

Metal-Nitrido Photo-oxidants: Synthesis, Photophysics, and Photochemistry of $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})](\text{X})_3$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3$)

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$[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})](\text{X})_3$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3$) which is strongly emissive both in solid state and in fluid solutions at room temperature ($\tau_0 \sim 1.5 \mu\text{s}$ in MeCN) is readily synthesised by Ce^{IV} oxidation of $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in water; the $(d_{xy})^1 (d_{\pi}^*)^1$ ($d_{\pi}^* = d_{xz}, d_{yz}$) excited state of *trans* $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})]^{3+}$ is a powerful one-electron oxidant $\{[\text{Os}^{\text{V}}\equiv\text{N}]^{3+} + e^- \rightarrow [\text{Os}^{\text{V}}\equiv\text{N}]^{2+}, E_f^0 \sim 2.1 \text{ V vs. normal hydrogen electrode}\}$ in aqueous solution, reacting with organic substrates through an electron-transfer pathway.

The design of strongly luminescent transition metal complexes with high excited state redox potentials for uses in photo-induced multi-electron transfer processes has recently been the subject of extensive studies.¹ The co-ordination complexes of the third row transition metals, such as platinum, osmium, and iridium are of particular interest because these heavy metal ions usually possess long-lived spin-forbidden excited states. Our interest in this area concerns the development of the photochemistry of d^2 Os^{VI} complexes with the metal ion multiply-bonded to other heteroatoms. *e.g.* sulphur, oxygen, or nitrogen.² These osmium complexes, if suitably designed, are believed to be versatile reagents for photo-induced multi-electron atom transfer reactions. We have demonstrated that *trans* dioxo-osmium (vi) complexes are capable of performing photo-induced oxygen atom transfer reactions.^{2c} Herein are described $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})](\text{X})_3$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3$) complexes[†] which are prototypes of the $\text{Os}^{\text{V}}\equiv\text{N}$ system, with

high energy and long-lived excited states in fluid solutions at room temperature.

Oxidation of $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with excess of $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ in water at room temperature gave $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})\text{Cl}]^{2+}$,³ which precipitated as a bright yellow chloride salt upon addition of 6 M HCl. Stirring *trans*- $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})\text{Cl}]\text{Cl}_2$ (**1**) in neat $\text{CF}_3\text{SO}_3\text{H}$ followed by addition of diethyl ether led to the formation of light yellow *trans*- $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})](\text{CF}_3\text{SO}_3)_3$ (**2**). Complexes (**1**) and (**2**) are air stable solids with correct elemental analyses. As expected for the d^2 - Os^{VI} system with the $(d_{xy})^2$ ground state electronic configuration,[‡] they are diamagnetic ($\mu_{\text{eff}} \sim 0 \mu_{\text{B}}$) at room temp. Their i.r. spectra show intense $\nu(\text{Os}\equiv\text{N})$ stretches at $\sim 1090 \text{ cm}^{-1}$.^{3,5} They behave as 1:3 electrolytes in water in accordance with the expected strong σ -*trans* effect of nitrido group, which should labilize the co-ordinated chloride or trifluoromethanesulphonate. Both (**1**) and (**2**) exhibit irreversible electrochem-

[†] The $[\text{Os}^{\text{VI}}(\text{NH}_3)_4(\text{N})]^{3+}$ ion had previously been reported by Taube and co-workers in their earlier work (ref. 3). However, no pure sample, with satisfactory elemental analyses, was obtained by these workers.

[‡] The energy of d-orbitals of $\text{Os}^{\text{VI}}\equiv\text{N}$ complexes assuming a C_{4v} symmetry are in the order, $b_2(d_{xy}) < e(d_{xz}, d_{yz}) \sim b_1(d_{x^2-y^2}) - y_2 < a_1(d_{z^2})$ (ref. 4).

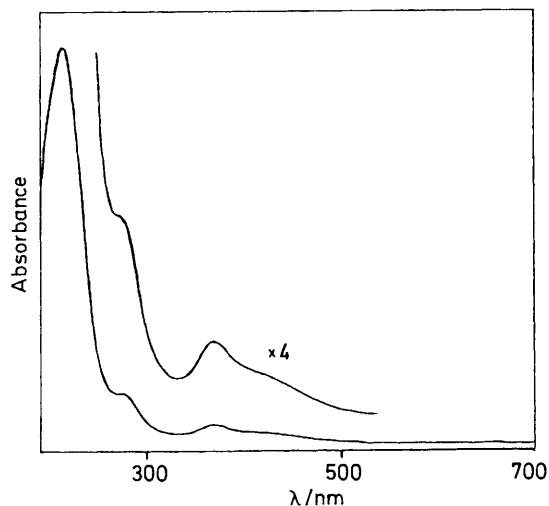


Figure 1. U.v.-visible absorption spectrum of *trans* [Os^{VI}(NH₃)₄(N)] [CF₃SO₃]₃ (**2**) in MeCN.

Table 1. Photophysical data for *trans* [Os^{VI}(NH₃)₄(N)] [CF₃SO₃]₃ (**2**).^a

	Emission ^b λ _{max} /nm.	Lifetime/μs ^c
Solid	610	1.4
MeCN	545	1.5
MeOH	520	0.6
H ₂ O	520	0.1
D ₂ O	520	0.4

^a The quantum yield of the phosphorescence was ~0.14 in MeCN; standard, quinine sulphate. ^b The emission spectrum was recorded on a Hitachi 650-60 spectrophotometer. ^c Lifetime measurements were performed with a Nd : YAG DCR 3 pulsed laser; excitation, 355 nm. Concentration of the osmium complex, 1.3 × 10⁻³ mol dm⁻³.

istry. Complex (**2**) is irreversibly reduced at a potential (E_{pc}) of -0.31 V vs. normal hydrogen electrode (NHE) in 0.1 M CF₃SO₃H {-1.0 V vs. AgNO₃ (0.1 M)/Ag in 0.1 M [Et₄N][BF₄ acetonitrile solution}. The u.v.-visible spectrum of (**2**) in acetonitrile (Figure 1) is dominated by some intense high energy bands ($\epsilon_{max.} > 10^3$ mol⁻¹ dm³ cm⁻¹) in the 200–300 nm region, possibly due to p_{π} (N³⁻) → d_{π}^* ($d_{\pi}^* = d_{xz}, d_{yz}$) charge-transfer transition.[‡] There are also weak electronic transitions at 370 and 410 nm(sh). With reference to previous spectroscopic work,⁴ the 410 nm shoulder ($\epsilon_{max.} < 10^2$ mol⁻¹ dm³ cm⁻¹) which tails down to 500 nm is assigned to the spin-orbit component of the (d_{xy})² → (d_{xy})¹ (d_{π}^*)¹ transition, which is likely to be due to ¹A₁ → E(³E).⁴

Excitation of (**1**) or (**2**) at 300–350 nm results in an intense orange emission; photophysical data are summarized in Table 1. Unlike the [Os(N)X₄]⁻ (X = Cl, Br) complexes which emit only in the solid state,⁶ emission from fluid solutions of (**1**) or (**2**) is observed at room temperature (Figure 2). The large difference in excitation and emission energies suggests that the emissive state is the (d_{xy})¹ (d_{π}^*)¹ triplet, likely to be the E(³E) spin-orbit component. This is in accordance with Gray's spectroscopic work⁶ on [Os(N)X₄]⁻ and the measured lifetimes of 1.4–1.5 μs (Table 1), which indicate that the transition involved is a spin-forbidden process. The emission lifetime decreases from MeCN to MeOH and water and is quenched by H⁺. The large kinetic

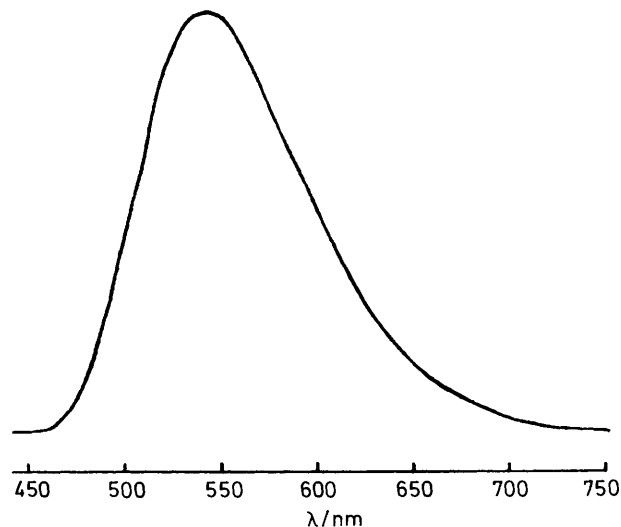


Figure 2. Emission spectrum of *trans* [Os^{VI}(NH₃)₄(N)] [CF₃SO₃]₃ (**2**) in a degassed MeCN solution. Excitation, 320 nm.

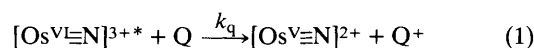
Table 2. Rate constants for the quenching of *trans* [Os^{VI}(NH₃)₄(N)] [CF₃SO₃]₃ (**2**) (1.4 × 10⁻³ M) in degassed acetonitrile solution at 25 °C.

Quencher (Q)	E ₄ (Q ^{+/Q})/V vs. SCE ^c	k _q ^a /mol ⁻¹ dm ³ s ⁻¹
<i>α-trans</i> -methylstyrene	1.94 ^b	1.5 × 10 ⁶
1,2-dimethoxybenzene	1.45 ^c	2.8 × 10 ⁷
1,4-dimethoxybenzene	1.34 ^c	5.6 × 10 ⁷
<i>N</i> -methylaniline	1.03 ^d	1.2 × 10 ⁹
Triphenylamine	0.86 ^c	1.5 × 10 ⁹
Diphenylamine	0.83 ^c	2.1 × 10 ⁹
Phenothiazine	0.53 ^c	8.3 × 10 ⁹
<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine	0.10 ^c	6.3 × 10 ⁹

^a The second-order quenching rate constants were obtained by lifetime-quenching methods. ^b T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, 1988, **110**, 1953. ^c C. K. Mann and K. K. Barnes, in 'Electrochemical Reaction in Non-aqueous Systems,' Marcel Dekker, New York, 1970. ^d T. Hino, H. Akazawa, H. Masuhara, and N. Mataga, *J. Phys. Chem.*, 1976, **80**, 33. ^e Standard Calomel Electrode.

isotope effect (k_H/k_D) of 4 for the lifetime in water suggests that interaction of the Os≡N moiety with the OH group of the solvent may provide an efficient relaxation pathway for these excited osmium complexes. From the electrochemical results [E_{pc} for Os^{VI}: H₂O, >-0.31 V vs. NHE; MeCN, >-1.0 V vs. AgNO₃ (0.1 M/Ag)] and the estimated E_{0-0} emission (~2.4 eV) of the [Os^{VI}(NH₃)₄(N)]Cl₃ solid at 77 K, the (d_{xy})¹ (d_{π}^*)¹ triplet of Os^{VI}≡N is an extremely powerful one-electron oxidant; the reduction potential of [Os^{VI}≡N]^{3+*} is likely to be >2.0 V vs. NHE in H₂O [1.4 V vs. AgNO₃ (0.1 M)/Ag in MeCN].

The emission can be quenched by organic substrates (Q) including aromatic amines, arenes, and alkenes; steady-state quenching results for (**2**) by lifetime measurements are in Table 2. No ground-state reaction between the substrates and (**2**) is observed in acetonitrile. Since the k_q values increase monotonically with decreasing oxidation potentials of Q, the quenching processes electron-transfers as illustrated in equation (1)



Flash-photolysis of (2) with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (tmpd) in degassed acetonitrile yields a transient [tmpd]⁺ signal ($\lambda_{\text{max}} \sim 600 \text{ nm}$).⁷

The present work demonstrates that highly oxidizing osmium nitrido complexes with long lifetimes in fluid solutions can easily be generated through light excitation. This opens up a new area for the oxidation chemistry of metal-nitrido complexes. Since promotion of an electron to the antibonding d_{π}^* levels should weaken the Os \equiv N bond,⁶ the $(d_{xy})^1 (d_{\pi}^*)^1$ excited triplet of the present Os^{VI} \equiv N system, which is long-lived in fluid solutions, has the potential of performing nitrogen atom transfer reactions.⁸

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References

- 1 See, for example; D. G. Nocera, A. W. Maverick, J. R. Winkler, C. M. Che, and H. B. Gray, *A. C. S. Symp. Series*, 1983, **211**, 21.
- 2 (a) C. M. Che and W. K. Cheng, *J. Am. Chem. Soc.*, 1986, **108**, 4644; (b) C. M. Che, V. W. W. Yam, K. C. Cho, and H. B. Gray, *J. Chem. Soc., Chem. Commun.*, 1987, 948; (c) V. W. W. Yam, C. M. Che, and W. T. Tang, *ibid.*, 1988, 100.
- 3 See also, J. D. Buhr, J. R. Winkler, and H. Taube, *Inorg. Chem.*, 1980, **19**, 2416.
- 4 C. D. Cowman, W. C. Trogler, K. R. Mann, C. K. Poon, and H. B. Gray, *Inorg. Chem.*, 1976, **15**, 1747.
- 5 See also, M. J. Wright, and W. P. Griffith, *Transition Met. Chem.*, 1982, **7**, 53.
- 6 M. D. Hopkins, V. M. Miskowski, and H. B. Gray, *J. Am. Chem. Soc.*, 1986, **108**, 6908.
- 7 G. T. Pott and J. Kammanedeur, *J. Chem. Phys.*, 1969, **47**, 395; A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, 1955, **77**, 4454.
- 8 See also, J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **105**, 2073; J-P. Mahy, P. Battioni, and D. Mansuy, *ibid.*, 1986, **108**, 1079.