Synthesis, characterization and photophysical properties of $[OsO_2(mes)_2(NC)Ru(bpy)_2(CN)]$

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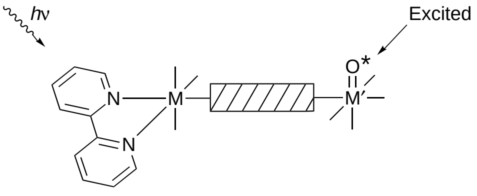
A novel heterometallic complex comprising of a d^2 $OsO_2(mes)_2$ and a d^6 $Ru(bpy)_2(CN)_2$ fragment is prepared and characterized by X-ray analysis; its photophysical properties are measured.

The design of new heterometallic complexes for photoinduced atom transfer reactions has received current interest. One of our approaches is to link a low-valent metal–polypyridine to a high-valent metal–oxo fragment *via* self-assembly reactions.[1] The former would serve as a good light absorber while the latter functions as an oxygen atom transfer agent.



In this context, the cyanide ion, which is known to form stable complexes with metal ions in both high and low oxidation states would be a good bridging ligand.[2] Described herein are the structure and photophysical properties of the first heteronuclear $Ru^{II}Os^{VI}$ $[OsO_2(mes)_2(NC)Ru(bpy)_2(CN)]$ **1** formed by reaction of $[OsO_2(mes)_2]$ (mes = mesityl)[3] with $[Ru(bpy)_2(CN)_2]$ (bpy = 2,2′-bipyridine).[2]

Upon slow evaporation of a solution of $[OsO_2(mes)_2]$ and $[Ru(bpy)_2(CN)_2]$ in dichloromethane–methanol at 0 °C, brown needle crystals† of **1** were obtained (yield 95%) and the structure was characterized by X-ray analysis.‡ Fig. 1 shows a perspective view of the molecule. The osmium atom adopts a distorted square-pyramidal geometry with an average Os–O distance of 1.700 Å and O–Os–O angle of 144.9(2)°. These are comparable to values of 1.720 Å and 147.5(3)° in the related complex $[\{OsO_2(mes)_2\}_2(pyz)]$[4] which has a square-pyramidal geometry at the Os atom. Although the measured N–C–Ru angle of 177.7(4)° is close to 180°, the Os–N–C angle of 160.5(4)° reveals that the Ru–C≡N–Os array is not quite linear. The N–C and Ru–C distances for the bridging cyanide are both 0.04 Å shorter than that of the terminal cyanide. The IR data are in accord with the X-ray structure with ν(C≡N) stretches at 2088.5 and 2072.8 cm^{-1}, at higher frequencies relative to $[Ru(bpy)_2(CN)_2]$ [ν(C≡N) 2067.4, 2052.9 cm^{-1}]. The ν(Os=O) stretches are at 893.1 and 884.6 cm^{-1}, which are comparable to the related value of 900 cm^{-1} for $[\{OsO_2(mes)_2\}_2(\mu\text{-pyz})]$.

Complex **1** is soluble in common organic solvents such as dichloromethane and methanol. Similarly to the reported $[OsO_2(mes)_2L]$ complexes (L = 1,10-phenanthroline or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine),[5] the equilibrium reaction [eqn. (1)] exists in solution and dissociation is suppressed by addition of an excess of $[OsO_2(mes)_2]$.

$$[OsO_2(mes)_2(NC)Ru(bpy)_2(CN)] \rightleftharpoons [OsO_2(mes)_2] + [Ru(bpy)_2(CN)_2] \quad (1)$$

Fig. 2 shows the absorption spectra of solutions of $[Ru(bpy)_2(CN)_2]$ in the presence of various concentrations of $[OsO_2(mes)_2]$. The MLCT band of $[Ru(bpy)_2(CN)_2]$ shifts to a higher energy (461 to 436 nm) upon addition of $[OsO_2(mes)_2]$ (0 to 10-fold excess). A similar experiment with $[Ru(bpy)_3]Cl_2$ has also been done but its MLCT band does not change even in the presence of tenfold excess of $[OsO_2(mes)_2]$. Thus the progressive blue shift is evidence for the formation of the dimeric species **1** in solution.[6]

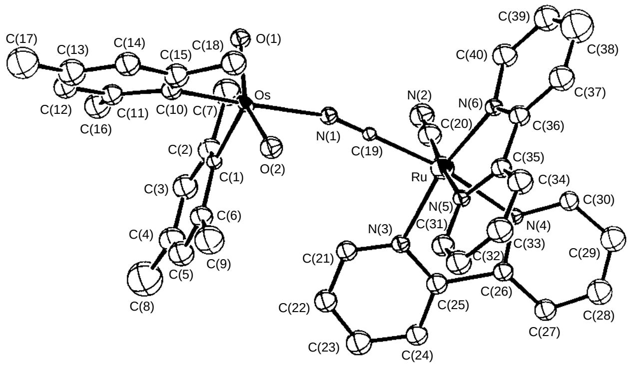


Fig. 1 A perspective view of **1** (thermal ellipsoids at 40% probability level). Selected bond lengths (Å) and angles (°): Os–O(1) 1.704(3), Os–O(2) 1.696(3), Os–N(1) 2.235(4), Os–C(1) 2.063(5), Os–C(10) 2.108(4), Ru–N(3) 2.064(4), Ru–N(4) 2.113(4), Ru–C(19) 1.972(4), Ru–C(20), 1.992(4), N(1)–C(19) 1.143(6), N(2)–C(20) 1.145(6); O(1)–Os–O(2) 144.9(2), O(1)–Os–N(1) 88.5(1), O(1)–Os–C(1) 110.4(2), O(1)–Os–C(10) 91.5(2), N(1)–Os–C(1) 87.1(2), N(1)–Os–C(10) 173.4(2), C(1)–Os(1)–C(10) 99.1(2), C(19)–Ru–C(20) 89.5(2), Os–N(1)–C(19) 160.5(4), Ru–C(19)–N(1) 177.7(4), Ru–C(20)–N(2) 178.6(4).

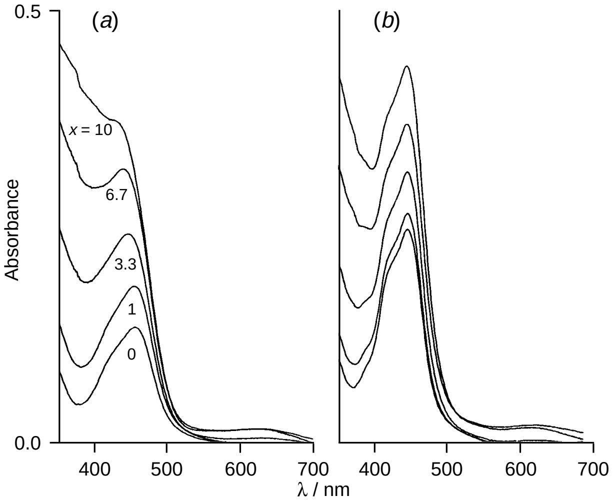


Fig. 2 UV–VIS absorption spectra of (*a*) $[Ru(bpy)_2(CN)_2]$ (2.0×10^{-5} mol dm^{-3}) and (*b*) $[Ru(bpy)_3]Cl_2$ (2.0×10^{-5} mol dm^{-3}) at various concentrations of $[OsO_2(mes)_2]$. Ratio of the $OsO_2(mes)_2$: Ru complexes = 1 : *x*.

Complex **1** in the solid state is non-emissive at 298 and 77 K. In solution, it gives an emission at the same energy as that of [Ru(bpy)$_2$(CN)$_2$] measured under similar conditions. However, the lifetime and intensity of the emission are much reduced. Fig. 3 shows ϕ_0/ϕ and τ_0/τ *vs.* [quencher] plots for [Ru(bpy)$_2$(CN)$_2$] and [Ru(bpy)$_3$]Cl$_2$ with [OsO$_2$(mes)$_2$] as quencher (ϕ and τ are emission intensity and decay lifetime, respectively). It is interesting that the decay time Stern–Volmer quenching constant, $K_{SV}{}^{\tau}$ {deduced from the slope of the plot of τ_0/τ *vs.* concentration of [OsO$_2$(mes)$_2$]} for both complexes are similar (1038 and 1098 dm^3 mol^{-1}). The value of the Stern–Volmer quenching constant, $K_{SV}{}^{\Phi}$ {deduced from the slope of the plot of ϕ_0/ϕ *vs.* concentration of [OsO$_2$(mes)$_2$]} for [Ru(bpy)$_3$]Cl$_2$ (1842 dm^3 mol^{-1}) is slightly larger than the $K_{SV}{}^{\tau}$ value, presumably this is due to the overlap of the absorption spectrum of [OsO$_2$(mes)$_2$] with the excitation spectrum of [Ru(bpy)$_2$(CN)$_2$]. Interestingly, the Stern–Volmer plots for [Ru(bpy)$_2$(CN)$_2$] are not linear and exhibits upward curvature characteristic of a system showing both static and dynamic quenching.[7] The static quenching is assigned to ground-state complex formation of [OsO$_2$(mes)$_2$(NC)Ru(bpy)$_2$(CN)] from [OsO$_2$(mes)$_2$] and [Ru(bpy)$_2$(CN)$_2$] in solution. This heterometallic complex in the solid state is non-emissive suggesting that the long-lived emissive MLCT state of the Ru(bpy)$_2$(CN)$_2$ chromophore is completely quenched by the OsO$_2$(mes)$_2$ unit *via* the bridging cyano group. Because the $K_{SV}{}^{\tau}$ values for [Ru(bpy)$_3$]Cl$_2$ and [Ru(bpy)$_2$(CN)$_2$] are similar, we propose that the dynamic quenching mechanism which represents the collision of [OsO$_2$(mes)$_2$] and the excited ruthenium partner through diffusion would be outer sphere in terms of electron- and/or energy-transfer.

Previous studies showed that the Ru(bpy)$_2$(CN)$_2$ chromophore could be easily functionalized *via* cyanide bridge formation with a suitable choice of adducts [Pt(dien)^{2b} or Ru(NH$_3$)$_5$^{2b}] but Ru–CN–M (M = Lewis acid) adduct formation were found not to substantially modify the excited-state properties of the Ru(bpy)$_2$(CN)$_2$ chromophore.[2b,6] In this work, the excited state of **1** which localizes at the ruthenium centre should be MLCT in nature. This excited state is rapidly quenched by intramolecular energy and/or electron transfer pathways. If intramolecular energy transfer proceeds, the quenching product is [OsO$_2$(mes)$_2$]*. If intramolecular electron transfer proceeds, the quenching product is either the reduced or oxidized species of [OsO$_2$(mes)$_2$]. In any case, the energetic or reactive site shifts from ruthenium to the Os–oxo moiety. The rich oxidation chemistry and photochemistry of high-valent osmium–oxo complexes are well documented in literature.[9] Thus formation of an activated five-coordinate osmium–oxo complex through intramolecular electron- and/or energy-transfer would provide an entry to a new class of metal–oxo photooxidants with good light absorbing properties.

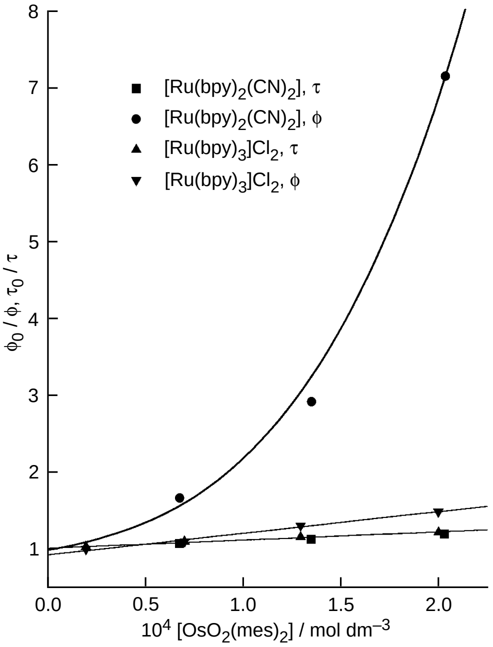


Fig. 3 Plots of ϕ_0/ϕ and τ_0/τ *vs.* [OsO$_2$(mes)$_2$] for complex **1**

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Footnotes

† A mixture of [OsO$_2$(mes)$_2$] (60 mg, 0.13 mmol) and [Ru(bpy)$_2$(CN)$_2$] (50 mg, 0.11 mmol) in dichloromethane–methanol (1 : 1, 10 ml) was stirred for 1 h. The solvent was slowly evaporated to dryness in a water bath (25 °C) to give a brown microcrystalline solid which was washed with diethyl ether (3 × 10 ml). This was recrystallized by slow evaporation of a dichloromethane–methanol mixture at 0 °C to afford brown needle crystals; yield 97 mg (95%). ^{1}H NMR (CD$_3$OD): δ (bpy) 9.61 (d, 2), 8.52 (d, 2), 8.46 (d, 2), 8.09 (t, 2), 7.94 (t, 2), 7.58 (m, 4), 7.29 (t, 2), (mes) 6.92 (s, 4), 2.43, (s, 6), 2.32 (s, 12). IR ν(C≡N) 2088.5s, 2072.8s; ν(Os=O) 893.1s, 884.6s, 849.1m. Anal. Calc. for C$_{40}$H$_{38}$N$_6$O$_2$OsRu: C, 51.88; N, 9.08; H, 4.14. Found: C, 50.91; N, 8.90; H, 3.98%.

‡ *Crystal data*: [C$_{40}$H$_{38}$N$_6$O$_2$OsRu·2CH$_3$OH]; M_r = 990.133, monoclinic, space group $P2_1/c$ (no. 14), a = 17.421(3), b = 10.194(3), c = 23.259(3) Å, β = 95.91(2)°, U = 4108(1) Å^3, Z = 4, D_c = 1.601 g cm^{-3}, μ(Mo-Kα) = 35.03 cm^{-1}, F(000) = 1968, T = 301 K. A brown crystal of dimensions 0.25 × 0.20 × 0.30 mm was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). 7804 unique reflections were obtained from a total of 33 227 measured reflections. 5747 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. All 54 non-H atoms were refined anisotropically. Hydrogen atoms of the methanol molecules were not found but 38 H atoms of the complex molecule at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 487 variable parameters by least-squares refinement on F with $w = 4F_o{}^2/\sigma^2(F_o{}^2)$, where $\sigma^2(F_o{}^2) = [\sigma^2(I) + (0.018\ F_o{}^2)^2]$ for 5747 reflections with $I > 3\sigma(I)$ was reached at R = 0.035 and wR = 0.043 with a goodness-of-fit of 1.61 $(\Delta/\sigma)_{max}$ = 0.04 for atoms of the complex molecule. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.66 and 1.24 eÅ^{-3} respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference nubmer 182/350.

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