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Mononuclear and Dinuclear Osmium(II) Compounds Containing 2,2′-Bipyridine and 3,5-Bis(pyridin-2-yl)-1,2,4-triazole: Synthesis, Electrochemistry, Absorption Spectra, and Luminescence Properties

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The synthesis, structure, electrochemical behavior, absorption spectra, luminescence spectra (from 90 to 298 K), luminescence lifetimes (from 90 to 298 K), and photoreactivity of the complexes Os(bpy)$_2$(bpt)$^+$ (**1**) and [Os(bpy)$_2$]$_2$(bpt)$^{3+}$ (**2**), where bpy = 2,2′-bipyridine and Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole, are reported. The properties exhibited by **1** and **2** are compared with those of Os(bpy)$_3^{2+}$ and of the analogous Ru(II) complexes. For both **1** and **2**, the lowest energy absorption band and the luminescence band are attributed to Os → bpy metal-to-ligand charge-transfer (MLCT) singlet and triplet excited states, respectively. Electrochemical oxidation is centered on the metal(s), and electrochemical reduction is centered on the ligands, with bpy being reduced at less negative potentials than bpt$^-$. Because of the stronger σ-donor ability of bpt$^-$ compared with bpy, the Os → bpy CT absorption and emission bands of **1** (λ_{max}^{abs} = 486 nm and λ_{max}^{em} = 762 nm in CH$_3$CN at room temperature) are red-shifted compared with those of the parent Os(bpy)$_3^{2+}$ complex. In nitrile rigid matrix at 90 K, the emission lifetimes are 250 and 340 ns for **1** and **2**, respectively. For both complexes, increasing temperature causes a decrease of the emission lifetime (55 ns for **1** and 33 ns for **2** at room temperature), but the ln $(1/\tau)$ vs $1/T$ plots between 90 and 298 K do not exhibit the highly activated decay processes characteristic of the ^{3}MLCT → ^{3}MC crossover. In agreement with this result, no photodecomposition was observed in CH$_2$Cl$_2$ solutions containing Cl$^-$ ions. The ln $(1/\tau)$ vs $1/T$ plots for **1** and **2** are noticeably different in fluid solution, indicating that an additional radiationless decay channel intervenes for **2** above 150 K.

Introduction

There is currently an increasing interest in luminescent and redox-reactive transition-metal complexes, especially in view of their use as building blocks for the design of photochemical molecular devices that perform useful light-induced functions such as energy migration and charge separation.[2-4] Most of the investigations have so far concerned Ru(II)-polypyridine complexes,[5-9] but the Os(II)-polypyridine complexes also exhibit quite interesting photochemical, photophysical, and redox properties.[10-13] For both families of complexes, oxidation processes are metal centered, reduction processes are ligand centered, and the lowest (luminescent and long-lived) excited state is a triplet metal-to-ligand charge-transfer (^{3}MLCT) level.

The design of polynuclear complexes capable of performing photoinduced energy migration or charge separation requires the assembly, in an appropriate spacial sequence, of building blocks that exhibit different excited-state energies or redox potentials. From this point of view, the two families of Ru(II)- and Os(II)-polypyridine complexes nicely complement each other because the Os(II) complexes can be oxidized at less positive potentials than the Ru(II) analogues, which also implies that the luminescent ^{3}MLCT level of an Os(II) complex lies lower in energy than that of an analogous Ru(II) complex. For the latter reason, the Os complexes are also expected and found to be more stable toward photodissociation.

The number of investigations concerning the photochemical and photophysical behavior of dinuclear or polynuclear complexes is rapidly growing.[14-16] Key components in polynuclear complexes are the bridging ligands, since the interaction between the bridged units and, thereby, the properties of the polynuclear complex, are critically dependent on the size, shape, and electronic nature of the bridge.[17] In several instances, the bridge is also directly involved in electrochemical reduction and/or light excitation and emission processes. The anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole,[18] bpt$^-$, is a particularly interesting bridge because, contrary to most of the previously used polypyridine bridges, it carries a negative charge, which results in a high σ-donor and a low π-acceptor ability. Furthermore, its two bidentate functions are chemically distinct, because the central triazole ring uses the N^1 (or N^2) and N^4 nitrogen atoms for coordination (Figure 1).

In previous papers, we have reported the synthesis, characterization, X-ray structure, electrochemical properties, absorption spectra, luminescent behavior, and photochemical reactivity of the mononuclear Ru(bpy)$_2$(bpt)$^+$ and dinuclear [Ru(bpy)$_2$]$_2$bpt^{3+} complexes.[15,19,20] In this paper, we report a study on the analogous Os(bpy)$_2$(bpt)$^+$ (**1**) and [Os(bpy)$_2$]$_2$bpt^{3+} (**2**) complexes. The results obtained are discussed and compared with those of the analogous Ru complexes and of the parent Os(bpy)$_3^{2+}$ complex.

Experimental Section

Materials. 3,5-Bis(pyridin-2-yl)-1,2,4-triazole (Hbpt)[18] and *cis*-Os(bpy)$_2$Cl$_2$ were prepared according to literature methods.[21] All the

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(1) (a) Istituto FRAE—CNR. (b) University of Bologna. (c) Leiden University. (d) Dublin City University.

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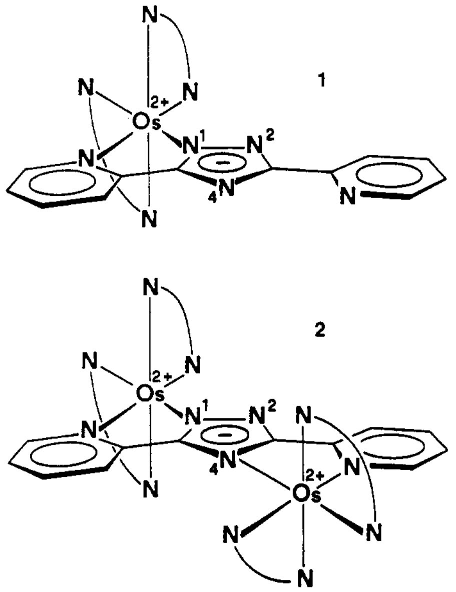

Figure 1. Schematic representation of the complexes studied. For **2** only one isomer is shown.

solvents used were of the best grade commercially available.

Os(bpy)$_2$(bpt)PF$_6$·H$_2$O (1). A 2-mmol sample of Os(bpy)$_2$Cl$_2$ and 2.4 mmol of Hbpt were refluxed for 48 h in EtOH/H$_2$O (1/1). The hot solution was filtered and evaporated until dryness, and 10 mL of water was added to the solid. The solution was put onto a Sephadex SP-25 column and eluted with 0.1 M NaCl solution. The first dark fraction was isolated, after which the compound was precipitated by addition of an excess of an aqueous NH$_4$PF$_6$ solution. Another dark band was present at the top of the column, which was most likely the dinuclear species. After filtration of the precipitate, the compound was further purified by column chromatography on neutral alumina with ethanol as eluent. Finally, the complex was crystallized from acetone/water. Anal. Calcd for Os(bpy)$_2$(bpt)PF$_6$·H$_2$O: C, 43.29; H, 2.93; N, 14.20; P, 3.47. Found: C, 42.85; H, 2.80; N, 14.02; P, 3.41.

[Os(bpy)$_2$]$_2$(bpt)(PF$_6$)$_3$·2H$_2$O (2). This compound was prepared in a similar manner, except that 1.1 mmol of Os(bpy)$_2$Cl$_2$ and 0.5 mmol of Hbpt were refluxed in ethanol/water for 120 h. Purification and isolation took place as described for the mononuclear compound, except that, after elution with 0.1 M NaCl (to remove the mononuclear impurities), the dinuclear complex was obtained by use of 3 M NaCl solution with the Sephadex SP-25 material. Anal. Calcd for [Os(bpy)$_2$]$_2$(bpt)(PF$_6$)$_3$·2H$_2$O: C, 36.78; H, 2.61; N, 10.72; P, 5.48. Found: C, 36.39; H, 2.06; N, 10.37; P, 5.51.

Physical Measurements. Proton NMR spectral measurements and COSY experiments were performed on a Bruker 300-MHz spectrometer. The measurements were carried out in acetone-d_6 with TMS as internal standard. Further experimental details for the COSY measurements have been given in a previous paper.[19]

Electrochemical measurements were carried out with a minicell (capacity 3 mL) at room temperature, in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. All experiments were performed on an EG&G PAR C Model 303 instrument equipped with an EG&G 384B polarographic analyzer. A glassy carbon electrode was used as working electrode, a platinum wire as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. The redox potentials were estimated by using differential pulse polarography (dpp) at a scan rate of 4 mV s^{-1} with a pulse height of 20 mV. Cyclic voltammograms (CV) were obtained at a scan rate of 100 mV s^{-1}. The separation between cathodic and anodic peaks and the relative intensities of the cathodic and anodic currents were taken as criteria for reversibility of the redox process.

The absorption spectra were recorded with a Perkin-Elmer Lambda 5 or Kontron Uvikon 860 spectrophotometer. Uncorrected emission spectra were obtained with a Perkin-Elmer MPF-44B spectrofluorimeter equipped with a Hamamatsu R928 tube.

The temperature dependence experiments were carried out in a mixture (hereafter called "nitrile") of freshly distilled propionitrile/butyronitrile (4/5 v/v). A dilute solution of each complex was sealed under vacuum in a 1-cm quartz cell after repeated freeze-pump-thaw cycles. The cell was placed inside a Thor C600 nitrogen flow cryostat, equipped with a Thor 3030 temperature controller. The absolute error in the temperature is estimated to be ±2 K. The emission lifetimes were measured by an Edinburgh 199 single-photon-counting apparatus. A single-exponential analysis was satisfactorily applied to the decay of the luminescence intensity over the full temperature range explored, including the glass-to-fluid temperature interval of the solvent (approximately 100–150 K). In the latter temperature range, the deactivation of the luminescence of MLCT emitters is affected by repolarization processes of the solvent. Time-resolved studies have shown that the emission energy shifts from a higher level, corresponding to that obtained in frozen solvent, to a lower level, corresponding to that obtained in completely fluid solvent.[22] According to the results of recent studies, the time dependence of the luminescence energy shift shows a more complex behavior in alcoholic than in nitrile (aprotic) solvents, presumably because of specific solvent effects.[22] For the restricted 100–150 K temperature interval, the shortening of the luminescence lifetime in passing from frozen solution (100 K) to fluid solution (150 K) is ascribed to an increment in radiationless decay rate, B, due to the shift to lower energy displayed by the steady-state luminescence maximum ("energy gap law" effect[10]), $1/\tau = k + B$.[8] Either conformational changes of the luminescent species or solvent rearrangements can be responsible for the relaxation of the luminescent level to lower energy.[8,10,22] The single-exponential analysis was performed with nonlinear programs,[23] and the quality of the fit was assessed by the χ^2 value close to unity and by a regular distribution of the residuals along the time axis. The experimental error in the lifetime is estimated to be ≤8%. Standard iterative nonlinear programs[23] were also employed to extract the parameters for the temperature dependence of the lifetime.

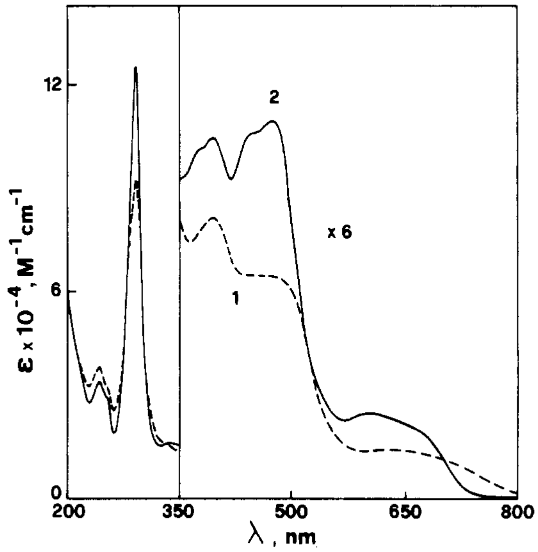

Figure 2. Absorption spectra in acetonitrile solution at room temperature: **1** = Os(bpy)$_2$(bpt)$^+$; **2** = [Os(bpy)$_2$]$_2$(bpt)$^{3+}$.

The photochemical experiments were carried out on **1**, **2**, and Os(bpy)$_3^{2+}$ (as PF$_6^-$ salts, 6.5 × 10^{-4} M) at room temperature in air-equilibrated CH$_2$Cl$_2$ solutions containing an excess (0.005 M) of Cl$^-$ ions as benzyltriethylammonium chloride. Excitation was performed with a tungsten halogen lamp. The irradiated solution was contained in a 3-mL spectrophotometric cell housed in a thermostated holder.

Results

The X-ray analysis of Ru(bpy)$_2$(bpt)PF$_6$ showed that the metal ion is bound via N^1 of the triazole ring.[20] Since the NMR spectrum of **1** is very similar to that of the analogous ruthenium compound, it is concluded that also in the case of **1** the metal center is coordinated via N^1 (Figure 1). The two metal ions of [Ru(bpy)$_2$]$_2$(bpt)$^{3+}$ are bound via N^1 and N^4 to the triazole bridge, as indicated by the NMR spectrum[19] and by a preliminary X-ray investigation.[24] The NMR spectrum of **2** is quite similar to that of the analogous ruthenium compound, suggesting the same type of coordination (Figure 1). We have previously reported the

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Table I. Absorption and Luminescence Properties

	absorption,[a] 298 K		emission[b] 90 K		emission[b] 298 K	
	λ_{max}, nm	ϵ_{max}, $M^{-1}\,cm^{-1}$	λ_{max}, nm	τ, ns	λ_{max}, nm	τ,[c] ns
$Os(bpy)_3^{2+}$	479	11 100	712	940	725	62
$Os(bpy)_2(bpt)^+$	486	11 000	750	250	762	55
$[Os(bpy)_2]_2(bpt)^{3+}$	475	18 000	765	340	762	33

[a] Acetonitrile solution. [b] Nitrile solution. [c] Deaerated solution.

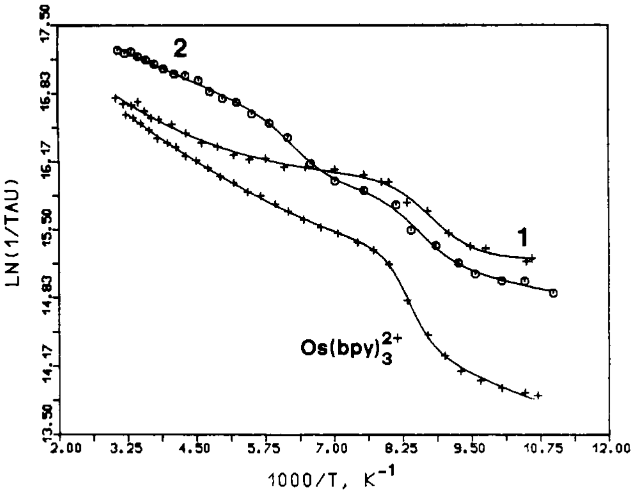

Figure 3. Temperature dependence of the luminescence lifetime. **1** = $Os(bpy)_2(bpt)^+$; **2** = $[Os(bpy)_2]_2(bpt)^{3+}$. The behavior of $Os(bpy)_3^{2+}$ is also shown for comparison.

separation and characterization of two geometrical isomers of the ruthenium dinuclear compound.[19] The spectroscopic properties of the two isomers were the same within the accuracy of the performed measurements. No attempt was made to isolate the two geometrical isomers of **2**, since there are no reasons to believe that the properties of the two isomers of the osmium dinuclear compound will be different.

The electronic absorption spectra of **1** and **2** in acetonitrile at room temperature are shown in Figure 2. A pH titration in a Britton Robinson buffer of **1** yielded a pK_a value of 4.1 ± 0.1, which is practically the same as that reported for the analogous mononuclear ruthenium compound (4.0).[19]

The wavelengths and molar extinction coefficients of the lowest energy absorption maxima at 298 K, the wavelengths of the emission maxima at 90 and 298 K, and the luminescence lifetimes at 90 and 298 K are listed in Table I. The emission lifetimes and the luminescence spectra were examined in the entire temperature range between 90 and 298 K, and some obtained results are shown in Figures 3 and 4. The data for $Os(bpy)_3^{2+}$ are also shown for comparison.

In CH_2Cl_2 solutions containing 0.005 M Cl^-, irradiation (see Experimental Section) did not cause any change in the absorption and emission spectra of **1** and **2**. Under the same conditions, both the $Ru(bpy)_3^{2+}$ and the $[Ru(bpy)_2]_2(bpt)^{3+}$ complexes were rapidly photodecomposed.[15] By comparison, an upper limit for the quantum yield of photodecomposition for **1** and **2** was estimated to be 10^{-5}.

Electrochemical measurements in the potential window from +2.00 to −2.80 V vs SCE showed several reversible waves. Irreversible waves were observed below −2.0 V. The data concerning the reversible waves are gathered in Table II, where the available data for $Os(bpy)_3^{2+}$[25] and for the analogous Ru(II) complexes[15] are also reported for comparison.

Discussion

Absorption and Emission Spectra. Previous studies[15,19] have shown that bpt^- is more difficult to reduce than bpy and exhibits

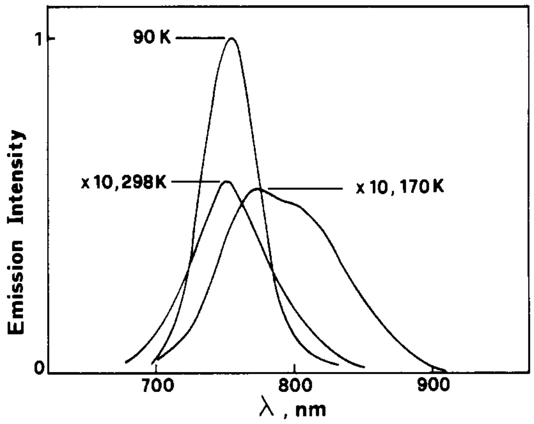

Figure 4. Temperature dependence of the luminescence band of **2**.

Table II. Electrochemical Potentials[a] (V)

	E_{ox}		E_{red}		
$Ru(bpy)_3^{2+}$[b]	+1.24		−1.35	−1.54	−1.79
$Ru(bpy)_2(bpt)^+$[c]	+0.85		−1.47	−1.72	
$[Ru(bpt)_2]_2(bpt)^{3+}$[c]	+1.04	+1.34	−1.40	−1.62	−1.67
$Os(bpy)_2^{2+}$[d]	+0.83		−1.28	−1.55	
$Os(bpy)_2(bpt)^+$	+0.49		−1.41	−1.69	
$[Os(bpy)_2]_2(bpt)^{3+}$	+0.64	+0.85	−1.34[e]	−1.58	−1.68

[a] Acetonitrile solutions, vs SCE. [b] Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675. [c] Reference 15. [d] Reference 25. [e] Two-electron wave.

better σ-donor and poorer π-acceptor properties. This is confirmed by the absorption and emission spectra of **1** and **2**. Replacement of a bpy ligand of $Os(bpy)_3^{2+}$ by bpt^- to give $Os(bpy)_2(bpt)^+$ causes small red shifts of the metal-to-ligand (Os → bpy) charge-transfer[26,27] absorption and emission bands (Table I). Coordination of a second $Os(bpy)_2^{2+}$ unit to the bpt^- bridging ligand implies the sharing of its negative charge between two $Os(bpy)_2^{2+}$ units, with an expected decrease of electronic density on the metal ions and a consequent blue shift of the Os → bpy CT levels. This effect, however, is negligible (Table I), whereas it was noticeable for the analogous Ru complexes. Apparently, for Os there is some compensation effect related to the more covalent character of the M-bpy bond. Anyway, the observed behavior contrasts with that of most of the polypyridine-type bridging ligands where the LUMO orbital is a π* orbital localized on the bridge and, as a consequence, the lowest CT band and the emission band move to lower energy in going from the mononuclear to the dinuclear compound.

It should also be recalled that in the dinuclear complex the coordination environment of the two Os(II) ions is not exactly the same, because the coordinating atoms N^4 and N^1 ($=N^2$) of the triazole ring are not equivalent. More specifically, in the bpt^- ligand the σ-donor ability of the N^1 (or N^2) position is greater than that on the N^4 position,[19] as confirmed by electrochemical measurements carried out on the two isomers of $Ru(bpy)_2$(pyridyltriazole)$^+$.[28] On these grounds, in **2** the lowest energy luminescent ^{3}MLCT state (of Os → bpy origin) is expected to be centered on the Os-containing unit attached to the N^1 (or N^2) position, and another ^{3}MLCT state localized on the other moiety of the molecule is expected at slightly higher energy. For the analogous Ru(II) complex, no evidence was found for the presence of this second ^{3}MLCT level. For **2**, however, the interpretation of the temperature dependence of the luminescence, discussed in the next section, appears to require the presence of two distinct emitting levels.

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Table III. Kinetic Parameters for Radiative and Radiationless Decay[a]

	$10^{-6}k_0$,[b] s^{-1}	$10^{-7}A_1$,[c] s^{-1}	ΔE_1,[c] cm^{-1}	$10^{-6}B_1$,[d] s^{-1}	T_{B_1}, K	$10^{-7}A_2$,[e] s^{-1}	ΔE_2,[e] cm^{-1}	T_{B_2}, K
$Os(bpy)_3^{2+}$	0.62	6.4	330	2.4	122			
$Os(bpy)_2(bpt)^+$	3.9	7.8	440	4.7	116			
$[Os(bpy)_2]_2(bpt)^{3+}$	1.7	1.8	170	3.5	119	4.2	220	160

[a] Nitrile solutions. Estimated uncertainties in derived quantities are 20% for energy and 10% for ln (rate). [b] Decay rate constant at 90 K, eq 2. [c] Frequency factor and activation energy of the Arrhenius term describing a nonradiative process taking place over the full T range. [d] Increase in the nonradiative rate constant related to solvent melting around $T = T_{B_1}$, eq 5. [e] Frequency factor and activation energy of an additional Arrhenium term, eq 6, describing a nonradiative process taking place for $T > T_{B_2}$.

Excited-State Decay. To account for the temperature dependence of the luminescence lifetime of $Ru(bpy)_3^{2+}$ and several other coordination compounds,[8] $1/\tau$ was expressed as a sum of a temperature-independent and some temperature-dependent terms:

$$1/\tau = k_0 + \sum_i k_i(T) \qquad (1)$$

The temperature-independent term can be expressed by

$$k_0 = k^r + k_0^{nr} \qquad (2)$$

where k^r is the radiative rate constant (usually taken to be temperature independent above 77 K[29]) and k_0^{nr} is a radiationless rate constant related to deactivation to the ground state via a weak-coupling mechanism.

For $Ru(bpy)_3^{2+}$ and other Ru(II)–polypyridine complexes,[8] the temperature-dependent terms were associated with different types of radiationless processes depending on the temperature range under observation, as discussed in the following.

In single crystals or frozen solvents ($T \leq 100$ K for alcoholic or nitrile solvents) and above the glass-to-fluid transition region of the solvent, the luminescence intensity has been found to decay according to a single-exponential law. For these cases, the involved radiationless processes could be described by an Arrhenius-type equation

$$k_i^{nr} = A_i \exp(-\Delta E_i/RT) \qquad (3)$$

The use of the above equation is consistent with thermal equilibration among a cluster of close-lying ($<10^2$ cm^{-1}) ^{3}MLCT energy levels.[8,10,30] In this case, Boltzmann population factors are numerically negligible and have been disregarded. The same treatment was applied to (i) thermal equilibration between the above mentioned set of states and high-lying (300–800 cm^{-1}) energy levels of similar electronic nature[31] and (ii) the crossover between the luminescent ^{3}MLCT cluster of states and nonluminescent ^{3}MC levels, which resulted in energy separations of 2000–4000 cm^{-1}.[8,10] A single-exponential decay of the luminescence was experimentally observed for all the above mentioned cases.

For the glass-to-fluid temperature interval, the radiationless processes could be related to effects (e.g., solvent repolarization) that do not occur at low temperature because of the frozen environment;[22,32-34] this second type of thermally activated process can be expressed by the empirical equation[32]

$$k_i^{nr} = \frac{B_i}{1 + \exp[C_i(1/T - T_{B_i})]} \qquad (4)$$

which describes a stepwise change of lifetime centered at a certain temperature T_{B_i}. In eq 4, C_i is a temperature related to the smoothness of the step and B_i is the increment for k_i^{nr} at $T \gg T_{B_i}$. This equation is particularly useful to describe the behavior of a system in the glass-fluid region of a solvent matrix.

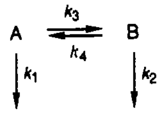
The ln ($1/\tau$) vs $1/T$ plots for $Os(bpy)_3^{2+}$[35] and **1** could be fitted by the equation

$$1/\tau = k_0 + A_1 \exp(-\Delta E_1/RT) + \frac{B_1}{1 + \exp[C_1(1/T - 1/T_{B_1})]} \qquad (5)$$

as is usually the case for mononuclear complexes that undergo luminescence from MLCT levels.[8] Such an equation, however, was not able to fit the plot of **2**. Addition to eq 5 of another "stepwise" term, eq 4, also gave unsatisfactory results. A good fitting (see Figure 3) was obtained by addition to eq 5 of a term:

$$k_2^{nr} = \frac{A_2 \exp(-\Delta E_2/RT)}{1 + \exp[C_2(1/T - 1/T_{B_2})]} \qquad (6)$$

The use of the above empirical equation for the fit of the experimental points of complex **2** requires some comments, as the spectral behavior of **2** is related to the presence of two luminescent excited states (see below). The photophysical behavior of a system composed of two such states is well-known.[36,37] When they exhibit energy-separate luminescence spectra, the expected decay of the emission is doubly exponential at any given wavelength covering the two luminescence regions. In this case, both decay constants are complex functions of four kinetic constants:



In the present case, however, we were unable to obtain a detailed resolution of the two decay constants, likely because the emission spectra related to the two states were overlapping. As a consequence, the reported results for complex **2** at $T > 170$ K were obtained by analyzing the luminescence decay according to a single-exponential law.

The values obtained for the various parameters from the best fitting procedure are shown in Table III. The ln ($1/\tau$) vs $1/T$ plots of the three complexes exhibit a comparable stepwise behavior in the temperature range 110–120 K. In the same temperature range, the emission maximum, E_{em}, moves to lower energy by 450, 200, and 330 cm^{-1} for $Os(bpy)_3^{2+}$, **1**, and **2**, respectively. Further heating to room temperature results in the raising of the luminescence level with respect to the value attained at 150 K; see Table I. The increment B_1 for k_1^{nr} at $T \gg T_{B_1}$ is quite similar (Table III) for the three complexes, suggesting that this step is related to the same physical process in all cases. As previously discussed for $Ru(bpy)_3^{2+}$,[38] this behavior can be related to repolarization rearrangements of the solvent molecules when the matrix begins to melt. On increasing temperature after this first step, the behavior of **2** differs considerably from that of $Os(bpy)_3^{2+}$ and **1**, showing a second step. Although the presence of two steps

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has been previously observed for other complexes,[15,32] this second step is rather unusual, since, as we have seen before, it cannot be described by an eq 4 type term. The behavior of the luminescence spectrum in the same temperature region is also unusual. As shown in Figure 4, at 170 K the emission maximum is slightly red-shifted and a large shoulder is present on the red side. On further increase of temperature, the emission spectrum moves to the blue and the shoulder disappears. This suggests that two closely lying MLCT excited states, differently influenced by the solvent repolarization, may be involved in the luminescence emission of **2**. One of the two states can be described as involving electron promotion from the Os center easier to oxidize (the one bound to N^1) to a proximate bpy ligand (bpy)(bpy$^-$)Os^{III}[N^1]bpt[N^4]Os^{II}(bpy)$_2^{3+}$ (state A). The nature of the other MLCT state, however, is less clear. We can speculate that such a state may correspond to one of the following transitions: (i) MLCT involving the same metal and ligand centers as for state A, but at higher energies (state B); (ii) MLCT involving the Os center bound to N^4 and a proximate bpy ligand, (bpy)$_2$Os^{II}[N^1]bpt[N^4]Os^{III}(bpy)(bpy$^-$)$^{3+}$ (state C); (iii) MLCT from the Os center bound to N^1 to a remote bpy ligand, (bpy)$_2$Os^{III}[N^1]bpt[N^4]Os^{II}(bpy)(bpy$^-$)$^{3+}$ (state D). Conversion from state A to state C and/or D would require a stronger solvent repolarization than the conversion from state A to state B. The need of an eq 6 type term to fit the photophysical results for $T > 170$ K (where the solvent is sufficiently fluid) suggests that state C or D could be responsible for the observed behavior.

The different behavior of the analogous dinuclear Ru complex[15] may be related to the different energy gap between the involved ^{3}MLCT levels and/or to the presence of fast deactivation via MC levels (see below). It should also be noted that the ln $(1/\tau)$ vs $1/T$ plot of mononuclear Ru(bpy)$_2$(bpt)$^-$ was found to exhibit a two-step behavior,[15] attributed to specific interactions of the vacant coordination sites with the solvent. The lack of such a behavior for **1** may be due to the more covalent character of the Os–N bonds (greater π-back-bonding in Os complexes compared to Ru complexes[10]) and, consequently, to the decreased amount of charge transferred (and consequent minor solvent interaction) in the ^{3}MLCT level.

It is important to point out that for the three osmium complexes the ln $(1/\tau)$ vs $1/T$ plots at high temperature ($T > 250$ K) do not exhibit the steep linear behavior shown by the plots of most Ru complexes.[8,15] This is in agreement with the fact that the energy gap between MLCT and MC excited states is much larger in the Os complexes than in the Ru complexes[10] and, as a consequence, the deactivation channel involving activated surface crossing to the upper lying ^{3}MC excited levels cannot enter into play. This is probably the reason for the lack of photochemical decomposition in the examined complexes.

Electrochemical Behavior. The electrochemical properties of **1** and **2** (Table II) are similar, as expected, to those of the analogous Ru complexes:[15,19] (i) the (metal-centered) oxidation potential becomes less positive going from Os(bpy)$_3^{2+}$ to Os(bpy)$_2$(bpt)$^+$, because bpt$^-$ is a better σ-donor and a worse π-acceptor than bpy; (ii) on coordination of a second Os(bpy)$_2^{2+}$ unit to Os(bpy)$_2$(bpt)$^+$, the first oxidation wave moves to more positive potentials, probably because of the increase in the positive charge of the molecule; (iii) the two separated oxidation waves of the dinuclear complex may be due to the nonequivalence of the chelating sites of the bridge and to electronic interactions between the two metal centers; (iv) the energy separation between the two waves (0.21 V) of **2** is smaller than that previously found for the analogous dinuclear Ru complex (0.30 V), suggesting that in the monooxidized Os complex there is less delocalization between the two metal centers;[39] (v) the first and second reduction potentials of Os(bpy)$_2$(bpt)$^+$ correlate well with the first and second reduction potentials of Os(bpy)$_3^{2+}$ and can thus be assigned to reduction of the coordinated bpy ligands; (vi) the shift toward negative potentials in going from Os(bpy)$_3^{2+}$ to Os(bpy)$_2$(bpt)$^+$ is again explained by the differences in the coordination properties of bpy and bpt$^-$; (vii) on coordination of another Os(bpy)$_2^{2+}$ unit to Os(bpy)$_2$(bpt)$^+$, the reduction waves for bpy split into two components and move to less negative potentials because of the large positive charge of the bimetallic complex; (viii) from **1** to **2** the wave splitting on reduction is much smaller (actually, the first reduction is a bielectronic process) than that observed on oxidation because the two centers involved in the reduction are more separated than the two centers involved in the oxidation.

Conclusions

The mononuclear M(bpy)$_2$(bpt)$^+$ and dinuclear [(M(bpy)$_2$]$_2$(bpt)$^{3+}$ complexes (M = Ru[15] or Os) show quite interesting photophysical, photochemical, and electrochemical properties. The π^* LUMO orbital, which is responsible for the lowest energy MLCT singlet and triplet excited levels and for the less negative reduction potentials, is centered on a terminal bpy ligand.

In other words, the briding ligand bpt$^-$ is not a trap for energy and electrons and thus it appears a convenient bridge for polynuclear complexes which can exhibit photoinduced energy or electron migration. The luminescence and redox properties of the mononuclear and dinuclear complexes are substantially those of the M(bpy)$_2^{2+}$ unit, perturbed to a different degree in the monomer and dimer.

A detailed study of the temperature dependence of the luminescence (spectra and lifetimes) has evidenced substantial differences in the radiationless decay paths of the various complexes. The most important point is that the Ru monomer[15] and the Os mononuclear and dinuclear compounds do not undergo surface crossing to the reactive ^{3}MC level at room temperature. This is also shown by the lack of photodecomposition reactions for such compounds.

From the results obtained, it appears that the Ru–Os mixed-metal dinuclear complexes could be quite interesting compounds for an investigation of intracomponent energy- and electron-transfer processes. Investigations in this direction are now in progress in our laboratories.

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