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Osmium(II)/Ruthenium(II) Trimetallics Incorporating Polyazine Bridging Ligands: Isovalent Near-IR Absorbers with Unique Electrochemical Behavior

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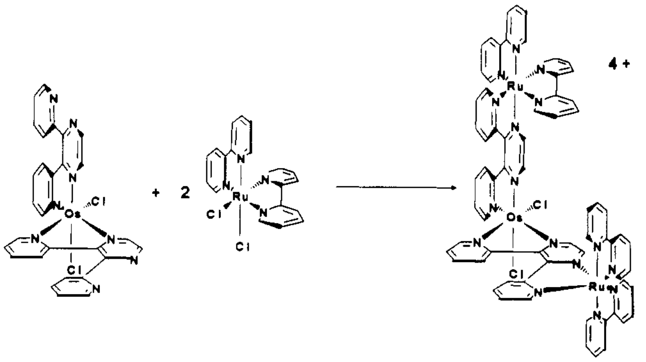
A series of mixed-metal Os(II)/Ru(II) trimetallic complexes bridged by polypyridyl ligands have been prepared of general form $\{[(bpy)_2Ru(BL)]_2OsCl_2\}^{4+}$ (where BL = 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)-quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb), and bpy = 2,2′-bipyridine). The compounds have been characterized by UV/vis absorption and near infrared spectroscopy, cyclic and Osteryoung square-wave voltammetry, and spectroelectrochemistry. The complexes display absorptions throughout the visible region of the spectrum and exhibit complicated electrochemical behavior. All of the systems studied possess both osmium- and ruthenium-based oxidative processes with the ruthenium-based oxidation occurring at significantly more positive potentials. The lowest lying bridging ligand-based π^* orbital shifts to lower energies as the π delocalization of the bridging ligand increases giving bridging ligand-based reductions which shift to more positive potentials on going from dpp to dpq to dpb (−756, −388, and −260 mV, respectively). Unlike previously prepared mono- and mixed-metal bimetallic complexes utilizing these bridging ligands, the metal-based Os(II/III) oxidation in these trimetallics varies dramatically depending upon the bridging ligand employed. The electrochemical behavior of these species is also unique for polymetallic systems in that the bridging ligands are only reduced by one electron each prior to reduction of the bpy ligands. In addition, the two equivalent terminal ruthenium metal centers in the dpq and dpb complexes oxidize at different potentials, although they are separated by a BL–Os–BL network. The lowest lying excited state of these molecules is an Os(dπ) → BL(π^*) MLCT based on the central metal center. This transition shifts to the red as the easier to reduce dpq and dpb ligands are incorporated into the trimetallic system. In fact, this MLCT occurs in the near-IR region of the spectrum at 966 nm for the dpq-bridged system and 1059 nm for the dpb-bridged system.

Introduction

As a result of their unique photophysical and photochemical properties, an enormous amount of emphasis has been placed on the excited state properties of polypyridyl-ruthenium and -osmium complexes, most notably $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and its derivatives.[1] This interest has been due in part to the variety of excited state electron and energy transfer properties these complexes possess.[1]

A major problem often encountered in the utilization of compounds such as $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ for excited-state electron and energy transfer photosensitization is the need for the excited state of the bipyridyl complexes to collide with an energy or electron acceptor and then transfer energy or electrons during the excited state lifetime of these complexes. This requirement often leads to inefficient photosensitization. Polymetallic systems, on the other hand, are designed to bring together all of the reaction partners so that a bimolecular collisional process is not required to initiate the excited state electron or energy-transfer reaction.[2-8] Another advantage in the use of polymetallic complexes is their ability to act as "electron reservoirs" which opens up the possibility of using these systems in schemes which require multielectron processes.

In order to design polymetallic systems with tunable ground- and excited-state properties, it is necessary to assemble and probe such systems. Mixed-metal complexes are of interest due to their multicomponent nature. Within this framework we have synthesized compounds of the general form $\{[(bpy)_2Ru(BL)]_2OsCl_2\}^{4+}$ (where BL = 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)-quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb), and bpy = 2,2′-bipyridine). A schematic for the synthesis of $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$ is shown as follows:



This series of complexes can be prepared in good yield using the synthetic methodology outlined above. The bridging ligands used

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(1) See, for example: (a) Navon, G.; Sutin, N. *Inorg. Chem.* **1974,** *13,* 2159. (b) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972,** *94,* 8238. (c) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976,** *98,* 6536. (d) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974,** *96,* 4710. (e) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B.P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979,** *101,* 4815. (f) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978,** *No. 168,* 1. (g) Meyer, T. J. *Acc. Chem. Res.* **1978,** *11,* 94. (h) Sabbatini, N.; Balzani, V. *J. Am. Chem. Soc.* **1972,** *94,* 7587. (i) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1972,** *93,* 1800. (j) Kane-Maguire, N. A. P.; Langford, C. H. *J. Am. Chem. Soc.* **1972,** *94,* 2121. (k) Burstall, F. H. *J. Chem. Soc.* **1936,** 173.

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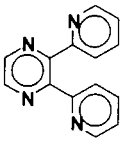
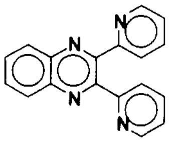
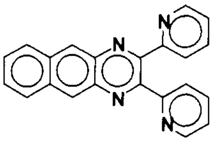
are similar to bpy but have the added ability to coordinate additional metal centers through the remote nitrogens, making possible the development of these multimetallic systems. These three ligands differ from one another only by the addition of electron-withdrawing benzene rings fused to the side of the pyrazine ring, shown as follows:



dpp



dpq



dpb

This results in a net stabilization of the lowest-unoccupied π^* orbital.

The trimetallic complexes reported herein clearly demonstrate how the ground-state electrochemical and metal-to-ligand charge-transfer (MLCT) excited-state properties of these mixed-metal systems are dependent upon the nature of the bridging polypyridyl ligand and the synthetic design of the molecule as well as how this complex behavior can be elucidated by synthetic variations.

Experimental Section

Materials. 2,3-bis(2-pyridyl)pyrazine (dpp)[9] was purchased from Aldrich Chemical Co. 2,3-Bis(2-pyridyl)quinoxaline (dpq),[9] 2,3-bis(2-pyridyl)benzoquinoxaline (dpb),[9] and $[Ru(bpy)_2Cl_2]$[10] were synthesized according to the literature procedures. The acetonitrile used in the electrochemical measurements was spectroquality (Burdick and Jackson), and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), was prepared from tetrabutylammonium bromide (Aldrich) and HPF_6 (Aldrich), recrystallized several times from ethanol, and stored in a vacuum desiccator prior to use. All other chemicals were Fisher Scientific and used without further purification.

$Os(BL)_2Cl_2$. The monometallic bis-bridging ligand precursor complexes were prepared by a modification of the method of Buckingham et al. for the synthesis of $Os(bpy)_2Cl_2$.[11] A 1-equiv amount of K_2OsCl_6 was combined with 2 equiv of either dpp, dpq, or dpb in DMF, and the mixture was heated at reflux for a period of 1 h. The solution was then removed from the heating source, and a saturated solution of $Na_2S_2O_4$ was added. The flask was cooled in an ice bath. Upon cooling, a microcrystalline product formed in each case, which was then collected by vacuum filtration and washed with copious amounts of deionized water, acetone, and ethanol. The compounds were used, after washing, in the synthesis of the trimetallic species. Yield: dpp, 52%; dpq, 45%; dpb, 84%.

$\{[(bpy)_2Ru(dpp)]_2OsCl_2\}(PF_6)_4\cdot 3H_2O$. The dpp-based trimetallic was prepared by reacting 1 equiv of $Os(dpp)_2Cl_2$ (0.143 g, 0.197 mmol) with 5 equiv of $Ru(bpy)_2Cl_2$ in 50 mL of 2:1 (v/v) ethanol/water. The solution was heated at reflux under argon for approximately 72 h. The flask was then removed from the heat, and a saturated solution of aqueous KPF_6 (60 mL) was added with stirring to induce precipitation. The precipitate was then collected by vacuum filtration. The product was purified by column chromatography on Sephadex LH-20 (Pharmacia) using 95% ethanol as the eluent. To accomplish this the product was first metathesized to the chloride salt by dissolving the compound in a minimal amount of acetone and adding the solution to a saturated solution of tetrabutylammonium chloride in acetone. The metathesized product was collected by vacuum filtration, air dried, and dissolved in a minimal amount of ethanol to be placed on the Sephadex column. The black product band was the first to elute. The product band was collected, concentrated by rotary evaporation, dissolved in a minimal amount of water, and then metathesized to the hexafluorophosphate salt. The precipitate was collected by vacuum filtration, washed with diethyl ether, and dried under vacuum. Yield: 63%. Anal. Calcd: C, 37.28; H, 2.67; N, 10.23. Found: C, 37.34; H, 2.49; N, 10.27.

$\{[(bpy)_2Ru(dpq)]_2OsCl_2\}(PF_6)_4\cdot 3H_2O$. The dpq-based trimetallic was prepared and purified as above substituting $Os(dpq)_2Cl_2$ (0.259 g, 0.312 mmol) for $Os(dpp)_2Cl_2$. The blue/green product band was the first to elute. Yield: 67%. Anal. Calcd: C, 39.84; H, 2.72; N, 9.78. Found: C, 39.87; H, 2.59; N, 9.61.

$\{[(bpy)_2Ru(dpb)]_2OsCl_2\}(PF_6)_4\cdot 2H_2O$. The dpb-based trimetallic was prepared and purified as above by substituting $Os(dpb)_2Cl_2$ (0.205 g, 0.215 mmol) for $Os(dpp)_2Cl_2$. The forest green product band was the first to elute. Yield: 58%. Anal. Calcd: C, 42.52; H, 2.71; N, 9.45. Found: C, 42.49; H, 2.71; N, 9.60.

Electrochemistry. Cyclic and Osteryoung square-wave voltammograms were recorded in acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The apparatus used has been described in detail elsewhere.[12] Half-wave potentials are reproducible to within 0.02 V.

Spectroscopy. The UV/vis apparatus used has been described in detail elsewhere.[12] Near-IR spectra were performed on a Perkin-Elmer 330 spectrophotometer. All spectra were recorded in acetonitrile at room temperature. The resolution of this instrument is 2 nm.

Spectroelectrochemistry. The apparatus used for the spectroelectrochemical experiments has been described in detail elsewhere.[13] All electrochemical experiments were carried out in acetonitrile which had been passed over activated neutral Alumina (Fisher) to remove trace water and stored over activated molecular sieves. Solutions of the trimetallic complexes were ca. 0.1 mM and were electrolyzed at a Pt mesh electrode. Spectroelectrochemistry results for the monometallic $[Os(bpy)_2(BL)](PF_6)_2$ and mixed metal bimetallic $[(bpy)_2Os(BL)Ru(bpy)_2](PF_6)_4$ complexes have been previously reported.[12]

Results and Discussion

Electrochemistry. The cyclic voltammograms of the monometallic Os(II) and Ru(II) complexes, $[M(bpy)_2(BL)]^{2+}$ (M = Os, Ru; BL = dpp, dpq, dpb), are consistent with three ligand-based reductions and one metal-based oxidation.[4,6,12a,14] The first reduction in each case corresponds to reduction of the bridging ligand, while the second and third reductions correspond to sequential reductions of the two bipyridine ligands.[4,6,12a,14] Cyclic voltammograms of the bimetallic Os(II)/Ru(II) mixed-metal complexes, $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$ (BL = dpp, dpq, dpb), are consistent with two reversible metal-based oxidations and six reversible ligand-based reductions. In all of the bimetallic complexes the first and second reductions have been shown to be BL based.[12b] The subsequent four reductions have been assigned to sequential reduction of the four bpy ligands.[12b]

The electrochemical data for the three mixed-metal trimetallic complexes are given in Table I, and the cyclic and Osteryoung square wave voltammograms are shown in Figure 1. The proposed Scheme I for the oxidative and reductive processes for the trimetallic complexes is unique. (Please note: In Scheme I the chlorides attached to the osmium center have been omitted for clarity.)

The electrochemistry of the trimetallic complexes is complicated due to the presence of three metal centers, two bridging ligands, and four bipyridine ligands, all of which are electroactive. On the basis of previously prepared mono-, bi-, and higher order multimetallic complexes, it is expected that the oxidations will be metal centered with the Ru(II/III) couple occurring at more positive potentials than the Os(II/III) couple.[3,4,6,12,14-16] Also, it

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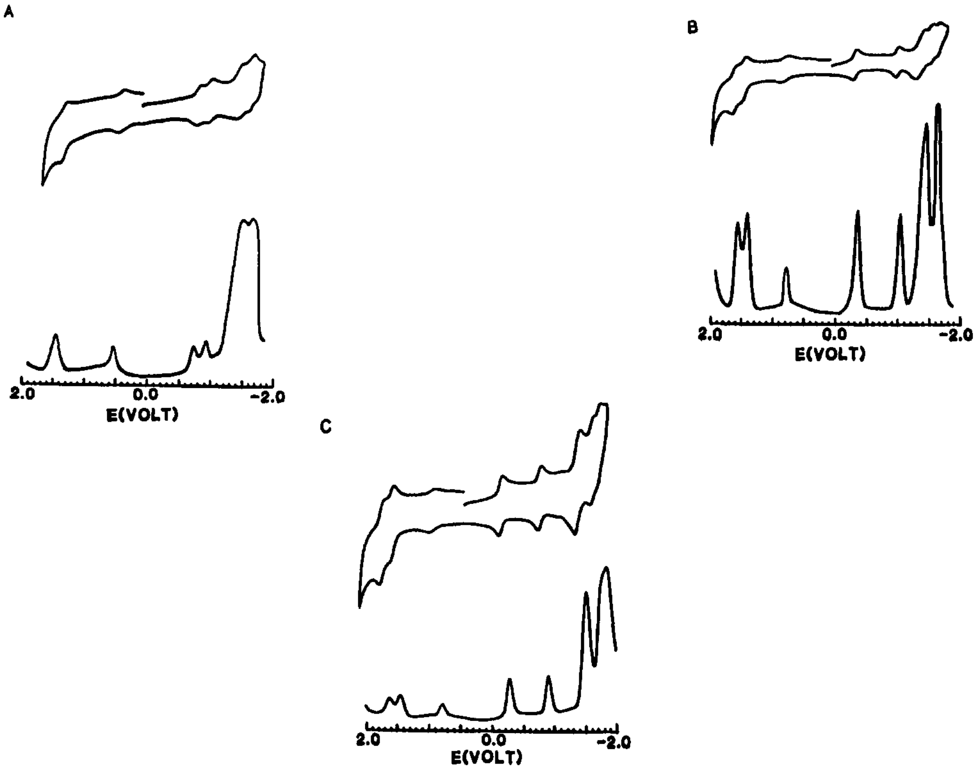

Figure 1. Cyclic and Osteryoung square-wave voltammograms (CH_3CN containing 0.1 M Bu_4NPF_6): (A) $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}(PF_6)_4$; (B) $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}(PF_6)_4$; (C) $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}(PF_6)_4$.

Table I. Cyclic Voltammetric Data for a Series of Trimetallic Os(II),Ru(II) Complexes Containing Polyazine Bridging Ligands[a]

complex	$E_{1/2}$ (V)	assgnt
$\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$	+1.51[b]	Ru^{II}/Ru^{III}
	+0.50	Os^{II}/Os^{III}
	−0.76	$dpp,dpp/dpp,dpp^-$
	−0.97	$dpp,dpp^-/dpp^-,dpp^-$
	−1.49[b]	bpy/bpy^-
	−1.73[b]	bpy/bpy^-
$\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$	+1.57	$Ru^{II},Ru^{III}/Ru^{III},Ru^{III}$
	+1.46	$Ru^{II},Ru^{II}/Ru^{II},Ru^{III}$
	+0.74	Os^{II}/Os^{III}
	−0.39	$dpq,dpq/dpq,dpq^-$
	−1.12	$dpq,dpq^-/dpq^-,dpq^-$
	−1.54[b]	bpy/bpy^-
	−1.75[b]	bpy/bpy^-
$\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$	+1.63	$Ru^{II},Ru^{III}/Ru^{III},Ru^{III}$
	+1.46	$Ru^{II},Ru^{II}/Ru^{II},Ru^{III}$
	+0.83	Os^{II}/Os^{III}
	−0.26	$dpb,dpb/dpb,dpb^-$
	−0.90	$dpb,dpb^-/dpb^-,dpb^-$
	−1.50[b]	bpy/bpy^-
	−1.74[b]	bpy/bpy^-

[a] Potentials were recorded versus a Ag/AgCl reference electrode (0.268 V vs SHE) in 0.1 M Bu_4NPF_6 in CH_3CN at a scan rate of 200 mV/s. [b] Waves correspond to reduction or oxidation of two equivalent centers by one electron each ($n = 2$).

Scheme I

$$\begin{tikzcd}
\{(bpy)_2Ru^{III}(BL)Os^{III}(BL)Ru^{III}(bpy)_2\}^{7+} \arrow[d, shift left, "+1e^-"] \\
\{(bpy)_2Ru^{III}(BL)Os^{III}(BL)Ru^{II}(bpy)_2\}^{6+} \arrow[u, shift left, "-1e^-"] \arrow[d, shift left, "+1e^-"] \\
\{(bpy)_2Ru^{II}(BL)Os^{III}(BL)Ru^{II}(bpy)_2\}^{5+} \arrow[u, shift left, "-1e^-"] \arrow[d, shift left, "+1e^-"] \\
\{(bpy)_2Ru^{II}(BL)Os^{II}(BL)Ru^{II}(bpy)_2\}^{4+} \arrow[u, shift left, "-1e^-"] \arrow[d, shift left, "+1e^-"] \\
\{(bpy)_2Ru^{II}(BL^-)Os^{II}(BL)Ru^{II}(bpy)_2\}^{3+} \arrow[u, shift left, "-1e^-"] \arrow[d, shift left, "+1e^-"] \\
\{(bpy)_2Ru^{II}(BL^-)Os^{II}(BL^-)Ru^{II}(bpy)_2\}^{2+} \arrow[u, shift left, "-1e^-"] \arrow[d, shift left, "+2e^-"] \\
\{(bpy)(bpy^-)Ru^{II}(BL^-)Os^{II}(BL^-)Ru^{II}(bpy^-)(bpy)\} \arrow[u, shift left, "-2e^-"]
\end{tikzcd}$$

is expected that the first and second reductions in these trimetallic complexes will correspond to sequential one-electron reductions of each of the bridging ligands, and this is indeed what is observed. As noted above, in the mixed-metal Os/Ru bimetallic systems, $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$, the second reduction has been shown to correspond to the second reduction of the bridging ligand.[12b] The bridged system in the trimetallic complexes is different in that the central osmium site is coordinated to two chloride ligands. This decreases the σ acidity of this metal and increases its π basicity. This would be expected to shift the BL-based reductions to more negative potentials as compared to the $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$ analogs. The third and fourth reductions occur at relatively constant potentials in each of the three complexes regardless of the bridging ligand employed and are assigned as bpy based. Thus, these trimetallics exhibit unique electrochemical behavior for multimetallic complexes with these bridging ligands in that each bridging ligand is reduced by only one electron prior to bpy reduction.

As noted above, the two bridging ligands are reduced separately. This separation between the two bridging ligand based reductions is indicative of the electronic coupling of the two equivalent bridging ligands via the osmium metal center. The trimetallic complexes display $\Delta E_{1/2}$ ($\Delta E_{1/2} = E_{1/2}{}^{red}(1) - E_{1/2}{}^{red}(2)$) values

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of 0.21, 0.73, and 0.64 V for the dpp, dpq, and dpb complexes, respectively. The $\Delta E_{1/2}$ values for the dpq and dpb systems are extremely large, far in excess of any previously studied polyazine bridging ligand complexes. The analogous Ir,Ru trimetallic complexes, $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$ (BL = dpp, dpq, dpb), display $\Delta E_{1/2}$ values ranging from 0.15 to 0.14 V, significantly smaller than the osmium-containing complexes.[19] The significantly enhanced coupling in these osmium-based systems is a result of the higher energy d orbitals on the osmium metal center, which can facilitate BL,BL coupling. The $\Delta E_{1/2}$ values for the first reduction of the BL in the Os,Ru complexes are significantly different for the dpp, dpq, and dpb complexes with the dpp complex displaying a much lower degree of coupling than either the dpq or dpb systems. This could be due to the fact that the LUMO in dpp complexes is spread over both the pyridine and pyrazine portions of the bridging ligand while in the dpq and dpb the LUMO is spread over the quinoxaline and benzoquinoxaline portions of the BL.[19] The increased negative charge density could be polarized away from the osmium center in the dpp complex on to the remote pyridine moiety leading to decreased coupling.

The oxidative processes involve oxidation of Os(II) to Os(III) and Ru(II) to Ru(III) with the Ru oxidations occurring at significantly more positive potentials than the corresponding Os oxidation.[2,3,9-11,17-20] In a comparison of the Os(II/III) oxidation in $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$ (+0.50 V) with the dpq- and dpb-bridged trimetallic systems (+0.74 and +0.83 V, respectively) there is a significant shift in the potential of the osmium-based oxidations as a function of the bridging ligand employed. This is in direct contrast to the monometallic, $[Os(bpy)_2(BL)]^{2+}$, and heterobimetallic, $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$, dpp, dpq, and dpb complexes, where the osmium-based oxidation remains essentially constant (+0.94, +0.99, +1.00 V for the monometallics and +1.01, +1.09, and +1.10 V for the bimetallics, respectively). The title trimetallic complexes have higher lying metal d orbitals. Thus, these systems can have more pronounced interaction with the BL-based π^* orbitals. This will result in a more dramatic dependence of the metal-based oxidation on the nature and energy of the BL-based π^* orbital. The π-accepting ability of dpb is greater than dpq than dpp. Thus, the osmium metal center should be harder to oxidize in the dpb trimetallic as compared to the dpq and dpp, as is observed.

The potentials of the ruthenium(II/III) couples remain more constant (+1.51 V for the dpp system, +1.46 and +1.57 mV for the dpq system and +1.46 and +1.64 mV for the dpb system), consistent with the lower energy ruthenium dπ orbitals having a decreased interaction with the BL orbitals. The appearance of two separate ruthenium oxidation potentials in the dpq and dpb systems is somewhat surprising since this is an indication that the two terminal ruthenium atoms are coupled through the BL–Os–BL framework. This type of coupling of the terminal ruthenium centers has not been observed in previously studied complexes, namely, the all-ruthenium trimetallic systems incorporating dpp,[16,31] $\{[(bpy)_2Ru(dpp)]_2RuCl_2\}^{4+}$, and complexes similar to those reported herein substituting Ir for the osmium metal center.[19] This newly observed coupling of the terminal ruthenium centers in the present compounds results from a central osmium metal center with higher energy dπ orbitals. This facilitates mixing with the BL-based π^* orbitals, giving a pathway for Ru coupling.

Electronic Absorption Spectra. Mixed-polypyridyl complexes of Ru(II) and Os(II) exhibit multiple absorptions in the visible region of the spectrum, where the separation between the bands reflects the difference between the π systems of the ligands.[4,20] The UV/vis data for each of the trimetallic complexes studied are shown in Figure 2 and summarized in Table II, and the near-IR data for $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$ and $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$ are shown in Figure 3.

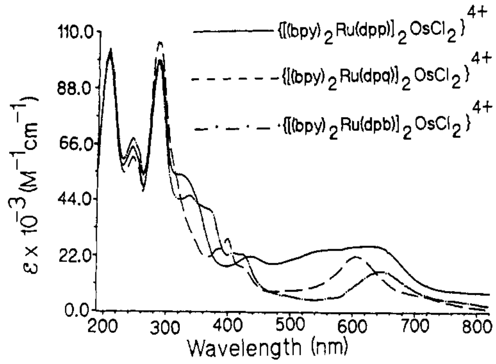

Figure 2. Electronic absorption spectra for a series of trimetallic Os(II),Ru(II) polypyridyl complexes in CH_3CN.

Table II. Electronic Spectral Data for a Series of Trimetallic Os(II),Ru(II) Complexes Containing Polyazine Bridging Ligands[a]

complex	λ_{max}^{abs} (nm)	$10^{-3}\epsilon$ (M^{-1} cm^{-1})	assgnt
$\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$	286	99.1	π–π^*(bpy)
	322	54.0	π–π^*(dpp)/^{1}MLCT
	436	21.8	^{1}MLCT(Ru → bpy)
	542	24.1	^{1}MLCT(Ru → dpp)
	630	26.2	^{1}MLCT(Os → dpp)
$\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$	286	105.6	π–π^*(bpy)
	340 (sh)	44.7	π–π^*(dpq)
	382 (sh)	24.7	^{1}MLCT(Ru → dpq)
	398	28.7	^{1}MLCT(Ru → dpq)
	422 (sh)	17.6	^{1}MLCT(Ru → bpy)
	604	21.9	^{1}MLCT(Ru → dpq)
	966	39.6	^{1}MLCT(Os → dpq)
$\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$	286	97.8	π–π^*(bpy)
	336	45.7	^{1}MLCT(Ru → bpy)
	368	40.2	π–π^*(dpb)
	406	22.9	^{1}MLCT(Ru → dpb)
	422	22.5	^{1}MLCT(Ru → bpy)
	642	15.9	^{1}MLCT(Ru → dpb)
	1059	30.2	^{1}MLCT(Os → dpb)

[a] Spectra were recorded in CH_3CN at room temperature.

The electronic absorption spectra of the trimetallic systems are complicated, as expected, with transitions stretching into the near-IR region of the spectrum (1059 nm). The intense higher energy bands, in the UV region of the spectrum, are assigned as $\pi \rightarrow \pi^*$ bpy- and BL-centered transitions by analogy to the free ligand spectra as well as the previously prepared $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$ systems.[12b]

In the visible region of the spectrum, one would expect to see transitions corresponding to both Os(dπ) and Ru(dπ) → BL(π^*) ^{1}MLCT.[3,12,17,18,21] The lowest energy MLCT, which is assigned as Os(dπ) → BL(π^*), is clearly red shifted in the $\{[(bpy)_2Ru(BL)]_2OsCl_2\}^{4+}$ complexes as compared with the dpp-, dpq-, and dpb-bridged bimetallic complexes, $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$, and occurs in the near-IR for the dpq- and dpb-bridged complexes. This is a result of the destabilization of the Os orbitals due to the change in the coordination environment (2 Cls and 4 Ns vs 6 Ns). The analogous Ru-based MLCT occurs at slightly higher energy in the trimetallics as compared to the Ru,Os bimetallic complexes. This is consistent with the observed destabilization of the BL-based π^* orbitals in the trimetallic complexes as compared to the $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$ systems due to the enhanced π-back-bonding ability of the electron-rich central osmium metal center.

At slightly higher energies than the lowest energy ^{1}MLCT bands are a series of additional charge-transfer bands. However, unlike the bridging ligand-based MLCT bands, the energy of

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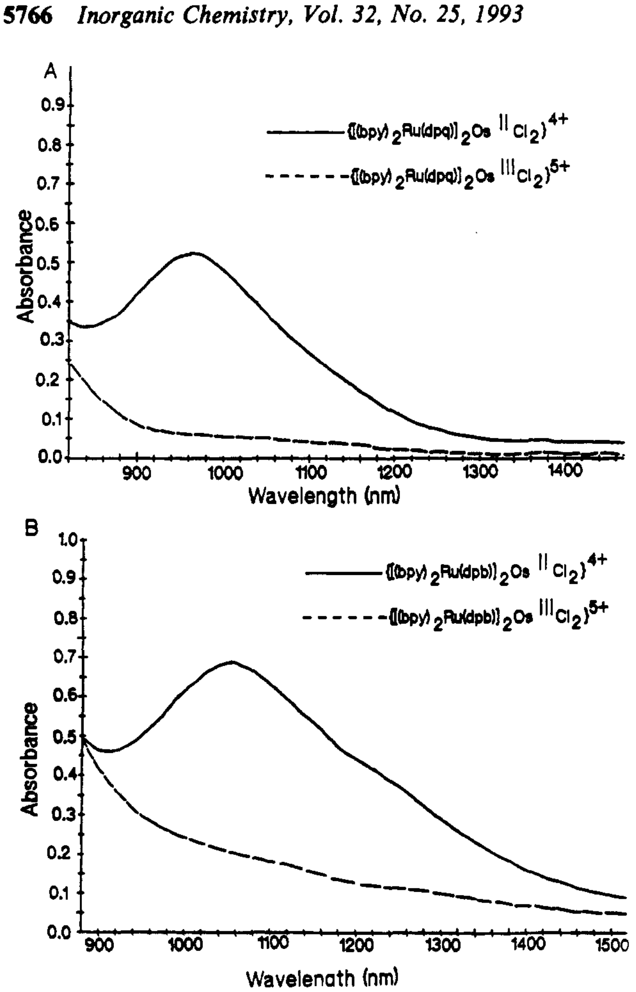

Figure 3. Near-infrared spectroelectrochemical results for (A) $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}(PF_6)_4$ and (B) $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}(PF_6)_4$.

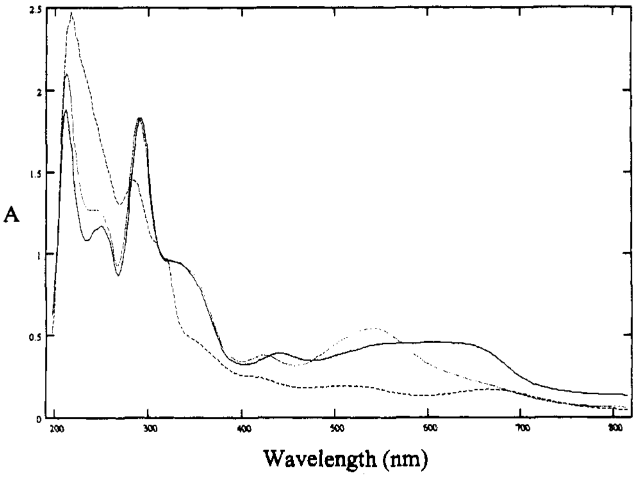

Figure 4. Spectroelectrochemical results for $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}(PF_6)_4$ in CH_3CN: —, $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$; ···, $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{5+}$; - - -, $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{7+}$.

these transitions remains essentially constant as the properties of the bridging ligand are varied from dpp to dpq to dpb (436, 422, and 422 nm, respectively) consistent with Ru ($d\pi$) → bpy(π^*) MLCT transitions. Additional details on the spectroscopy of these systems can be gained through spectroelectrochemical analysis.

Spectroelectrochemistry. With each complex it was possible to reversibly oxidize through the first metal centered oxidation (Os(II/III)). Oxidation of $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$ to +700 mV and $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$ and $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$ to +1300 mV resulted in a color change of black to purple for the dpp complex and relatively no color changes for the dpq and dpb complexes after passage of approximately 1 equiv of charge each. In all cases the oxidation could be reversed by changing the electrolysis potential to 0.0 V with greater than 95% regeneration of the original species. Spectroelectrochemical results are shown in Figures 3–8. $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$ exhibits absorption maxima at 286, 322, 436, 542, and 630 nm. The lowest energy transition at 630 nm is lost upon one-electron

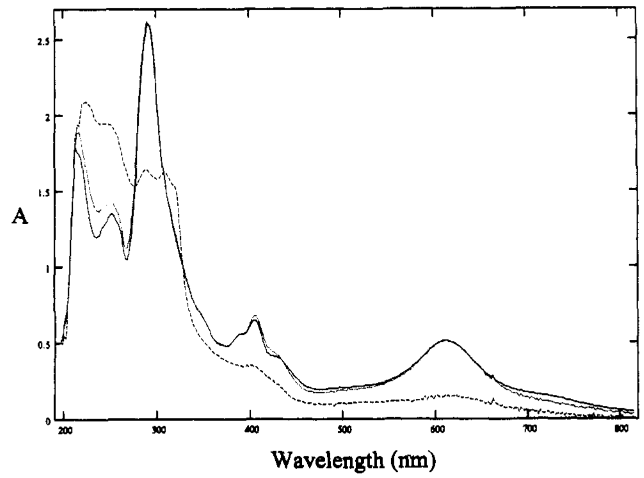

Figure 5. Oxidative spectroelectrochemical results for $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}(PF_6)_4$ in CH_3CN: —, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$; ···, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{5+}$; - - -, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{7+}$.

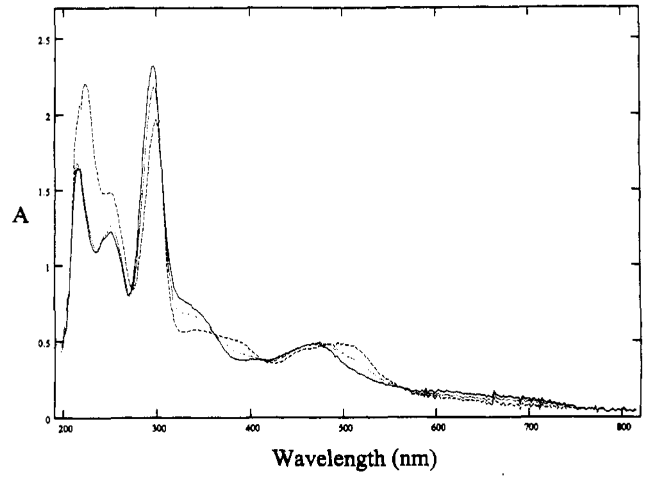

Figure 6. Reductive spectroelectrochemical results for $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}(PF_6)_4$ in CH_3CN: —, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{3+}$; ···, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{2+}$; - - -, $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{0}$.

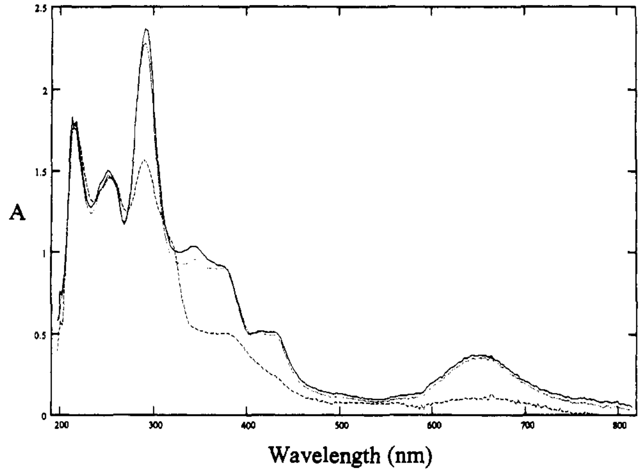

Figure 7. Oxidative spectroelectrochemical results for $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}(PF_6)_4$ in CH_3CN: —, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$; ···, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{5+}$; - - -, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{7+}$.

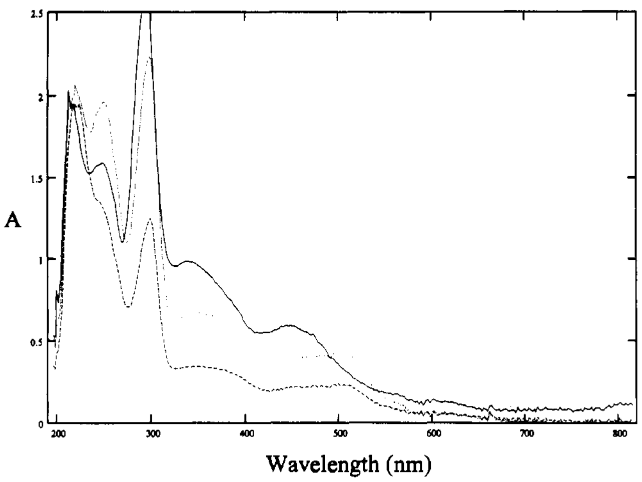

Figure 8. Reductive spectroelectrochemical results for $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}(PF_6)_4$ in CH_3CN: —, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{3+}$; ···, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{2+}$; - - -, $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^0$.

oxidation of the osmium center confirming its assignment as Os(dπ) → BL(π^*) in nature. The ruthenium component of this broad band is maintained upon osmium oxidation consistent with its assignment as a Ru(dπ) → BL(π^*) charge-transfer transition. Additionally, the transition at 432 nm experiences a slight blue shift as the osmium metal center is oxidized. The decreased π-back-bonding ability of the electrogenerated Os(III) center to the BL will give rise to enhanced back-bonding between the Ru(II) centers and BL. This should cause the Ru → bpy MLCT transition to shift to higher energy. Oxidation of the Os center has no noticeable effect on transitions less than 400 nm, consistent with their assignment as internal ligand transitions.

Generation of the Ru(III)/Os(III)/Ru(III) complex (three electron oxidation) resulted in a color change of black to light purple after passage of 3 equiv of charge for the dpp complex. Upon three-electron oxidation, loss of the low-energy transition at 542 nm is observed confirming its assignment as a Ru(dπ) → BL(π^*) charge-transfer transition. The higher energy transition at 436 nm is also lost confirming its Ru(dπ) → bpy(π^*) MLCT nature. The shoulder at 322 nm experiences a decrease in intensity upon oxidation of the Ru centers indicating this region may contain contributions from higher energy Ru-based MLCTs as well as ligand-based π–π^* transitions. The transition at 286 nm splits into two components with one shifting to lower energy upon oxidation of the Ru centers consistent with this band containing overlapping n–π^* and π–π^* transitions based on bpy.[19] Upon three-electron oxidation, a new peak at ca. 680 nm appears which has been observed in complexes of the type $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$ and has been assigned as a dpp → Ru LMCT made possible upon oxidation of the metal-based dπ orbitals.[19] Metal-to-metal charge-transfer (MMCT) transitions are possible in the partially oxidized complexes, although these have not been observed in any of the trimetallics studied. It was not possible to reversibly reduce and reoxidize $\{[(bpy)_2Ru(dpp)]_2OsCl_2\}^{4+}$.

Oxidation of $\{[(bpy)_2Ru(dpq)]_2OsCl_2\}^{4+}$ and $\{[(bpy)_2Ru(dpb)]_2OsCl_2\}^{4+}$ to form the Ru(II)/Os(III)/Ru(II) species resulted in loss of very few transitions in the visible region of the spectrum and essentially no color change in either solution. In fact, the lowest lying visible absorbance does not appear to be affected at all. These results are indicative of the lowest energy MLCT transition in the visible spectrum of these complexes as not being due to Os → BL based transitions confirming their assignment as Ru → BL MLCTs. Upon one-electron oxidation of the Os center, loss of the transitions at 966 and 1059 nm in the dpq and dpb complexes, respectively, are observed confirming the assignment of these near-IR bands as Os(dπ) → BL(π^*) MLCT in nature. Oxidation of the osmium metal center in the dpq- and dpb-bridged complexes results in a slight blue shift of the transitions at 422 nm consistent with their Ru → bpy MLCT assignment. As was observed in the Os,Ru bimetallic complexes, the bands in the UV do not appear to be affected by oxidation of the osmium center consistent with their assignments as being bpy and BL internal ligand transitions. Oxidation of each complex to +1800 mV, corresponding to oxidation by three electrons and generation of the Ru(III)/Os(III)/Ru(III) species, resulted in total loss of the lowest energy MLCT transitions at 605 and 625 nm in the dpq and dpb complexes, respectively, after passage of approximately 3 equiv of charge each. This supports the assertion that this transition is Ru(dπ) → BL(π^*) MLCT in character.

One-electron reduction to −600 mV in the dpq complex (blue/green to pale gold) and −500 mV in the dpb complex (forest green to golden yellow) results in loss of the lowest energy visible and near-IR transitions consistent with their assignment as MLCTs terminating on BL-based π^* orbitals. Upon reduction to −1100 mV (two-electron reduction) in both the dpq and dpb systems total loss of the lowest energy transitions is observed. In both the singly and doubly reduced species there is an increase in absorbance in the 400–550-nm region of the spectrum. This parallels the observed behavior in the bimetallic $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$ complexes and has been assigned to low-energy ligand-based π^* → π^* transitions made possible upon electrochemical occupation of the BL based π^* orbitals.[12b] Transitions at higher energies, between 320 and 400 nm, show a decrease in intensity upon reduction by one and two electrons, which indicates that these high-energy transitions are in part BL based.

Reduction of either the dpq or dpb complex by four electrons is ca. 60% reversible and results in spectroscopic changes consistent with bpy reduction and inconsistent with BL-based reductive processes. Both complexes experience reduction in the intensity of the bpy-based π → π^* at 286 nm. This supports the assertion that the bridging ligands are only reduced by one electron prior to bpy reduction in these polymetallic complexes.

Correlation of Spectroscopic and Electrochemical Results. A plot of energies for the lowest energy MLCT transitions (E_{abs} (eV)) versus the difference in redox potentials between the first metal-based oxidation and first bridging ligand-based reduction, $\Delta E_{1/2}$ ($E_{1/2}$(Os(II)/Os(III)) − $E_{1/2}$(BL/BL$^-$)), for the Os(II) monometallic complexes, $[Os(bpy)_2(BL)]^{2+}$, the Os/Ru bimetallic complexes, $[(bpy)_2Os(BL)Ru(bpy)_2]^{4+}$, the Os/Os bimetallic complexes, $[(bpy)_2Os]_2(BL)^{4+}$, and the title trimetallic complexes gave a linear correlation in which a linear least-squares analysis yielded

$$E_{abs} = -0.162 + 1.45\Delta E_{1/2} \qquad r = 0.853$$

where r is the correlation coefficient. Separate analysis of the trimetallics yields

$$E_{abs} = -4.58 + 4.85\Delta E_{1/2} \qquad r = 0.990$$

with the remaining mono- and bimetallic complexes yielding

$$E_{abs} = 0.385 + 1.11\Delta E_{1/2} \qquad r = 0.970$$

The linear nature of the plot indicates that the same dπ–π^* MLCT orbitals are involved in both the optical and electrochemical processes.[12,22-30] The enhanced fit of this data when the trimetallics are treated separately may result from the unique nature

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of these trimetallic complexes displaying a large degree of perturbation of the Os(dπ) orbitals as a function of the bridging ligand employed.

Conclusions

The electrochemistry of the complexes reported herein is unique among polymetallic systems as a result of the central $Os(BL)_2Cl_2$ core. Unlike previously prepared mono- and bimetallic Os and Ru complexes, the metal-based Os(II/III) oxidation in these complexes varies as a function of the bridging ligand employed. Also, the bridging ligands are only reduced by one electron prior to reduction of the bpy ligands due to the influence of the electron-rich $Os(BL)_2Cl_2$ center. The terminal ruthenium centers in the dpq and dpb complexes oxidize at different potentials, indicative of long-range communication through the BL–Os–BL framework. The utilization of synthetic variation and the stability of several oxidation states in these complexes has made it possible to clarify both the electronic spectra and electrochemical data for these supramolecular complexes. With the complexation of additional metal centers to the $[Os(BL)_2Cl_2]$ parent compounds it has been shown that it is possible to systematically synthesize trimetallic and, potentially, even higher order mixed-metal supramolecular complexes and to significantly alter their ground- and excited-state properties. Since these complexes are stable in a variety of oxidation states, they could provide multiple reducing equivalents for a substrate. Further studies which look at the photochemical and electrocatalytic reactivity are currently underway and will be the subject of a forthcoming report.

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