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Mono- and Dinuclear Complexes of Ruthenium(II) and Osmium(II) with a 3,5-Bis(2-pyridyl)-1,2,4-triazole Cyclohexyl-Bridged Spacer. Absorption Spectra, Luminescence Properties, and Electrochemical Behavior

Gaetano Giuffrida,[1a] Giuseppe Calogero,[1a] Giovanni Guglielmo,[1a] Vittorio Ricevuto,[1a] Mauro Ciano,[1b] and Sebastiano Campagna*,[1a]

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, v. Sperone 31, I-98166 Vill. S. Agata, Messina, Italy, and Istituto FRAE-CNR, v. Castagnoli 1, I-40126 Bologna, Italy

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Two novel dinuclear complexes of Ru(II) and Os(II) with a bis-chelating bridging ligand based on 3,5-bis(2-pyridyl)-1,2,4-triazole moieties have been synthesized, and their absorption spectra, electrochemical behavior, and luminescence properties have been studied. For comparison purposes, the parent mono-chelating ligand and its mononuclear complexes have also been synthesized and their properties have been studied. The investigated complexes are $(bpy)_2M(dpt\text{-}cy''\text{-}dpt)M(bpy)_2^{4+}$ and $(bpy)_2M(dpt\text{-}cy')^{2+}$ ($M = Ru^{2+}$ or Os^{2+}; bpy = 2,2′-bipyridine; dpt-cy″-dpt = *trans*-1,4-cyclohexanebis(N^4-3,5-bis(2-pyridyl)-1,2,4-triazole)amide; dpt-cy′ = N^4-cyclohexane-3,5-bis(2-pyridyl)-1,2,4-triazole). Their absorption spectra exhibit intense bands (ϵ in the range 10^4–10^5 M^{-1} cm^{-1}) in the UV region due to bpy-centered transitions and moderately intense bands (ϵ in the range 10^3–10^4 M^{-1} cm^{-1}) in the visible region that can be assigned to metal-to-bpy charge-transfer (MLCT) transitions. The extinction coefficients of the bands of the dinuclear complexes are about twice those of the corresponding bands of the mononuclear species. All the complexes exhibit reversible, metal-based oxidation processes and reversible, bpy-based reduction processes in the potential window investigated (−1.8 V/+1.7 V vs SCE). In particular, the differential pulse voltammograms of the dinuclear compounds exhibit only one oxidation peak at approximately the same potential of the oxidation processes of the corresponding mononuclear species (+1.30 V and +0.80 V for Ru and Os compounds, respectively). This indicates that the metal ions of the dinuclear compounds undergo simultaneous oxidation. Complexes and ligands are luminescent both at room temperature in acetonitrile fluid solution and at 77 K in 4:1 MeOH/EtOH (v/v) rigid matrix. The ligands fluorescence, attributed to a π–π^* level, is completely quenched in the complexes. The luminescence of the complexes can be attributed to the lowest energy triplet M → bpy charge-transfer excited state(s). Luminescence energies and lifetimes are practically unchanged on passing from mono- to dinuclear species. The results obtained indicate that only a weak electronic interaction is possible between the metal units across the cyclohexyl-bridged spacer, so that the metal components maintain their own excited-state and redox properties when they are arranged into the (supramolecular) dinuclear arrays.

Introduction

Assembly of molecular components that exhibit suitable redox and excited state properties can lead to photochemical molecular devices capable to perform useful light-induced processes.[2] Such supramolecular species can be designed on the basis of (i) building blocks that exhibit suitable ground and excited state properties and (ii) spacers capable of linking the building blocks to form appropriate supramolecular arrays and providing the electronic coupling for the occurrence of intercomponent energy- and electron-transfer processes.[2,3]

Ru(II) and Os(II) complexes of polypyridine-type ligand are ideal building blocks[4,5] for the design of supramolecular systems capable to perform light-induced functions. In the last few years many supramolecular systems based on polynuclear Ru(II) and Os(II) polypyridine complexes have been synthesized and their intercomponent energy and electron transfer processes have been studied.[6,7] Recently, systems containing up to 22 Ru(II) polypyridine units have been reported.[7e] In most cases, the spacer between the metal units is a polychelating ligand and its structure is quite important in determining the geometrical arrangement of the polynuclear species and its properties. Therefore, much attention is currently devoted to the design and synthesis of novel spacers capable to play the role of bridging ligands.

Here we report syntheses, absorption spectra, electrochemical behavior, and luminescence properties of dinuclear Ru(II) and Os(II) complexes of a novel bridging ligand based on two 3,5-bis(2′-pyridyl)-1,2,4-triazole moieties connected by a cyclohexyl-

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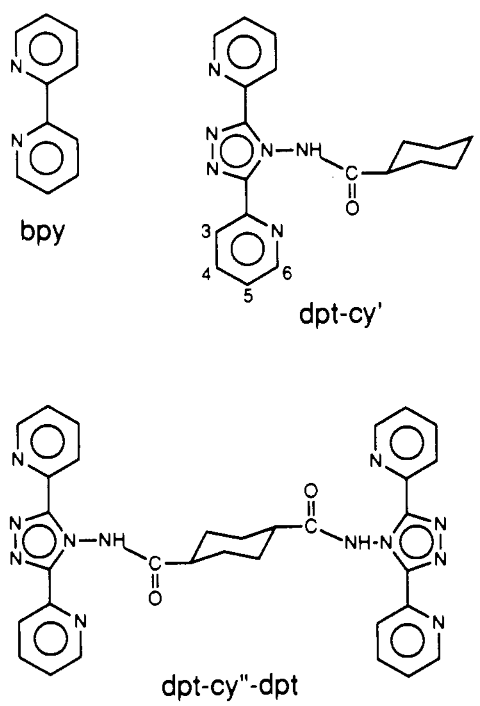

Figure 1. Structural formulas of the ligands. The positions of the pyridine ring are numbered to help ^{1}NMR assignments (see text).

derivative spacer (dpt-cy"-dpt, see Figure 1). The properties of the mononuclear parents, as well as those of the free bischelating bridging ligand and of its monochelating unit (dpt-cy′, Figure 1) have also been studied.

Experimental Section

General Information. $Ru(bpy)_2Cl_2$[8] and $Os(bpy)_2Cl_2$[9] were prepared according to literature methods. 4-Amino-3,5-bis(2′-pyridyl)-1,2,4-triazole and the other chemicals were purchased from Aldrich and used as received. All reactions were carried out under argon. Absorption spectra in the UV and visible region were performed with a Kontron Uvikon 860 spectrophotometer. Luminescence spectra were recorded with a Perkin Elmer LS-5B spectrofluorimeter equipped with a red sensitive Hamamatsu R928 phototube, and luminescence lifetimes were measured with an Edinburgh FL 900 single-photon counting spectrometer. For the low-temperature measurements, a homemade finger dewar was employed. The electrochemical behavior was studied in acetonitrile solution by cyclic voltammetry and differential pulse voltammetry; the ferrocene/ferrocenium redox couple was used as an internal standard, SCE as the reference electrode and tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Further details and procedures for electrochemical experiments and elemental analyses and IR spectra have been previously reported.[7b,10]

Syntheses. Dpt-cy′. To a solution of 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole (0.100 g, 0.42 mmol) in benzene (20 mL) was added cyclohexanecarbonyl chloride (0.064 mL, 0.48 mmol). A white powder was obtained, filtered, washed with diethyl ether 1:2 (v/v), and then purified by crystallization from 1:2 ethanol/diethyl ether (v/v). ^{1}NMR (CD_3Cl): δ 8.78 (m, *H*6), 8.48 (m, *H*5 or *H*4), 8.19 (m, *H*4 or *H*5), 7.69 (m, *H*3), 3.20 (broad, N*H*), 1.80 (m, aliphatic *H*), 1.35 (m, aliphatic *H*). Anal. Calcd for $C_{19}H_{20}N_6O$: C, 65.51; H, 5.74; N, 24.13. Found: C, 65.40; H, 5.70; N, 24.25. Yield after purification: 86%.

Dpt-cy"-dpt. To a solution of *trans*-1,4-cyclohexanedicarboxylic acid (0.200 g, 1.16 mmol) in benzene (25 mL) was added thionyl chloride (2 mL), and the mixture was refluxed for 30 min. The excess of thionyl chloride was eliminated by distillation. The solution was rotary evaporated in vacuo and the *trans*-1,4-cyclohexanedicarbonyl chloride obtained as a white solid was dissolved in benzene (25 mL). A solution of 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole (0.560 mg, 2.32 mmol) in benzene (25 mL) was added, and the white powder obtained was isolated by filtration and purified by repeated crystallizations from 1:2 ethanol/diethyl ether (v/v). ^{1}NMR characterization was forbidden because of the low solubility in CD_3Cl. Anal. Calcd for $C_{32}H_{28}N_{12}O_2$: C, 62.74; H, 4.57; N, 27.45. Found: C, 62.75; H, 4.44; N, N, 27.60. Yield after purification: 82%.

$[Ru(bpy)_2(dpt\text{-}cy')](PF_6)_2\cdot 2H_2O$ (1). A solution of $Ru(bpy)_2Cl_2\cdot 2H_2O$ (0.030 g, 0.062 mmol) in ethanol (20 mL) was refluxed for 3 h, and then dpt-cy′ (0.025 g, 0.072 mmol) was added. The mixture was refluxed for another 2 h, cooled, and rotary evaporated in vacuo to 5 mL. A small excess of solid KPF_6 was added. After 30 min a brown red solid was obtained that was filtered, washed with diethyl ether, and recrystallized several times from 1:3 ethanol/acetonitrile (v/v). The product was chromatographed on alumina (eluant 1:2:1 dichloromethane/ethanol/diethyl ether), redissolved in dichloromethane, filtered, rotary evaporated in vacuo, washed with ethanol, and recrystallized from 1:2 ethanol/diethyl ether (v/v). Anal. Calcd for $C_{39}H_{40}N_{10}O_3P_2F_{12}Ru$: C, 43.05; H, 3.67, N, 12.87. Found: C, 42.89; H, 3.65; N, 12.50. Yield after purification: 60%.

$[(bpy)_2Ru(\mu\text{-}dpt\text{-}cy''\text{-}dpt)Ru(bpy)_2](PF_6)_4\cdot 2H_2O$ (2). The synthetic procedure was analogous to that described for **1**. Employed quantities: $Ru(bpy)_2Cl_2\cdot 2H_2O$, 0.040 g, 0.082 mmol; ethanol, 25 mL; dpt-cy"-dpt, 0.021 g, 0.035 mmol; red-brown powder. Anal. Calcd for $C_{72}H_{64}N_{20}O_4P_4F_{24}Ru_2$: C, 42.06; H, 3.11; H, 13.63. Found: C, 42.10; H, 3.18; N, 14.05. Yield after purification, 58%.

$[Os(bpy)_2(dpt\text{-}cy')](PF_6)_2$ (3). A solution of $Os(bpy)_2Cl_2$ (0.016 g, 0.029 mmol) in ethanol (20 mL) was refluxed for 6 h, and then dpt-cy′ (0.020 g, 0.058 mmol) was added. The mixture was refluxed for another 7 h, rotary evaporated in vacuo, and chromatographed on alumina (eluant 1:2:1 dichloromethane/ethanol/diethyl ether). The first fraction to be eluted was a violet compound that was discarded. The second fraction to be eluted was the desired product, obtained as a green species. An orange fraction (unidentified compound) remained on the column. The green fraction was rechromatographed, and no traces of violet or orange compounds were found. The green fraction was collected, rotary evaporated, dissolved in ethanol (10 mL), and then precipitated as hexafluorophosphate salt by adding a KPF_6-saturated aqueous solution (5 mL), and recrystallized from ethanol/diethyl ether 1:2 (v/v). Anal. Calcd for $C_{39}H_{36}N_{10}OP_2F_{12}Os$: C, 41.04; H, 3.15; N, 12.27. Found: C, 41.52; H, 3.06; N, 12.45. Yield after purification, 40%.

$[(bpy)_2Os(\mu\text{-}dpt\text{-}cy''\text{-}dpt)Os(bpy)_2](PF_6)_4$ (4). The synthetic procedure was analogous to that described for **3**. Employed quantities: $Os(bpy)_2Cl_2$, 0.030 g, 0.052 mmol ethanol, 35 mL; dpt-cy"-dpt, 0.013 g, 0.021 mmol; brown powder. Anal. Calcd for $C_{72}H_{60}N_{20}O_2P_4F_{24}Os_2$: C, 39.33; H, 2.73; N, 12.74. Found: C, 39.10; H, 2.70; N, 12.50. Yield after purification, 65%.

Infrared spectra of all the new compounds gave results in agreement with the expectations.

Results

The synthetic procedures for obtaining the novel ligands and complexes are illustrated in Schemes I and II. The absorption spectra of dpt-cy′ and dpt-cy"-dpt free ligands in acetonitrile solution are quite similar in shape. They exhibit a strong absorption in the UV region with maxima at 288 nm (ϵ = 14 000 M^{-1} cm^{-1} and 23 000 M^{-1} cm^{-1} for dpt-cy′ and dpt-cy"-dpt, respectively) and 246 nm (ϵ = 10 800 M^{-1} cm^{-1} and 17 800 M^{-1} cm^{-1} for dpt-cy′ and dpt-cy"-dpt, respectively). A shoulder is also apparent at about 330 nm in the spectrum of the bischelating ligand. All the complexes exhibit very intense absorptions in the UV region (ϵ in the range 10^4–10^5 M^{-1} cm^{-1}), typical of bpy-containing complexes.[4] Beside such UV absorptions, the complexes display a moderately intense absorption in the visible region (ϵ in the range 10^3-10^4 M^{-1} cm^{-1}). The Os-containing complexes also exhibit a noticeable absorption in the red tail of the visible region. Table I collects data on the absorption properties of all

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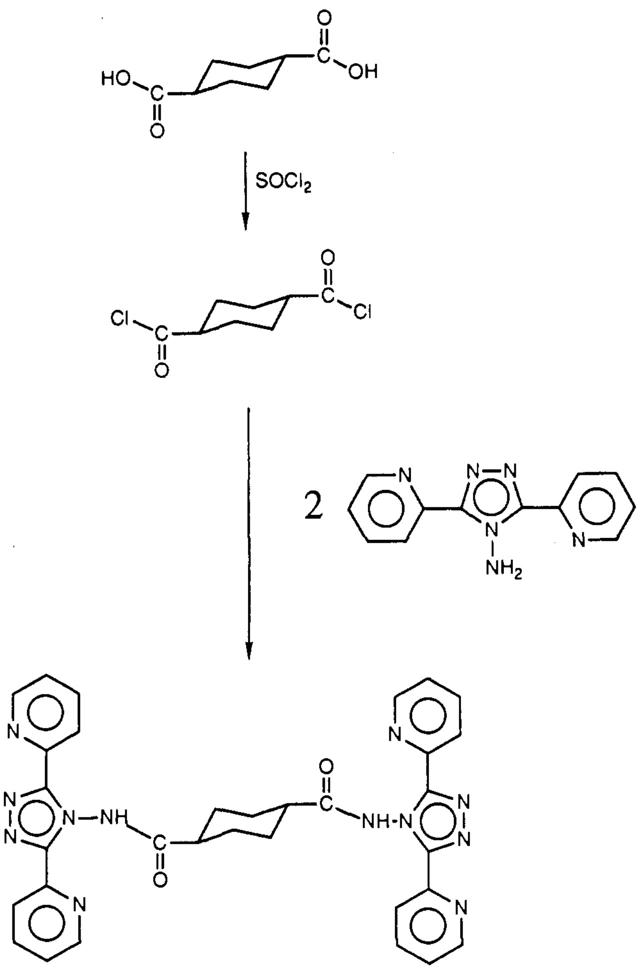
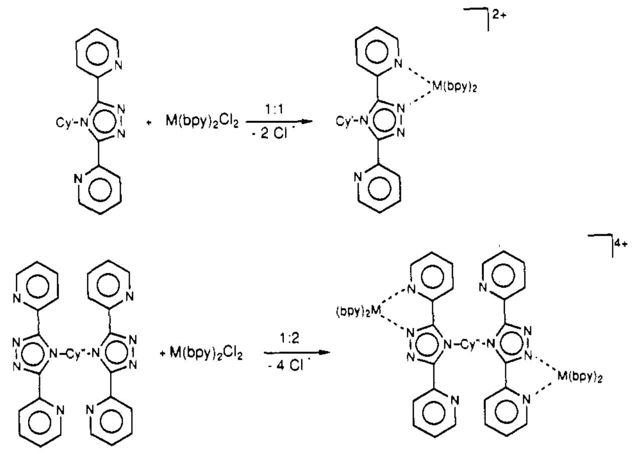
Scheme I



Scheme II



the new complexes and ligands. Figure 2 shows the absorption spectra of **3** and **4** in AN solution at room temperature.

Both complexes and free ligands exhibit luminescence in AN solution at room temperature and in 4:1 MeOH/EtOH (v/v) rigid matrix at 77 K. The luminescence lifetimes of the free ligands are shorter than the limit of our equipment (~2 ns), whereas the luminescence lifetimes of the complexes are in the microsecond range at 77 K and ten times shorter at room temperature. A vibrational progression (~1300 cm^{-1}) is apparent in the low temperature spectra. Data on luminescence properties are gathered in Table I, and luminescence spectra of **4** are shown in the inset of Figure 2.

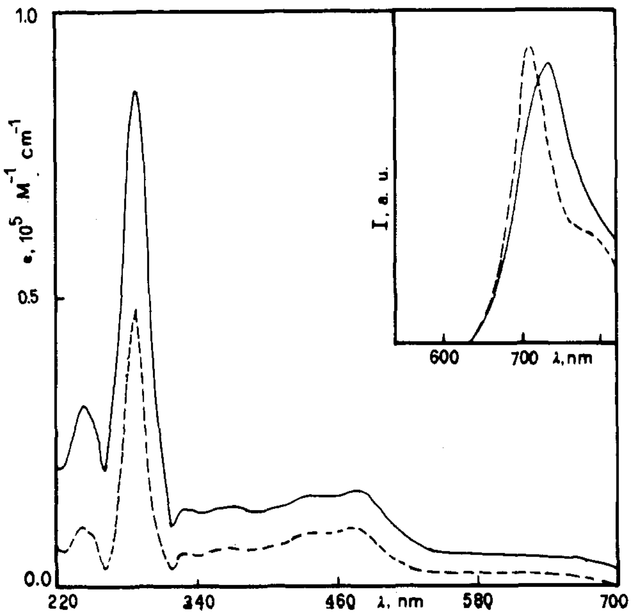


Figure 2. Absorption spectra of **4** (—) and **3** (- - -) in acetonitrile solution at room temperature and (inset) luminescence spectra of **4** in acetonitrile solution at room temperature (—) and in 4:1 MeOH/EtOH (v/v) rigid matrix at 77 K (- - -).

On oxidation, all the complexes exhibit only a reversible oxidation peak in the potential window examined (<+1.7 V vs SCE). Comparison with the intensity of the ferrocene/ferrocenium peak indicates that the oxidation peak of the dinuclear compounds comprises two one-electron processes. The reduction patterns are similar in all the complexes, displaying two reversible reduction peaks; as for oxidation, each reduction peak of the dinuclear compounds comprises two one-electron processes. The electrochemical data are collected in Table II.

Discussion

The spectroscopic, photophysical, and electrochemical properties of ruthenium and osmium polypyridine-like complexes are usually discussed with the approximation of localized molecular orbitals. Within this assumption, the excited states and electronic transitions are classified as metal centered (MC), ligand centered (LC), and charge transfer (either metal-to-ligand, MLCT, and ligand-to-metal, LMCT), while the redox processes can be defined as metal centered and ligand centered.[4,5]

Electrochemistry. By comparison with the well-known oxidation behavior of Ru(II) and Os(II) complexes of polypyridine ligands,[4,5] the oxidation peaks of the mononuclear complexes **1** and **3** can be assigned to oxidation of the Ru^{2+} and Os^{2+} metal ions, respectively. The potential values of the processes are in good agreement with the literature data, and confirm the expectation that Os^{2+} is easier to oxidize than Ru^{2+} in analogous compounds.[4b,5,7b,c]

To discuss the reduction patterns, one has to take into account that dpt ligands are electron-rich ligands, so that their reduction is expected to occur at very negative potentials.[11,12] Therefore, the reduction peaks at –1.25 V and –1.58 V of **3** and at –1.30 V and –1.54 V of **1** can be confidently assigned to the successive reductions of the two bpy ligands. This ligand-centered assignment is further confirmed by the very small changes of the reduction potentials of the complexes on passing from the Ru(II)

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Table I. Spectroscopic and Photophysical Data[a]

			luminescence			
		absorption	298 K		77 K[b]	
no.	compd	λ_{max}, nm[c] (ϵ, M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, μs
1	$[Ru(bpy)_2](dpt\text{-}cy')^{2+}$	445 (14 000)	632	100	585	5.10
2	$[Ru(bpy)_2]_2(dpt\text{-}cy''\text{-}dpt)^{4+}$	446 (25 000)	638	115	585	4.37
3	$[Os(bpy)_2](dpt\text{-}cy')^{2+}$	477 (9200)	730	50	715	1.06
4	$[Os(bpy)_2]_2(dpt\text{-}cy''\text{-}dpt)^{4+}$	477 (15 600)	725	42	716	0.95
	dpt-cy′	288 (14 000) 245 (10 800)	418	<10	410	<0.01
	dpt-cy″-dpt	288 (22 000) 246 (17 800)	420	<10	410	<0.01

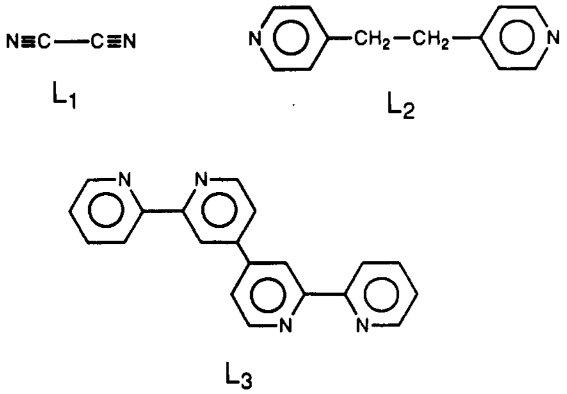
[a] Acetonitrile aerated solutions, unless otherwise noted. Experimental errors as follows: absorption maxima, ±2 nm; luminescence maxima, ±4 nm; extinction coefficients, 15%; luminescence lifetimes, 10%. [b] Methanol/ethanol 4:1 (v/v) rigid matrix. [c] Lowest energy maximum.

Table II. Electrochemical Data[a]

		$E_{1/2}$, V		
			redn	
no.	compd	oxidn		
1	$[Ru(bpy)_2](dpt\text{-}cy')^{2+}$	+1.32	−1.28	−1.52
2	$[Ru(bpy)_2]_2(dpt\text{-}cy''\text{-}dpt)^{4+}$	+1.33[b]	−1.30[b]	−1.54[b]
3	$[Os(bpy)_2](dpt\text{-}cy')^{2+}$	+0.84	−1.28	−1.56
4	$[Os(bpy)_2]_2(dpt\text{-}cy''\text{-}dpt)^{4+}$	+0.84[b]	−1.27[b]	−1.58[b]

[a] Acetonitrile solution, room temperature; $E_{1/2}$ values vs SCE; supporting electrolyte was tetraethylammonium perchlorate; experimental errors on peak potentials are ±10 mV. [b] Dielectronic peak.

Scheme III



to the Os(II) core, which indicates that the metal ions are not significantly involved in the reduction processes.

For dinuclear complexes, investigation of the oxidation behavior is very useful to determine the extent of electronic interaction between the metal units. In general, noticeable electronic interaction produces "stabilization" of the mixed-valence complex, with a splitting of the otherwise equivalent two metal-centered oxidation potentials.[13-17] Electronic interaction between metal units is mediated by the bridging ligand.[2c,d,14,15] Such a "communication" is mainly affected by the electronic properties of the spacer, e.g., the electronic overlap between the frontier orbitals of the spacer interfaced with the metal units, including geometric parameters such as orientation and distance.[2d] The more the bridging ligand is effective in transmitting electronic interaction, the larger is the difference between the first and second oxidation potentials of the dinuclear compound. The situation is examplified in its extreme cases by (i) complete delocalized systems such as $[(NH_3)_5Ru(L_1)Ru(NH_3)_5]^{4+}$ (for L_1, see Scheme III),[14d] in which one-electron oxidation leads to very stable and redox-resistant 5+/charged compounds having the same +2.5 formal charge residing in each metal ion, and (ii) systems exhibiting negligible electronic interaction between metal units, such as $[(NH_3)_5Ru(L_2)Ru(NH_3)_5]^{4+}$,[14d] and $[(bpy)_2Ru(L_3)Ru(bpy)_2]^{4+}$,[15l] in which oxidation of the two independent, non-interacting metal centers occurs at the same potential. The nature of the peripheral ligands can also affect the "communication" across the bridge.[10,18]

The dinuclear compounds studied in this work exhibit only one oxidation peak in the potential window examined (<1.7 V vs SCE), which by comparison with the oxidation peaks of the corresponding mononuclear species[19] is attributed in both cases to simultaneous one-electron oxidation of the two independent, weakly-interacting metal units.[20,21] Therefore, the cyclohexyl-bridged bis(pyridyl)triazole spacer is closer to case (ii) than to case (i), i.e. it assumes only weak coupling (at the best) between the metal components that it connects. However, it should be pointed out this does not mean that the dpt-cy″-dpt bridging ligand is an unsuitable spacer for energy- and/or electron-transfer processes between components of supramolecular systems, as fast energy- and/or electron-transfer processes need only electronic couplings as small as tens of cm^{-1}.[2c,d] This small electronic coupling is less than the limit necessary to cause a splitting of the oxidation potentials of the metal centers. A more valuable assessment of the electronic interaction and the allowness of energy- and electron-transfer processes between metal units across

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(13) This discussion refers to dinuclear compounds constituted by equivalent subunits, as are the $M(bpy)_2(dpt)^{2+}$ subunits in the present case ("symmetric" dinuclear compounds). The situation is more complicated, yet qualitatively equivalent, in the case of "asymmetric" dinuclear compounds.[10,17]

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(16) An electrostatic term depending on the distance between the metal units play also a role in splitting the oxidation potential of the metal units of polynuclear compounds.[11,12,14]

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(19) The procedure for comparing the oxidation peaks is the same as described in ref 7b for determining the number of electrons exchanged in a series of decanuclear metal complexes.

(20) Bard, Anson, and co-workers[21] have shown that molecules containing a number of identical noninteracting centers exhibit current–potential responses having the same shape as that obtained with the corresponding molecule containing a single center. Only the magnitude of the current is enhanced by the presence of additional electroactive centers.

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the dpt-cy″-dpt spacer needs the synthesis of asymmetric, heterometallic polynuclear compounds.

The reduction patterns of the dinuclear species are predictable from the results obtained from the mononuclear species and the non-interacting nature of the metal units as indicated by the oxidation behavior. Indeed, the differential pulse voltammograms and the cyclic voltammograms of both **2** and **4** exhibit a series of two reversible reduction peaks, each of them comprising two exchanged electrons. In both complexes, the first peak is attributed to simultaneous one-electron reduction of a bpy ligand of each of the two different metals, and the second peak refers to simultaneous reduction of the two remaining bpy ligands. The electron-rich dpt-cy″-dpt spacer is not reduced within the potential window investigated.

Absorption Spectra. The strong absorption bands that are present in the spectra of the free ligands can be assigned to π-π^* transitions involving the bis(pyridyl)triazole moieties. The very similar (but not identical) absorption spectra of the dpt-cy′ and dpt-cy″-dpt ligands and the constancy of the absorption maxima of the bands on passing from the monochelating to the bischelating ligand confirms a weak electronic coupling between the triazole-derivative units of dpt-cy″-dpt across the cyclohexyl spacer.

Since the electrochemical behavior of complexes and ligands and absorption spectra of the ligands suggest that the dinuclear compounds can be considered as constituted by two almost independent $M(bpy)_2(dpt)^{2+}$ moieties, the shapes of the absorption spectra of **2** and **4** are expected to be quite similar to those of **1** and **3**, respectively, with the molar absorptivity of the bands in the dinuclear compounds twice as much the molar absorptivity of the corresponding bands of the mononuclear ones. The experimental results are in good agreement with such a hypothesis (see Table I, Figure 2). The absorption bands with maxima at about 445 nm in the Ru(II) complexes and at 477 nm in the Os(II) complexes are assigned to metal-to-bpy CT transitions, while the intense bands at 285 nm (Ru complexes) and 289 nm (Os complexes) are attributed to bpy-centered π–π^* transitions. These assignments are based on the extinction coefficients, the electrochemical data, and previous results on similar complexes.[4,5,11,12] The ligand-centered absorptions due to dpt-cy′ and dpt-cy″-dpt ligands are probably obscured in the absorption spectra of the complexes by the much stronger bpy-centered transitions occurring in the same region.

The intense absorption tails of the spectra of **3** and **4** toward the red region, typical of Os(II) polypyridine complexes, are due to singlet–triplet MLCT transitions, which are partially allowed because of the strong spin–orbit coupling induced by the heavy osmium atom.[5,7d]

Luminescence. Emission of Ru(II)- and Os(II)–polypyridine complexes usually occurs from the lowest-lying, triplet MLCT excited state(s).[4,5] This assignment holds true for our complexes, with bpy playing the role of the acceptor ligand in the charge-transfer transition. The blue-shift of the emission energy on passing from fluid solution at room temperature to rigid matrix at 77 K (Table I, Figure 2) is typical of MLCT emitters[4,22] and is mainly due to the impossibility for the "frozen" solvent to reorganize around the excited molecule.[23] The circumstance that such an effect is more noticeable for the Ru complexes than for the Os compounds can be attributed to a smaller charge-transfer character of the MLCT excited state(s) in Os compounds because of the more covalent character of the Os–ligand bond.[5] The longer luminescence lifetimes at 77 K with respect to those at room temperature (Table I) are due to slowing down of the radiationless transitions (including matrix-assisted decay and thermal-activated population of short-lived, upper-lying excited states[4]) on decreasing temperature.

The vibrational progression (~1300 cm^{-1}) that can be noted in the low temperature emission spectra supports the MLCT assignment of the luminescence, since it corresponds to the C=C and C=N stretching modes, the dominating high-frequency energy acceptor modes of CT levels involving pyridine-type ligands.[4,24]

It is interesting to note that the constancy (within the experimental uncertainties) of the luminescence energies and lifetimes on passing from mono- to dinuclear species indicates that each metal component maintains its own excited state decay characteristics in the (supramolecular) dinuclear array.

Conclusions

We have reported the synthesis of a novel cyclohexyl-bridged binucleating ligand and of its dinuclear compounds with the Ru(bpy)$_2$– and Os(bpy)$_2$–metal units and studied the spectroscopic, photophysical, and electrochemical properties of such complexes. The results obtained suggest that the properties of each metal-based component are essentially maintained in the (supramolecular) dinuclear arrays. In particular, multielectron redox processes have been evidence to occur in the dinuclear species, indicating a weak interaction of the metal units across the cyclohexyl-bridged spacer. Such properties make these compounds interesting as potential light-active multielectron transfer catalysts.

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