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Polynuclear complexes of tris(bipyridine) bridging ligands. Energy transfer from Ru-based to Os-based components

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Abstract

The following complexes of the tris(bipyridine) ligand **1**, 1,3,5-tris[(((2,2'-bipyridyl-5'-yl)carbonyl)benzylamino)methyl]benzene, have been prepared: **1**$[Ru(bpy)_2]^{2+}$, **1**$[Ru(bpy)_2]_2{}^{4+}$, **1**$[Ru(bpy)_2]_3{}^{6+}$, **1**$[Os(bpy)_2]_3{}^{6+}$, and **1**$[Ru(bpy)_2]_2[Os(bpy)_2]^{6+}$. Their absorption spectra and luminescence properties have been investigated. Luminescence intensity and lifetime measurements show that in the mixed-metal complex **1**$[Ru(bpy)_2]_2[Os(bpy)_2]^{6+}$ efficient energy transfer takes place from the Ru-based components to the Os-based one.

1. INTRODUCTION

Much attention is currently devoted to photoinduced energy and electron migration in supramolecular systems [1-5]. Continuing our investigations on multicenter luminescent and redox-active species [6], we have synthesized the tris(bipyridine) ligand **1**, 1,3,5-tris[(((2,2'-bipyridyl-5'-yl)carbonyl)benzylamino) methyl]benzene, which is able to coordinate three (equivalent or different) metal-containing building blocks. We have then prepared some of its mono-, di-, and trimetallic complexes using $Ru(bpy)_2^{2+}$ and/or $Os(bpy)_2^{2+}$ building blocks, and we have studied their luminescence behavior. Our final aim is that of comparing energy and electron transfer processes in trinuclear complexes having "spacers" of different size, such as those shown in Fig. 1. To build up this series of compounds, we have decided to replace the previously used 5-ethoxycarbonyl-2,2'-bpy units [6] with unsubstituted 2,2'-bpy units because the latter assure a higher chemical stability and a stronger luminescence intensity to the Ru(II) and Os(II) complexes.

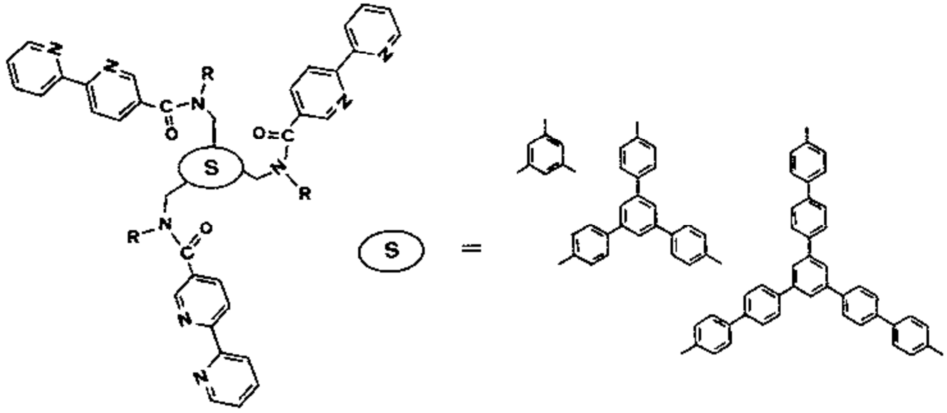

Figure 1. Schematic representation of tris(bipyridine) bridging ligands: S = benzene, 1; S = 1,3,5-triphenylbenzene, 2; S = 1,3,5(tri-5'biphenyl)benzene, 3.

2. EXPERIMENTAL

The synthesis of **1** and of its metal complexes will be described elsewhere. For the sake of simplicity, **1**$[Ru(bpy)_2]^{2+}$, **1**$[Ru(bpy)_2]_2^{4+}$, and **1**$[Ru(bpy)_2]_3^{6+}$ will be indicated by Ru, Ru_2, and Ru_3, and the same will also be done for **1**$[Os(bpy)_2]_3^{6+}$, Os_3, and for the mixed-metal **1**$[Ru(bpy)_2]_2[Os(bpy)_2]^{6+}$ complex, Ru_2Os, whose structure is schematized in Fig. 2.

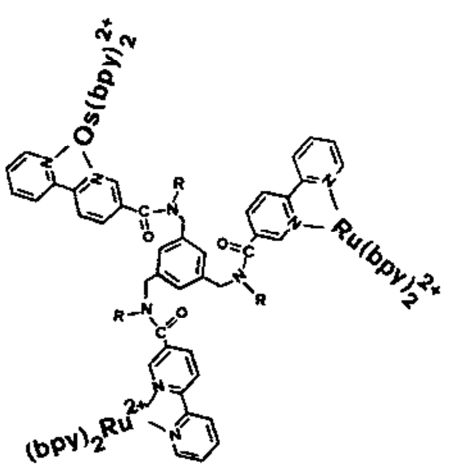

Figure 2. Schematic representation of $1[Ru(bpy)_2]_2[Os(bpy)_2]^{6+}$, Ru_2Os.

Absorption spectra were obtained with a Perkin Elmer Lambda 6 spectrophotometer and the luminescence spectra by a Perkin Elmer LS50 spectrofluorimeter. Luminescence lifetimes were obtained with an Edinburgh single-photon counting apparatus. Interference or cut-off filters were used to select appropriate spectral regions for lifetime measurements. In order to evaluate the quenching of the luminescence of the Ru(bpy)$_2$ components and the sensitization of the luminescence of the Os(bpy)$_2$ component in Ru$_2$Os, we have adopted the following procedure. Solutions of Ru$_2$Os and of a 2:1 mixture of Ru$_3$ and Os$_3$, 2Ru$_3$-1Os$_3$, having the same concentration, were prepared. They exhibited identical absorption spectra. The luminescence spectra of such solutions were then recorded under identical instrumental conditions (Fig. 3) and the results obtained were elaborated to evaluate the difference in intensity at 595 nm (77 K) or 650 nm (298 K), i.e. the quenching of the luminescence of the Ru-based chromophores by the Os-based one.

In order to estimate the sensitization of the luminescence of the Os-based unit, a more complex procedure had to be used because of the interference of the tail of the Ru-based luminescence on the weaker Os-based luminescence. The luminescence of the Ru-based chromophores was subtracted (using the Ru$_3$ luminescence spectrum as a standard) from the luminescence spectrum of both the Ru_2Os compound and the $2Ru_3$-$1Os_3$ mixture. The residual (Os-based) luminescence intensities of Ru_2Os and $2Ru_3$-$1Os_3$ were then compared.

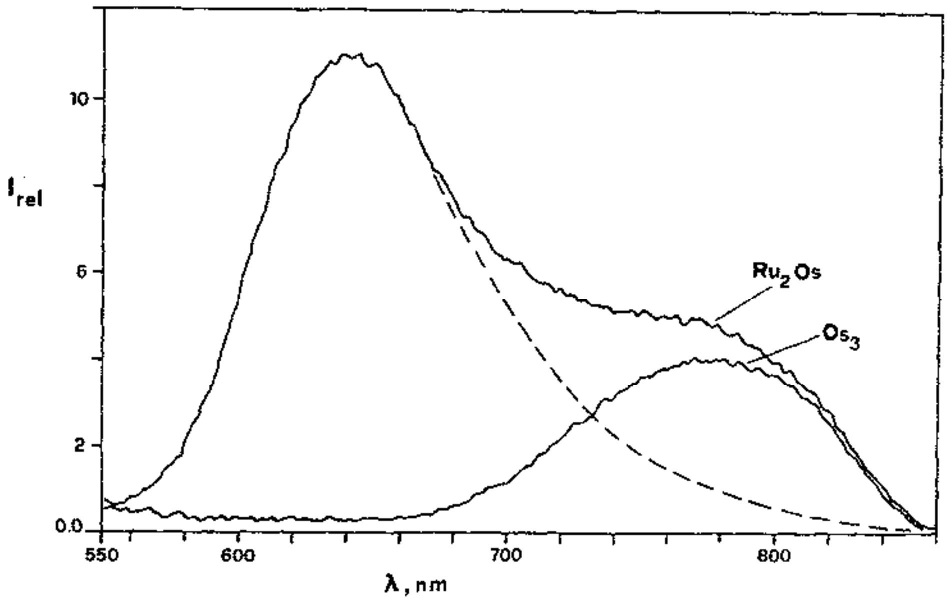

Figure 3 Emission spectra in CH_3CN of Ru_2Os; Os_3; dotted line Ru_3

3. RESULTS AND DISCUSSION

A summary of the absorption and luminescence data is shown in Table 1. As expected, the behavior of the mononuclear $\mathbf{1}[Ru(bpy)_2]^{2+}$ species, Ru, is quite similar to that of $Ru(bpy)_3^{2+}$ [7]. The behavior of the Ru_2 and Ru_3 species is identical to that of the Ru species, which indicates that there is no sizeable interaction between the various chromophoric groups. The behavior of the Os_3 species is very similar to that of $Os(bpy)_3^{2+}$ [8]. The Ru, Ru_2, and Ru_3 species are oxidized at the same potential, as will be discussed in detail elsewhere.

Comparison between the luminescence behavior of the Ru_2Os species and that of the $2Ru_3$-$1Os_3$ mixture (see experimental) shows that in the Ru_2Os

species the luminescence of the Ru-based chromophoric groups is quenched to less than 6% and that the efficiency of energy transfer from the Ru-based components to the Os-based one is close to 100%.

Preliminary results obtained for the analogous mixed-metal complex of the ligand **2**, which contains the larger 1,3,5-triphenylbenzene spacer (Fig. 1), indicate that the energy transfer efficiency reduces to ~50%. It is likely that no energy transfer occurs in the case of the mixed-metal complex of ligand **3**, which contains an even larger spacer (Fig.1).

Table 1 Luminescence data

	77 K[b]				298 K[c]					
compound[a]	λ, nm		τ, μs		λ, nm		τ, ns		I_{rel}[d]	
	Ru	Os	Ru	Os	Ru	Os	Ru	Os	Ru	Os
Ru	595	-	3.8	-	650	-	200	-	100	-
Ru_2	595	-	3.7	-	650	-	205	-	100	-
Ru_3	595	-	3.8	-	650	-	200	-	100	-
Os_3	-	720	-	0.68	-	780	-	23	-	1.1
$^2Ru_3\cdot 1Os_3$	595	720	3.5	1.8[e]	650	780	190	-	61	0.5
Ru_2Os	595	720	(4.5)[f]	0.70	650	780	(185)[f]	24	3.0	1.0

[a]For the abbreviations used, see text; [b]butyronitrile matrix; [c]acetonitrile solution; [d]excitation in the isosbestic point (450 nm); [e]strong overlap with the tail of Ru emission; [f]presumable impurity (< 6%) of a homometallic Ru species.

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