Metal Nitrido and Imido Photo-oxidants. Photophysics and Photochemistry of Nitrido and Imido Complexes of Osmium(VI) and *X*-Ray Crystal Structure of $[Ph_4As]_2[Os^{VI}(CN)_5N]$

Chi-Ming Che,[a] Michael Hon-Wah Lam,[a] and Thomas C. W. Mak[b]

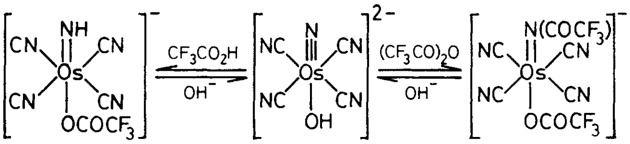
[a] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Terroritories, Hong Kong*

Nitrido- and imido-osmium(VI) complexes with cyanides as ligands have been synthesised and found to display intense photoluminescence in fluid solutions at room temperature; the *X*-ray structure of $[Ph_4As]_2[Os^{VI}(CN)_5N]$ has been determined with a measured Os≡N distance of 1.647(7) Å.

The design of metal photo-oxidants is an important area in photochemistry. We and Gray and co-workers[1—4] have found that d^2-metal complexes with the metal atom multiply bonded to a heteroatom, such as oxygen and nitrogen, usually have long-lived and high energy $(d_{xy})^1(d_{\pi*})^1$ ($d_{\pi*} = d_{xz}, d_{yz}$) excited states, suggesting that these classes of compounds may find important applications as photo-catalysts or in photo-induced atom transfer processes. Our recent studies have demonstrated the rich photochemistry of *trans*-$[Os^{VI}(TMC)(O)_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)[1] and $[Os^{VI}(NH_3)_4(N)]^{3+}$,[2] which are powerful photo-oxidants. Here we describe results which illustrate that the nitrido and imido complexes of tetracyano-osmium(VI) also possess novel photophysical and photochemical properties.

Treatment of $[Ph_4As][Os^{VI}(N)Cl_4]$ with a slight excess of NaCN in tetrahydrofuran/methanol gave *trans*-$[Os^{VI}(N)(CN)_4(OH)]^{2-}$, isolated as a yellow crystalline solid. In accordance with its formulation, $[Ph_4As]_2[Os^{VI}(N)(CN)_4(OH)]$ (**1**)† is diamagnetic ($\mu_{aff} = 0$) and is a 2 : 1 electrolyte in acetonitrile (Λ_M = 284 ohm^{-1} cm^2 mol^{-1}). The i.r. spectrum of (**1**) shows a broad $\nu_{(O-H)}$ at 3300 cm^{-1}, a sharp $\nu_{(C\equiv N)}$ at 2148 cm^{-1}, and an intense $\nu_{(Os\equiv N)}$ at 1050 cm^{-1}. Recrystallisation of (**1**) in methanol and in the presence of NaCN afforded $[Ph_4As]_2[Os^{VI}(CN)_5N]$ (**2**). The i.r. spectrum of (**2**) is very similar to that of (**1**) with $\nu_{(Os\equiv N)}$ at 1050 cm^{-1}. The structure of (**2**) has been determined by *X*-ray crystallography.‡ Figure 1 shows the ORTEP plot of the $[Os^{VI}(CN)_5N]^{2-}$ ion showing atom numbering. The co-ordination geometry about the osmium is distorted octahedral with the osmium atom displaced above the mean plane defined by the C(49), C(50), C(51), and C(52) atoms [the measured C(49)–Os(1)–C(51) and C(50)–Os(1)–C(52) angles are 168.5(3) and 162.2° respectively.]. The measured Os≡N distance of 1.647(7) Å is characteristic of osmium(VI) nitrido complexes.[5] The Os(1)–C(53) distance of 2.353(8) Å is at least 0.35 Å longer than the others, indicating the strong *trans*-effect of the nitrido group.

The optical spectra of (**1**) and (**2**) (Figure 2) in acetonitrile are virtually identical, showing an intense band at 294 nm, which tails down to 400 nm. Excitation of (**1**) or (**2**) at 300—400 nm leads to an intense phosphoresence at 550 nm (Figure 3, quantum yield is 0.10 for [(**1**)] = 10^{-4} M). With reference to previous works,[2,4] the emitting state is assigned to be $E_g[^3E_g]$, the spin–orbit substate of ^3Eg $\{[(d_{xy})^1(d_{\pi*})^1]\}$. Importantly, the measured lifetime (τ) of the emission



Scheme 1

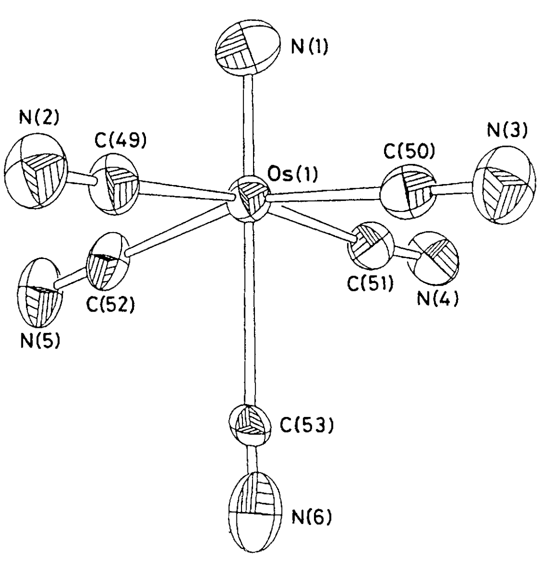


Figure 1. ORTEP plot of the $[Os(CN)_5N]^-$ ion showing atom numbering. Os(1)–N(1) 1.647(7), Os(1)–C(49) 2.086(8), Os(1)–C(50) 2.093(8), Os(1)–C(51) 2.067(8), Os(1)–C(52) 2.081(8), Os(1)–C(53) 2.353(8), C(49)–N(2) 1.131(10), C(50)–N(3) 1.142(11), C(51)–N(4) 1.156(10), C(52)–N(5) 1.105(10), C(53)–N(6) 0.868(13) Å. N(1)–Os(1)–C(49) 97.9(3), N(1)–Os(1)–C(50) 99.4(3), C(49)–Os(1)–C(50) 86.3, N(1)–Os(1)–C(51) 93.3(3), C(49)–Os(1)–C(51) 168.5(3), C(50)–Os(1)–C(51) 89.6(3), C(50)–Os(1)–C(52) 162.2(3), N(1)–Os(1)–C(53) 178.0(3), C(49)–Os(1)–C(53) 83.6(3), C(51)–Os(1)–C(53) 85.3(3)°.

---

† Satisfactory elemental analyses have been obtained for complexes (**1**) and (**3**).

‡ *Crystal data*: $(Ph_4As)_2[Os(CN)_5(N)]$, $C_{53}H_{40}N_6As_2Os$, M = 1100.98, monoclinic, space group $P2_1/n$, a = 9.034(3), b = 21.635(6), c = 24.127(4) Å, β = 97.79(2)°, U = 4672(2) Å^3, Z = 4, D_c = 1.565 g cm^{-3}, μ(Mo-K_α) = 41.8 cm^{-1}, F(000) = 2168. Intensities were measured at 20 °C on a Nicolet R3m/V diffractometer with graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å), ω-scan mode (3° ≤ 2θ ≤ 50°, scan rate 2.02—8.37 deg min^{-1}) using a crystal of dimensions 0.42 × 0.40 × 0.32 mm. Empirical absorption corrections (transmission factors 0.163—0.254) were applied, and of the 8310 unique reflections measured, 5428 observed data with $I > 3\sigma(I)$ were used in structure analysis. All non-hydrogen atoms were refined anisotropically, and the phenyl H atoms were allowed to ride on their respective parent C atoms with assigned isotropic temperature factors. The weighting function $w = [\sigma^2(F_0) + 0.0005|F_0|^2]^{-1}$ was used in full-matrix least-squares cycles, leading to R = 0.040, R_w^2 = 0.044, and S = 1.221 for 559 variables. Computations were performed with the SHELXTL-PLUS package on a DEC MicroVAX-II system. 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.

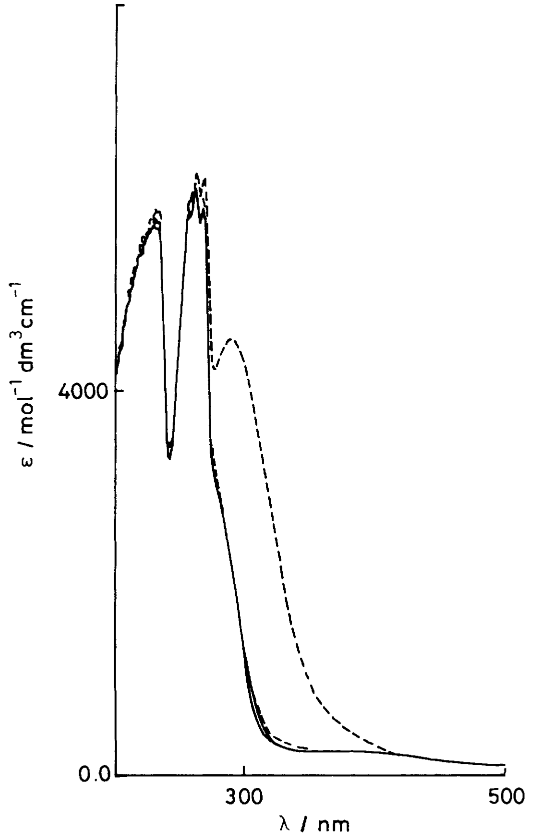


Figure 2. U.v.–vis. spectra of (**1**) (– – –) and (**4**) (——) in acetonitrile.

strongly depends on the concentration of the osmium complex. A linear Stern–Volmer plot between $1/\tau$ and [Os] has been obtained giving the self-quenching rate-constant (k_q) and τ_0 (lifetime at infinite dilution) to be 1.49×10^8 mol^{-1} dm^3 s^{-1} and 2.49 μs respectively. We tentatively assign the self-quenching to be as shown in equation (1). Such a postulation is not unreasonable, given the findings by Taube and coworkers,[6] who suggested that two Os≡N moieties may undergo coupling to give the Os–N≡N–Os complex under appropriate reaction conditions. Flash-photophysics experiments (excitation at 355 nm with a DCR-3 Nd-YAG laser) provide support for the proposed quenching mechanism. A long-lived transient signal showing an absorption peak at 460 nm (Figure 4) and which decays back to the starting Os^{VI} species has been recorded 20 μs after flashing a degassed acetonitrile solution of (**1**). Complex (**1**) proves to be a powerful oxidant. It undergoes reductive quenching [$Os^{VI*} + Q \rightarrow Os^{V} + Q^{+}$] with 1,4-dimethoxybenzene and triphenylamine to give quenching rate constants of 3.5×10^7 and 1.46×10^9 mol^{-1} dm^3 s^{-1} respectively.

$$[Os^{VI}{\equiv}N]^* + [N{\equiv}Os^{VI}] \rightarrow [Os{\equiv}N\cdots N{\equiv}Os] \rightarrow 2[Os^{V}{\equiv}N] \quad (1)$$

Addition of trifluoroacetic anhydride (TFAA) or trifluoroacetic acid to an acetonitrile solution of (**1**) or (**2**) results in the formation of a new osmium complex; the spectral trace of this reaction is shown in Figure 2. More importantly, this new species can be converted back to the starting Os^{VI} quantitatively upon addition of [Bu_4N]OH. Scheme 1 shows the proposed scheme for the reaction.

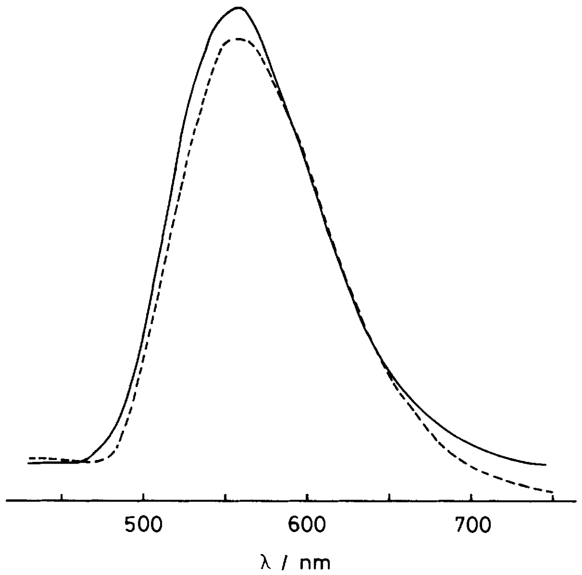


Figure 3. Emission spectra of (**1**) (– – –) and (**4**) (——) in acetonitrile at 25 °C. Excitation, 300—350 nm.

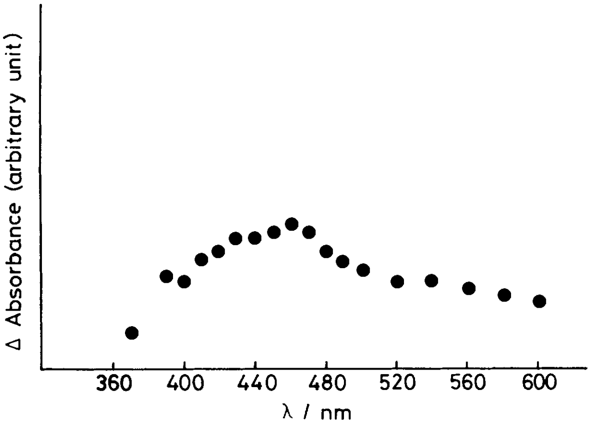


Figure 4. Transient absorption difference spectrum recorded 20 s after flashing a degassed acetonitrile solution of (**1**).

The [Ph_4As][$Os^{VI}(N\text{-}COCF_3)(CN)_4(CF_3CO_2)$] complex (**3**)† has been isolated by precipitation with diethyl ether. The i.r. spectrum of (**3**) shows two strong peaks at 1782 and 1736 cm^{-1} which can be assigned to the imidotrifluoroacetate and trifluoroacetate groups respectively.[7] The [$Os^{VI}(CN)_4(CF_3COO)(NH)$]$^-$ ion (**4**) is characterised by ^{1}H n.m.r. spectroscopy with (Os=NH) occurring at δ 2.46. As expected, the original $\nu_{(Os\equiv N)}$ at 1050 cm^{-1} disappears on the addition of TFAA or H$^+$ but the absorption peak attributed to $\nu_{(C\equiv N)}$ still occurs at 2146 cm^{-1}.

A feature of the osmium imido complexes is their photoluminescence behaviour. The emission spectra of (**3**) and (**4**) are virtually identical (excitation, 300—400 nm; λ_{max} at 554 nm, Figure 3) and are similar to those of (**1**) and (**2**). However, the lifetimes of their emissions at room temperature are very long (τ is 30 μs, [(**4**)] = 7.1×10^{-4} M], which is at least 15 times longer than that for (**1**) or (**2**). More importantly, the lifetime for (**3**) or (**4**) shows only a small dependence on the concentration of the osmium complex, with a self-quenching rate constant of 4.8×10^6 mol^{-1} dm^3 s^{-1} for (**4**) in acetonitrile. This is not unreasonable since co-ordination of CF_3CO or H^+ to the Os≡N moiety is likely to inhibit the coupling reaction. Preliminary studies showed that the emission of (**4**) is quenched by a variety of alkenes such as styrene and cyclo-octene, indicating the possibility of performing photo-induced nitrogen atom transfer reactions with this complex.

We acknowledge support from the University of Hong Kong and the Croucher Foundation. M. H. W. L. is the recipient of a Croucher Studentship administered by the Croucher Foundation.

Received, 12th April 1989; Com. 9/01486A

References

1 C. M. Che and W. K. Cheng, *J. Am. Chem. Soc.*, 1986, **108**, 4644; C. M. Che, V. W. W. Yam, K. C. Cho, and H. B. Gray, *J. Chem. Soc., Chem. Commun.*, 1987, 948; V. W. W. Yam, C. M. Che, and W. T. Tang, *ibid.*, 1988, 100; V. W. W. Yam and C. M. Che, *New J. Chem.*, in the press.

2 C. M. Che, H. W. Lam, T. C. Lau, and C. K. Poon, *J. Chem. Soc., Chem. Commun.*, 1989, 146.

3 J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 1373; *Inorg. Chem.*, 1985, **24**, 346.

4 M. D. Hopkins, V. W. Miskowski, and H. B. Gray, *J. Am. Chem. Soc.*, 1986, **108**, 6908.

5 D. Collison, C. D. Garner, F. E. Mabbs, and J. A. Salthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 1812; N. Zhang, S. C. Wilson, and P. A. Shapley, *J. Am. Chem. Soc.*, 1984, **106**, 7493.

6 J. D. Buhr and H. Taube, *Inorg. Chem.*, 1979, **18**, 2208.

7 See also related work on nitrido manganese(V) porphyrin complex, J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **105**, 2073.