Building Blocks for Polymetallic Ruthenium(II) and Osmium(II) Polypyridine Luminophores

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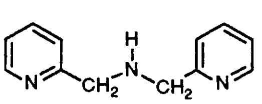
Three novel, mixed-ligand complexes of ruthenium and osmium are prepared; the key example [Ru(bpy)$_2$bpaH] (PF$_6$)$_2$ [bpy = 2,2′-bipyridine; bpaH = bis(picolyl)amine] **1** bears a 'dangling' pyridine ligand according to X-ray crystallography and has a luminescence lifetime comparable with that of [Ru(bpy)$_3$]$^{2+}$.

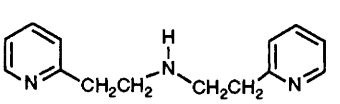
Despite certain limitations, [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine) continues to be a model luminophore, photosensitizer and electron-transfer reagent for numerous applications.[1–3] An increasing number of homo-[4] and hetero-binuclear[5] ruthenium and osmium polypyridine complexes have been studied to explore interactions between metal centres, mixed-valence states and multielectron-transfer processes.[5–7] The few known polymetallic ruthenium(II) and osmium(II) systems all involve conjugated, multidentate bridging ligands[4–6] lacking the flexibility needed to adjust the communication between metal centres affecting useful properties such as luminescence. As part of our programme to develop luminescent and electroactive oligometallic polypyridine systems, we have synthesized a number of ruthenium(II) and osmium(II) complexes of the type [M(bpy)$_2$L]$^{2+}$, where L is a non-conjugated tridentate ligand. Two ligands {L = bis(picolyl)-amine (bpaH) and bis[2-(2-pyridyl)ethyl]amine (beaH)} were chosen for this study because they (*i*) have established denticity and coordination capabilities,[8] (*ii*) might improve luminophore photostability by reducing ligand photodissociation,[2] (*iii*) can be immobilized or anchored to polymers[9] (for example, to develop a fibre-optic oxygen sensor[10]), and (*iv*) were of interest for their potential to form unusual seven-coordinate Ru^{II} and Os^{II} complexes.[11]

The mixed-ligand complexes were synthesized[12] by refluxing aqueous ethanolic solutions of *cis*-[Ru(bpy)$_2$Cl$_2$] or *cis*-[Os(bpy)$_2$Cl$_2$] and an excess of the tridentate ligand for 6–28 h under nitrogen. The complexes, precipitated as hexafluorophosphate salts (60–80%), are formulated as [M(bpy)$_2$L]$^{2+}$2PF$_6^-$ (**1** M = Ru, L = bpaH; **2** M = Ru, L = beaH; **3** M = Os, L = bpaH), on the basis of elemental analysis and positive fast atom bombardment-mass spectrometry (FAB$^+$-MS) data. A careful examination of the FAB$^+$-MS spectrum of [Ru(bpy)$_2$(bpaH)]$^{2+}$2PF$_6^-$ **1** prior to purification on a Sephadex LH-20 column revealed the presence of a molecular ion at *m*/*z* 1661 corresponding to a binuclear species [Ru(bpy)$_2$(bpaH)Ru(bpy)$_2$(bpaH)(PF$_6$)$_3$]$^+$.

The mononuclear complexes exhibit extremely complicated, though well-resolved ^{1}H NMR spectra. The presence of twenty-four resonances in the δ 6–10.5 region of the ^{1}H NMR spectrum of **1** (Fig. 1) indicates that all the aromatic protons in this molecule are anisochronous, in agreement with its expected asymmetry. The four methylene protons of the bis(picolyl)amine moiety are also nonequivalent and couple geminally (*J* 15–20 Hz) as well as with the secondary amine proton. The identity of the NH signal, which shifts downfield from δ 2.36 to 6.72 upon formation of the complex has been confirmed by proton-exchange studies.



bpaH



beaH

Table 1 Spectroscopic and electrochemical properties of complexes in acetonitrile at room temp.

Complex	Absorption λ_{max}/nm ($\varepsilon \times 10^3$ mol^{-1} cm^{-1})	Luminescence[a] Emission/nm	Luminescence[a] Life time τ/ns	Polarographic potential, $E_{1/2}$/V[b]
1	470 (3.0), 428sh (2.3), 342 (3.7), 292 (15.0), 246 (7.8)	630	496	1.14 — −1.39
2	476 (3.0), 428sh (2.0), 342 (3.3), 292 (18.0), 248 (8.4)	670	—	1.04 −1.61
3	486 (8.9), 432 (6.4), 358 (5.7), 290 (32.2), 256 (22.3)	724	50	0.91 −1.13

[a] 10^{-4} to 10^{-5} mol dm^{-3} in MeCN; excitation at 532 nm. [b] Aqueous solution containing 0.1 mol dm^{-3} tetraethylammonium hexafluorophosphate; *V vs.* SSCE. (SSCE = standard saturated calomel electrode).

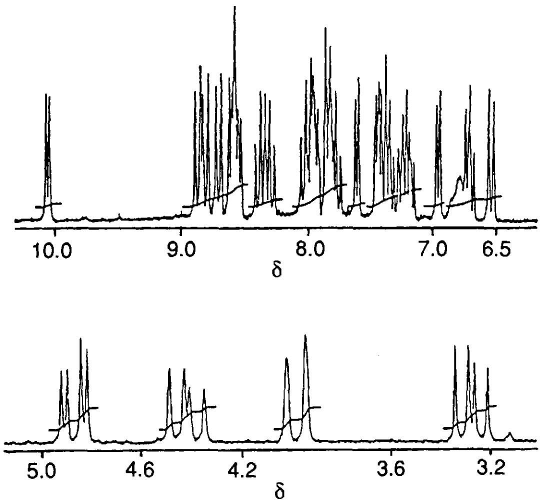


Fig. 1 ^{1}H NMR spectrum of **1**

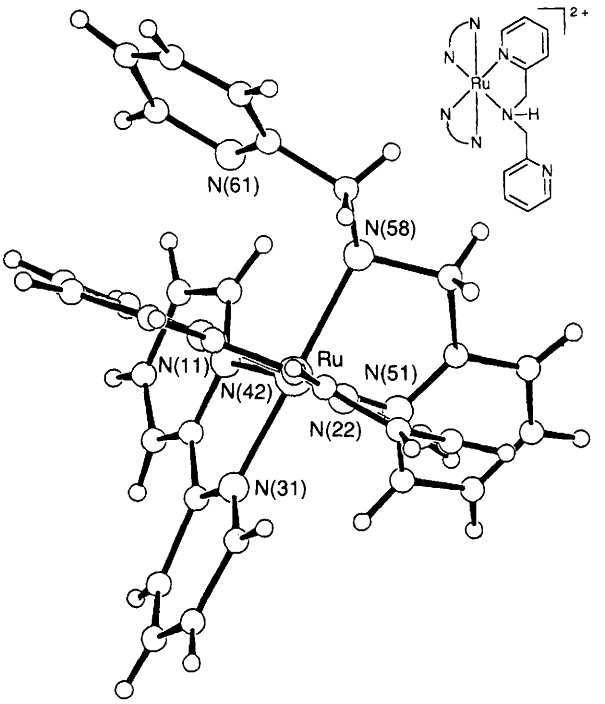


Fig. 2 A view of the $[Ru(bpy)_2(bpaH)]^{2+}$ cation in **1**. Molecular dimensions in the coordination sphere, distances (Å) and angles (°): Ru–N(11), 2.032(8) Å; Ru–N(22), 2.066(10) Å; ∠N(11)–Ru–N(22), 78.8(3); N(22)–Ru–N(31), 96.5(3); Ru–N(31), 2.072(9); Ru–N(42), 2.165(10); ∠N(31)–Ru–N(42), 77.0(3); N(42)–Ru–N(58), 96.6(3); Ru–N(51), 2.113(7); Ru–N(58), 2.199(8); ∠N(51)–Ru–N(58), 79.1(3); N(22)–Ru–N(51), 97.3(3); N(11)–Ru–N(58), 96.3(3).

The X-ray crystallographic structure† of **1** consists of discrete $[Ru(bpy)_2(bpaH)]^{2+}$ cations and PF_6^- anions. In the cation (Fig. 2), the metal atom is six-coordinate with a distorted octahedral environment consisting of two 2,2′-bipyridyl ligands [Ru–N 2.032(8), 2.066(10) and Ru–N 2.072(9), 2.165(10) Å] as well as to two nitrogen atoms of bis(picolyl) amine [Ru–N 2.113(7) and 2.199(9) Å]. It is perhaps significant that the longest Ru–N bond of the six around the metal atom is to the aliphatic nitrogen N(58), as also observed for other metal complexes of bis(picolyl)amine and 2-pyridylalkyleneamines.[13] This does not seem to be a result of the steric crowding of the unbonded or 'dangling' pyridine of bpaH, as the closest interatomic distance (2.57 Å) is between N(36) and N(56). The Ru–N(61) distance is 3.61(2) Å, indicating that there is no interaction with the seventh nitrogen atom. The electronic and emission spectra of **1**–**3** (Table 1) are similar to those observed for $[M(bpy)_3]^{2+}$, where M = Ru or Os. The luminescence quantum yield and excited state lifetime of **1** (Φ = 0.024, τ = 500 ns) are comparable with those of $[Ru(bpy)_3]^{2+}$ (Φ = 0.042, τ = 600 ns),[3] whereas the oxidation waves of all these complexes showed poor reversibility (ΔE_p 140–370 mV), even at temperatures as low as −40 °C.[7]

An interesting feature of complex **1** is its stability towards photodecomposition; irradiation of solutions in acetone or acetonitrile produces no change over periods of at least 24 h. Ligand photosubstitution in $[Ru(bpy)_3]^{2+}$ is presumed to proceed *via* a thermally activated radiationless transition from the luminescent metal-to-ligand charge-transfer (^{3}CT) level to a distorted metal-centred (^{3}MC) level, with subsequent cleavage of one Ru–N bond to form an intermediate containing a monodentate bipyridine ligand.[14] Photostability of **1** may be explained by the presence of a 'dangling' pyridine, which may enhance re-coordination to the five-coordinate intermediate formed by the cleavage of one Ru–N bond.

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† *Crystal data* for $[Ru(bpy)_2(bpaH)]^{2+}2PF_6$, **1**, $C_{32}H_{29}N_7F_{12}P_2Ru$: *M* = 902.2, *F*(000) = 1808, *a* = 12.408(11), *b* = 20.833(17), *c* = 13.986 (12) Å, β = 98.5(1)°, *U* = 3575.7 Å^3, D_c = 1.68 g cm^{-3}, D_m = 1.63 g cm^{-3}, *Z* = 4, λ(Mo-Kα) = 0.7107 Å (graphite monochromator), μ = 6.28 cm^{-1}, spacegroup $P2_1/n$. A dark-purple crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm (grown by evaporation of an aqueous solution) was used. 2418 Independent data above background [$(I) > 2\sigma(I)$] were measured on a Stoe-Stadi2 diffractometer. The structure was determined by the heavy-atom method and refined (Ru, F, P, anisotropic, N, C, H isotropic) to *R* = 0.064 (R_w = 0.067). All computations used SHELX76 package for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1976, and some of the programs on the Amdahl 5870 developed at the University of Reading. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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