N triple bond.

The irradiation of **I** (absorption spectrum:[5] $\lambda_{max} = 700$ nm ($\varepsilon = 4000\,M^{-1}cm^{-1}$) and 238 nm ($\varepsilon = 41\,000$) with a shoulder at 260 nm ($\varepsilon = 21\,000$)) results in a bleaching of the green color owing to the disappearance of the 700 nm absorption (Figure 1). Although **I** is not luminescent, the photoproduct shows an orange emission at $\lambda_{max} = 570$ nm (Figure 2) which grows with increasing irradiation time. The emission is attributed to the formation of $[Os^{VI}(NH_3)_4N]^{3+}$ (**II**).[7–9] This assignment is confirmed by the excitation spectrum of the

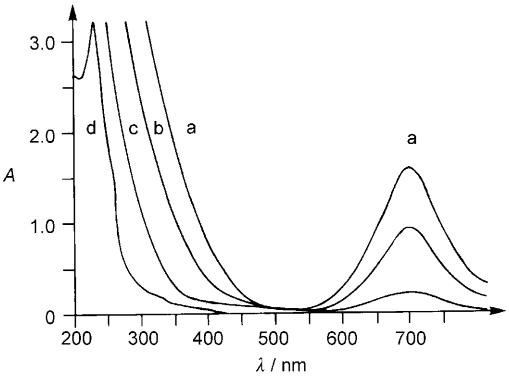


Figure 1. Spectral changes during the photolysis of $[(NH_3)_5Os^{II}(\mu\text{-}N_2)Os^{III}(NH_3)_5](CF_3SO_3)_5$ (4.1×10^{-4} M in 10^{-3} M CF_3SO_3H) under argon at room temperature after irradiation for 0 (a), 30 (b), 60 (c), and 120 min (d) with $\lambda = 250$–390 nm (UV filter Schott UG 11/2) in a 1 cm cell.

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photolyzed solution (Figure 2) which closely resembles the absorption spectrum[7–9,12] ($\lambda_{max} = 236$ nm ($3100\,\text{M}^{-1}\,\text{cm}^{-1}$) with shoulders at 270 nm (1350), 325 nm (75), and 410 nm ($\varepsilon = 25\,\text{M}^{-1}\,\text{cm}^{-1}$)]) and the excitation spectrum of an authentic sample of **II**.

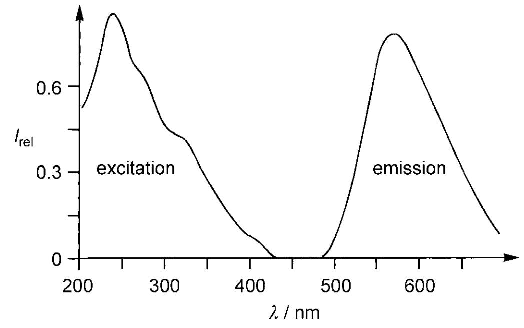

Figure 2. Electronic excitation ($\lambda_{em} = 570$ nm) and emission ($\lambda_{exc} = 380$ nm) spectrum of $[(NH_3)_5Os^{II}(\mu\text{-}N_2)Os^{III}(NH_3)_5](CF_3SO_3)_5$ (4.1×10^{-4} M in 10^{-3} M CF_3SO_3H) under argon at room temperature after 120 min irradiation with $\lambda_{irr} = 250$–390 nm (UV filter Schott UG 11/2), in a 1 cm cell.

The concentration of this complex in the photolyzed solution can be determined by measuring the emission intensity ($\lambda_{exc} = 380$ nm) taking into account the residual absorption of **I** at this wavelength. The photolysis of **I** does not take place upon irradiation of the $\lambda = 700$ nm band but only upon irradiation at shorter wavelengths ($\lambda < 450$ nm). The quantum yield amounts to $\phi = 0.002$ at $\lambda = 254$ nm and 0.003 at 365 nm. Complex **I** is not completely converted into **II**. The molar ratio of **I** to **II** was found to be 1:1.7 ± 10% after complete photolysis. Accordingly, a further Os complex must have been formed. It was assumed to be $[Os^{III}(NH_3)_5(H_2O)]^{3+}$ which cannot be identified in the photolyzed solution by its absorption spectrum because this spectrum consists only of a short-wavelength shoulder at $\lambda_{max} = 220$ nm of moderate intensity ($\varepsilon = 1100$). However, upon addition of iodide, this aqua complex undergoes a facile substitution yielding $[Os^{III}(NH_3)_5I]^{2+}$.[13] This complex shows a long-wavelength (ligand-to-metal charge transfer) LMCT band ($\lambda_{max} = 407$ nm ($\varepsilon = 1970$)). Indeed, this absorption appears in the spectrum of the photolyzed solution when iodide is added. The molar ratio of **I** to $[Os^{III}(NH_3)_5I]^{2+}$ was found to be 3:0.8 ± 10%. Neither **I** nor **II** were observed to react with iodide. Ammonia was detected as a further photoproduct of **I**. It was determined by a spectrophotometric procedure.[14] Any interference by **I** or the constituents of the photolyzed solution could be excluded. The molar ratio of **I** to NH_3 was found to be 1.8 ± 5%. Finally, the photolysis of **I** is not accompanied by the evolution of a gas. In contrast, the irradiation of $[Os^{II}(NH_3)_5(N_2)]^{2+}$ leads to the release of N_2[15] and at higher complex concentrations N_2 appears as gas bubbles even at the beginning of the photolysis.

The long-wavelength absorption of **I** at 700 nm has been assigned to an intervalence transition within the delocalized Os^{II}/Os^{III} system while the UV bands have been attributed to MLCT transitions to the bridging N_2 ligand.[5] These assignments are also reflected by the photoreactivity of **I**. Light absorption by the 700 nm band is not associated with any photoactivity. In contrast, MLCT excitation leads to the oxidation of the metal and reduction of N_2 as anticipated in Equation (1). Of course, MLCT excitation and product formation do not imply the transfer of six electrons to N_2, but only the shift of electron density owing to the covalent nature of the complexes. In contrast to **I**, MLCT excitation of $[Os^{II}(NH_3)_5(N_2)]^{2+}$ does not result in the reduction of N_2 but leads the release of N_2[15] probably because a simple photochemical mechanism yielding stable reduction products of N_2 is apparently not available in this case.

The distribution of the photoproducts of **I** as obtained by analytical measurements suggests that the presence of an excess electron in Equation (1) causes complications. It is reasonable to assume that the primary photochemical step takes place according to Equation (2) because thermal[10,11] and photochemical[8,9] processes corresponding to the reverse reaction have been observed. The release of ammonia [Eq. (2)] occurs as a result of the strong *trans*-effect of nitride.

$$[(NH_3)_5Os^{II}(N_2)Os^{III}(NH_3)_5]^{5+} \rightarrow [Os^{VI}(NH_3)_4N]^{3+} + [Os^{V}(NH_3)_4N]^{2+} + 2\,NH_3 \tag{2}$$

In contrast to $[Os^{VI}(NH_3)_4N]^{3+}$, the complex $[Os^{V}(NH_3)_4N]^{2+}$[16] is not stable and subsequent disproportionations may lead to product formation [Eq. (3) and Eq. (4)].

$$2\,[Os^{V}(NH_3)_4N]^{2+} \rightarrow [Os^{VI}(NH_3)_4N]^{3+} + [Os^{IV}(NH_3)_4N]^{+} \tag{3}$$

$$2\,[Os^{IV}(NH_3)_4N]^{+} + 3\,H^{+} + H_2O \rightarrow [Os^{V}(NH_3)_4N]^{2+} + [Os^{III}(NH_3)_5(H_2O)]^{3+} \tag{4}$$

These reactions or their modifications would result in the overall process given in Equation (5).

$$3\,[(NH_3)_5Os^{II}(N_2)Os^{III}(NH_3)_5]^{5+} + 3\,H^{+} + H_2O \rightarrow 5\,[Os^{VI}(NH_3)_4N]^{3+} + [Os^{III}(NH_3)_5(H_2O)]^{3+} + 6\,NH_3 \tag{5}$$

The analytical results roughly agree with this equation.

In general, $Os^{V}{\equiv}N$ complexes are not stable[7–9,16] because Os^{V} is strongly oxidizing and reducing.[17] In the absence of a suitable redox partner, Os^{V} undergoes disproportionation to Os^{VI} and Os^{IV} [see Eq. (3)]. Accordingly, it should be possible for other redox agents, such as oxygen, to intercept Os^{V}. Indeed, O_2 is apparently able to oxidize $[Os^{V}(NH_3)_4N]^{2+}$ to $[Os^{VI}(NH_3)_4N]^{3+}$ and take up the excess electron [see Eq. (1)]. In agreement with this assumption the photolysis of **I** in the presence of oxygen yields more $[Os^{VI}(NH_3)_4N]^{3+}$ and less $[Os^{III}(NH_3)_5(H_2O)]^{3+}$ than when performed under argon. The amount of $[Os^{VI}(NH_3)_4N]^{3+}$ increased by 13% when **I** (4×10^{-4} M) was photolyzed in the presence of oxygen. This result is close to a complete conversion (17%).

In the context of these observations the question arises what happens when $[(NH_3)_5Os^{III}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{6+}$[18] is irradiated. Does the photolysis take place according to the simple Equation (6)?

$$[(NH_3)_5Os^{III}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{6+} \rightarrow 2\,[Os^{VI}(NH_3)_4N]^{3+} + 2\,NH_3 \tag{6}$$

Unfortunately, $[(NH_3)_5Os^{III}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{6+}$ is rather labile and undergoes a facile decomposition in aqueous solution even at 5 °C.[5,18] Accordingly, a detailed study is very difficult to perform, but a qualitative experiment is quite revealing. In contrast to the photolysis of $[(NH_3)_5Os^{II}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{5+}$ (**I**), the irradiation of an aqueous solution of $[(NH_3)_5Os^{III}(\mu\text{-}N_2)Os^{III}(NH_3)_5]^{6+}$ is accompanied by the vigorous evolution of nitrogen, a process which also occurs place thermally but at much lower rate. The photochemical behavior of the 6+ ion can be explained by its excited-state properties. It is well established that MLCT transitions of Os^{III} complexes occur at much higher energies than those of Os^{II}.[19] A reactive ($Os \rightarrow N_2$) MLCT state of the 6+ ion is apparently not accessible by conventional light sources (wavelength > 230 nm). As an alternative or additional effect, ligand-field (LF) states of the 6+ ion are now populated which can initiate the release of N_2.

While the photoactivation of dinitrogen in **I** in an aqueous solution leading to the reductive cleavage of N_2 has been achieved it is of considerable importance to discover if the nitride ligand of the photoproduct can be utilized for the formation of useful nitrogen compounds.[4] It is well established that $Os^{VI}{\equiv}N$ complexes can undergo nitrogen-atom transfer reactions or reduction to Os^{II} or Os^{III} complexes.[17,20,21] In the latter case protonation of the nitride ligand yields NH_3. In this sense our observations can be directly related to the Haber–Bosch process which takes not in solution but at a solid surface. In this context it is of interest that Schrauzer[22] and Kisch and co-workers[23] observed the photoreduction of N_2 at TiO_2.

In summary, the photolysis of aqueous $[(NH_3)_5Os^{II}(N_2)Os^{III}(NH_3)_5]^{5+}$ induced by MLCT excitation leads to the reductive splitting of the bridging N_2 ligand yielding the nitride complex $[Os^{VI}(NH_3)_4N]^{3+}$ as the main photoredox product. It should be emphasized that the electronic charge-transfer excitation does not only provide a suitable intramolecular redox reaction but may also supply the necessary energy for activation and cleavage of the very stable N_2 molecule.

Experimental Section

The compounds $[(NH_3)_5Os^{II}(N_2)Os^{III}(NH_3)_5](CF_3SO_3)_5$ [5,6] and $[Os^{VI}(NH_3)_4N](CF_3SO_3)_3$ [7–9] were prepared according to published procedures. The photolyses were performed in aqueous solutions saturated by argon. Light sources were a low-pressure mercury lamp (Hanau, 6 W) and a high pressure mercury lamp (Osram HBO 200 W/2). The detection of ammonium was achieved by a commercially available quantitative test from Merck.[14]

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[1] S. Gambarotta, J. Scott, *Angew. Chem.* **2004**, *116*, 5412–5422; *Angew. Chem. Int. Ed.* **2004**, *43*, 5298–5308.
[2] M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200–202*, 379–409.
[3] E. Solari, C. Da Silva, B. Iacono, J. Hesschenbrouck, C. Rizzoli, R. Scopelliti, C. Floriani, *Angew. Chem.* **2001**, *113*, 4025–4027; *Angew. Chem. Int. Ed.* **2001**, *40*, 3907–3909.
[4] J. J. Curley, T. R. Cook, S. Y. Reece, P. Müller, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9394–9405.
[5] D. E. Richardson, J. P. Sen, J. D. Buhr, H. Taube, *Inorg. Chem.* **1982**, *21*, 3136–3140.
[6] P. A. Lay, R. H. Magnuson, J. Sen, H. Taube, *J. Am. Chem. Soc.* **1982**, *104*, 7658–7659.
[7] C.-M. Che, T.-C. Lau, H.-W. Lam, C.-K. Poon, *J. Chem. Soc. Chem. Commun.* **1989**, 114–116.
[8] C.-M. Che, H.-W. Lam, W.-F. Tong, T.-F. Lai, T.-C. Lau, *J. Chem. Soc. Chem. Commun.* **1989**, 1883–1884.
[9] H.-W. Lam, C.-M. Che, K.-Y. Wong, *J. Chem. Soc. Dalton Trans.* **1992**, 1411–1416.
[10] J. T. Buhr, H. Taube, *Inorg. Chem.* **1979**, *18*, 2208–2212.
[11] D. C. Ware, H. Taube, *Inorg. Chem.* **1991**, *30*, 4605–4610.
[12] J. T. Buhr, J. R. Winkler, H. Taube, *Inorg. Chem.* **1980**, *19*, 2416–2425.
[13] P. A. Lay, R. H. Magnuson, H. Taube, *Inorg. Chem.* **1989**, *28*, 3001–3007.
[14] Spectroquant Ammonium Cell Test, Merck KGaA, Germany.
[15] T. Matsubara, M. Bergkamp, P. C. Ford, *Inorg. Chem.* **1978**, *17*, 1604–1607.
[16] C.-M. Che, V. W.-W. Yam, *Adv. Inorg. Chem.* **1992**, *39*, 233–325.
[17] D. W. Pipes, M. Bakir, S. E. Vitols, D. J. Hodgson, T. J. Meyer, *J. Am. Chem. Soc.* **1990**, *112*, 5507–5514.
[18] P. A. Lay, R. H. Magnuson, H. Taube, *J. Am. Chem. Soc.* **1985**, *107*, 2551–2552.
[19] P. A. Lay, R. H. Magnuson, H. Taube, *Inorg. Chem.* **1988**, *27*, 2848–2853.
[20] M. Bakir, P. S. White, A. Dovletoglou, T. J. Meyer, *Inorg. Chem.* **1991**, *30*, 2835–2836.
[21] D. C. Ware, H. Taube, *Inorg. Chem.* **1991**, *30*, 4598–4605.
[22] G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.* **1977**, *99*, 7189–7193.
[23] H. Kisch, O. Linnik, *Mendeleev Commun.* **2008**, *18*, 10–11.