A Decanuclear Ruthenium(II)–Polypyridine Complex: Synthesis, Absorption Spectrum, Luminescence and Electrochemical Behaviour

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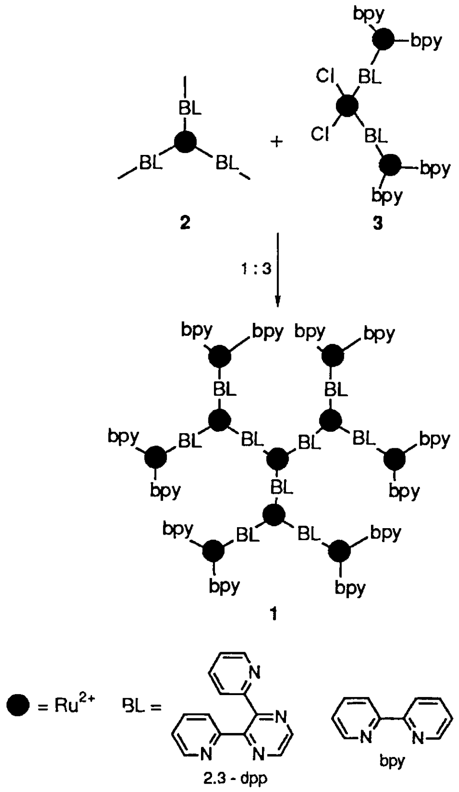
A novel oligonuclear Ru(II)–polypyridine complex, $Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3(PF_6)_{20}$ **1**, where dpp = bis(2-pyridyl)pyrazine and bpy = 2,2′bipyridine, has been prepared from the reaction of a $Ru(2,3\text{-dpp})_3{}^{2+}$ core **2** with three $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2{}^{4+}$ units; **1** shows a very intense absorption band at 541 nm ($\varepsilon = 1.25 \times 10^5$ $dm^3\ mol^{-1}\ cm^{-1}$), room temperature luminescence ($\lambda_{max} = 809$ nm, $\tau = 55$ ns, $\Phi = 10^{-3}$), and independent one-electron oxidation of the six peripheral Ru^{2+} ions at +1.43 V *vs.* saturated calomel electrode (SCE).

The synthesis of supramolecular species from molecular components that possess specific properties and contain appropriate 'pieces of information' is currently attracting much attention as a strategy to obtain advanced materials.[1–5] Ru(II)–polypyridine complexes can be used as building blocks to synthesize luminescent and redox-active polynuclear compounds where energy and/or electron-transfer processes can be induced by light.[5–7] A particularly convenient strategy to obtain such supramolecular species is that based on the use of bridging ligands (BL) like 2,3- and 2,5-dpp [dpp = bis(2-pyridyl)pyrazine], Scheme 1, to connect metal-containing units.[8–11] Continuing our studies on the synthesis and characterization of such polynuclear metal complexes,[12–16] we have obtained a decanuclear Ru(II)–polypyridine species (**1**, Scheme 1 and Fig. 1) which exhibits interesting spectroscopic and redox properties.

$Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3(PF_6)_{20}$ **1** was prepared as shown in Scheme 1, *i.e.* by reacting a $Ru(2,3\text{-dpp})_3{}^{2+}$ core **2**,[10a] which contains three free chelating sites, with three $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2{}^{4+}$ units **3**,[17] which contain easily replaceable Cl^- ligands. The trinuclear complex **3** is quite interesting since it can be used to introduce a trimetallic building block in species that have an unsaturated chelating site.

In principle, **1** can exist as different geometrical isomers, depending on the arrangement of the ligands around the metal ions. It can also be a mixture of several diastereoisomeric species, owing to the chiral nature of each metal centre. However, no evidence for the formation of different species has been obtained during the synthetic work. Furthermore, differences arising from the possible presence of geometrical or optical isomers are not expected to be significant in the electrochemical and luminescence experiments described below. Rather, it should be noticed that in **1** (Fig. 1, Scheme 1) there are three distinct types of metal ions [central (one), intermediate (three), and peripheral (six)], and two distinct types of bridging ligands [inner (three) and outer (six)], whereas the twelve bpy ligands are all equivalent.

Electrochemical investigations on mono-, bi-, tri-, tetra-, hexa- and hepta-nuclear compounds of the same family have shown that:[8–17] (*i*) oxidation is metal centred; (*ii*) reduction is ligand centred; (*iii*) the 2,3-dpp bridging ligands are reduced at less negative potentials than the terminal bpy ligands; (*iv*) interaction between equivalent metals or equivalent ligands is noticeable for metals coordinated to the same bridging ligand and for ligands coordinated to the same metal, whereas it is small for metals or ligands that are sufficiently far apart. Since bpy is a better electron donor than μ-2,3-dpp, one can expect that the density of charge on the metals of **1** increases in going from the centre to the periphery. Thus, the six equivalent peripheral Ru^{2+} ions should be the first metal ions to be oxidized. Since such peripheral metal ions are equivalent and only weakly interacting, they should undergo one-electron oxidation at nearly the same potential. Comparison with the oxidation wave of $Os(phen)_3{}^{2+}$ (phen = 1,10-phenanthroline) as an internal standard and with the 'four-electron' oxidation wave of the analogous hexanuclear compound[17] indicates that the first oxidation wave of **1** ($\Delta E_{\frac{1}{2}} = +1.43$ V *vs.* SCE) is, indeed, a 'six-electron' wave. Oxidation of the three intermediate and of the central Ru^{2+} ions is expected to occur at more positive potentials and it could not be observed in the potential window examined (< + 2.0 V). The reduction pattern, as expected, is extremely complicated because of the presence of as many as 21 reducible ligands. A first broad wave, which should correspond to the first one-electron reduction of the nine interacting bridging ligands, occurs at



Scheme 1

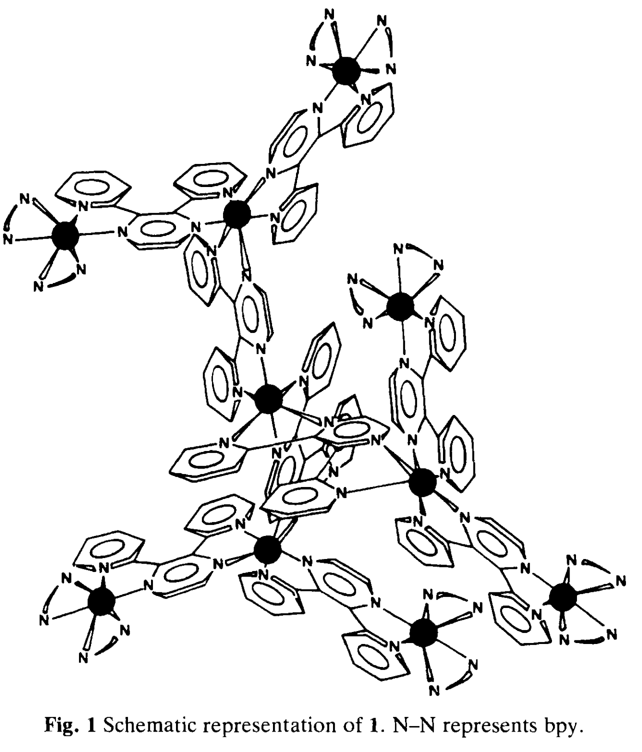


Fig. 1 Schematic representation of **1**. N–N represents bpy.

about −0.50 V. We plan to study **1** in DMF solution at 220 K in order to arrive at a complete and detailed interpretation of its reduction processes.

Compound **1** exhibits extremely intense bands in the UV region (λ_{max} = 283 nm, $\varepsilon_{max} = 3.5 \times 10^5$ dm^3 mol^{-1} cm^{-1}), that can be assigned to $\pi \rightarrow \pi^*$ transitions localized on the bpy and 2,3-dpp ligands, and quite intense bands in the visible region, that can be assigned to Ru → bpy (λ_{max} = 427 nm, $\varepsilon_{max} = 7.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and Ru → 2,3-dpp (λ_{max} = 541 nm, $\varepsilon_{max} = 1.25 \times 10^5$ dm^3 mol^{-1} cm^{-1}) charge-transfer transitions. The broadness of the latter band is due to the presence of non-equivalent Ru–BL couples, which leads to four different types of Ru → 2,3-dpp transitions.

The luminescence of **1** (77 K: λ_{max} = 732 nm, τ = 1.3 μs; 300 K: λ_{max} = 809 nm, τ = 55 ns, $\Phi = 1 \times 10^{-3}$) is typical of ^{3}MLCT emitters. On the basis of the electrochemical results and of the behaviour of parent compounds, emission can be assigned to the Ru → BL ^{3}CT level involving the peripheral Ru^{2+} ions. Energy migration from the centre to the periphery of the supramolecular system is quite efficient since the corrected excitation spectrum shows that the luminescent levels are reached with the same efficiency regardless of the excitation wavelength.

Oligonuclear complexes like **1** are interesting because they accumulate many chromophoric and redox centres in the same supramolecular entity and exhibit luminescence from a relatively long-lived excited state. Because of these properties, they are good candidates to play the roles of photosensitizers,[18,19] luminescent probes,[20,21] and multielectron-transfer catalysts.[22] By using different metals, bridging ligands, or terminal ligands it is also possible to control the direction of electronic energy migration in the supramolecular structure (antenna devices).[5,12,16]

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