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Spectroscopic and Electrochemical Properties of a Series of Mixed-Metal d^6,d^8 Bimetallic Complexes of the Form $[(bpy)_2M(BL)PtCl_2]^{2+}$ (bpy = 2,2′-Bipyridine; BL = dpq (2,3-Bis(2-pyridyl)quinoxaline) or dpb (2,3-Bis(2-pyridyl)benzoquinoxaline); M = Os^{II} or Ru^{II})

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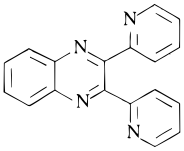
Introduction

The MLCT (metal-to-ligand charge transfer) nature of the excited states of ruthenium[1−3] and osmium[4,5] polypyridyl systems has led to a series of studies investigating their light-absorbing and photochemical reaction properties in intermolecular energy and electron transfer schemes. The synthesis of polyazine bridging ligands has led to the development of polymetallic complexes that maintain many of the desirable properties of these ruthenium and osmium chromophores.[6−13] Previously in our laboratory a series of trimetallic systems incorporating two light-absorbing metal centers and a catalytically active metal site have been synthesized, $\{[(bpy)_2Ru(BL)]_2MCl_2\}^{5+}$, where bpy = 2,2′-bipyridine, BL = 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), or 2,3-bis(2-pyridyl)benzoquinoxaline (dpb), and M = Ir^{III} or Rh^{III}.[14] Rillema and co-workers have prepared $\{Ru[(dpq)PtCl_2]_3\}(PF_6)_2$ and $[(bpy)_2Ru(bpm)PtCl_2](ClO_4)_2$, where bpm = 2,2′-bipyrimidine.[15] Their studies indicate that the coordination of platinum to the ruthenium monomeric species results in a red shift in MLCT absorption bands and BL-based reductions that occur at more positive potentials. Yam and co-workers recently synthesized $[(bpy)_2Ru(dpp)PtCl_2](PF_6)_2$.[16]

Covalent coupling of platinum to a ruthenium chromophore may be of use in the design of new anticancer agents. Square planar platinum complexes exhibit interactions with DNA.[17−19] The systems reported herein contain the *cis*-dichloro structural motif necessary for the anticancer activity of cis-$[Pt(NH_3)_2Cl_2]$.[17,18] The presence of the polypyridyl bridging ligands with extended π systems promotes intercalation into the DNA double helix. Murphy and co-workers reported the intercalation of $[(NH_3)_4Ru(dpb)Ru(NH_3)_4]^{4+}$ into DNA.[20]

Reported herein are the synthesis and spectroscopic and electrochemical characterization of a series of mixed-metal bimetallic complexes of the form $[(bpy)_2M(BL)PtCl_2](PF_6)_2$ (BL = dpq or dpb; M = Os^{II} or Ru^{II}).



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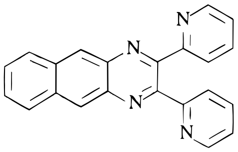

d p b

Experimental Section

Materials. Reagents were of Fisher reagent grade and were used without further purification. $[(bpy)_2Ru(BL)](PF_6)_2$,[6,7,13f] $[(bpy)_2Os(BL)](PF_6)_2$,[10,13] and $[Pt(DMSO)_2Cl_2]$[15] were prepared as described previously.

Electronic Absorption Spectroscopy. Electronic absorption spectroscopy was performed at room temperature on an HP 8452 diode array spectrophotometer with 2 nm resolution.

Electrochemical Studies. These measurements were performed using a BAS 100-W electrochemical analyzer. The working electrode was a platinum disk, the auxiliary electrode a platinum wire, and the reference electrode a Ag/AgCl electrode (0.29 V vs NHE). The solvent/electrolyte system was 0.1 M TBAH in acetonitrile.

Syntheses. $\mathbf{[(bpy)_2Ru(dpb)PtCl_2](PF_6)_2}$ was prepared by reaction of 0.105 g (0.0805 mmol) of $[(bpy)_2Ru(dpb)](PF_6)_2$ with 0.265 g (0.627 mmol) of $Pt(DMSO)_2Cl_2$ in deoxygenated methanol solution in the dark. The reaction mixture was heated at reflux, and the reaction, monitored by UV−vis spectroscopy, was complete after 36 h. The reaction mixture was cooled and the product collected by vacuum filtration. The resulting green solid was obtained in high yield but contained small amounts of $[Pt(DMSO)_2Cl_2]$. This was removed by repeated dissolution in a minimal amount of acetonitrile and flash precipitation in diethyl

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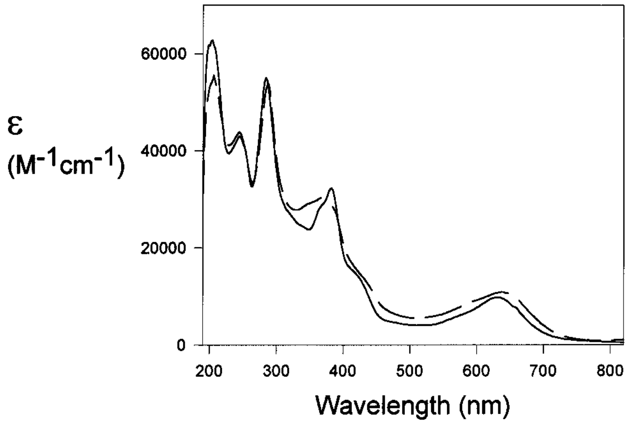

Figure 1. Electronic spectra recorded in acetonitrile at room temperature for (—) $[(bpy)_2Ru(dpb)PtCl_2](PF_6)_2$ and (– –) $[(bpy)_2Os(dpb)PtCl_2](PF_6)_2$ (bpy = 2,2′-bipyridine; dpb = 2,3-bis(2-pyridyl)benzoquinoxaline).

ether. The purified yield was 55%. FAB-MS (nitrobenzyl alcohol matrix); *m/z*: 1014, $[(bpy)_2Ru(dpb)PtCl_2]^+$; 978, $[(bpy)_2Ru(dpb)PtCl]^+$; 943, $[(bpy)_2Ru(dpb)Pt]^+$.

$[(bpy)_2Os(dpb)PtCl_2](PF_6)_2$ was prepared by heating at reflux $[Os(bpy)_2(dpb)](PF_6)_2$ (0.16 g, 0.14 mmol) and K_2PtCl_4 (0.36 g , 0.87 mmol) in deoxygenated acetonitrile. The reaction was monitored by UV–vis spectroscopy and was complete after 24 h. The reaction mixture was cooled and the product precipitated by addition to a saturated solution of aqueous KPF_6. The green solid that formed was collected by vacuum filtration, dissolved in a minimal amount of acetonitrile, and flash-precipitated in diethyl ether. The yield was 95%. FAB-MS (nitrobenzyl alcohol matrix), *m/z*: 1103, $[(bpy)_2Os(dpb)PtCl_2]^+$; 1067, $[(bpy)_2Os(dpb)PtCl]^+$; 1032, $[(bpy)_2Os(dpb)Pt]^+$.

$[(bpy)_2Ru(dpq)PtCl_2](PF_6)_2$ was prepared as above for the ruthenium-based dpb system but substituting $[(bpy)_2Ru(dpq)](PF_6)_2$ (0.134 g, 0.136 mmol) for $[(bpy)_2Ru(dpb)](PF_6)_2$. A typical yield was 67%. FAB-MS (nitrobenzyl alcohol matrix): *m/z*: 1109, $[(bpy)_2Ru(dpq)PtCl_2](PF_6)^+$; 964, $[(bpy)_2Ru(dpq)PtCl_2]^+$; 929, $[(bpy)_2Ru(dpq)PtCl]^+$; 893, $[(bpy)_2Ru(dpq)Pt]^+$.

$[(bpy)_2Os(dpq)PtCl_2](PF_6)_2$ was prepared by the reaction of $[(bpy)_2Os(dpq)](PF_6)_2$ (0.16 g, 0.15 mmol), with K_2PtCl_4 (0.42 g, 1.0 mmol) in acetonitrile as described for the osmium-based dpb analog. A typical yield was 90%. FAB-MS (nitrobenzyl alcohol matrix), *m/z*: 1198, $[(bpy)_2Os(dpq)PtCl_2](PF_6)^+$; 1053, $[(bpy)_2Os(dpq)PtCl_2]^+$; 1017, $[(bpy)_2Os(dpq)PtCl]^+$; 982, $[(bpy)_2Os(dpq)Pt]^+$.

Results and Discussion

Mixed-metal complexes of the form $[(bpy)_2M(BL)PtCl_2]^{2+}$ can be prepared easily from the appropriate Pt(II) salt and monometallic precursor, $[(bpy)_2M(BL)]^{2+}$ (M = Ru^{II} or Os^{II}). Electronic absorption spectra of the dpb-based bimetallic complexes are shown in Figure 1. The $[(bpy)_2M(BL)]^{2+}$ complexes (M = Os^{II}, Ru^{II}) possess intense bands in the UV attributed to bpy-based $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and dpq- and dpb-based $\pi \rightarrow \pi^*$ transitions at 350 and 390 nm.[6,7,13] The visible region possesses MLCT transitions to each ligand with the BL-based transitions occurring at lower energy. The Os-based $[(bpy)_2Os(BL)]^{2+}$ systems have Os → BL CT bands at 536 and 570 nm for dpq and dpb, respectively.[10,13] The analogous Ru systems have transitions at 517 and 550 nm for the dpq and dpb systems, respectively.[7,13f] This slight shift to lower energy of the Os → BL CT relative to the Ru system is the result of the higher energy $d\pi$ orbitals on Os. The shift of the M → dpb CT to lower energy compared to the analogous M → dpq CT within each series results from the lower energy π^*-acceptor orbitals on dpb relative to dpq.

For $[(bpy)_2M(BL)]^{2+}$ systems (M = Os^{II}, Ru^{II}) bimetallic formation results in a lowering in energy of the M → BL CT band.[6–13] Yam et al. recently reported that $[(bpy)_2Ru(dpp)PtCl_2]^{2+}$ possesses a Ru → bpy CT band at 422 nm and a Ru → dpp CT band at 509 nm.[16] This Ru → dpp CT is red-shifted relative to that of $[(bpy)_2Ru(dpp)]^{2+}$, which is at 468 nm.[6,16] In the homobimetallic system $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$, this Ru → dpp CT occurs at 526 nm.[6] Hence, the $Pt^{II}Cl_2$ coordination to the remote nitrogens on the dpp ligand is less stabilizing than the coordination of another $Ru^{II}(bpy)_2$ moiety.

Table 1. Cyclic Voltammetric Data for a Series of Mixed-Metal Bimetallic Complexes[a]

compd	$E_{1/2}$ (V vs Ag/AgCl)[b]		
	M^{II}/M^{III}	BL/BL^-	BL^-/BL^{2-}
$[(bpy)_2Ru(dpq)PtCl_2](PF_6)_2$	1.72	−0.28	−0.82
$[(bpy)_2Ru(dpb)PtCl_2](PF_6)_2$	1.61	−0.11	−0.75
$[(bpy)_2Os(dpq)PtCl_2](PF_6)_2$	1.11	−0.30	−0.92
$[(bpy)_2Os(dpb)PtCl_2](PF_6)_2$	1.05	−0.22	−0.80

[a] Recorded in CH_3CN, 0.1 M TBAH; Pt working electrode; Pt auxiliary electrode. [b] Potentials reported vs Ag/AgCl (0.29 V vs NHE).

The title mixed-metal bimetallic systems $[(bpy)_2M(BL)PtCl_2]^{2+}$ possess a Ru or Os chromophore in which the bridging ligand is also ligated to a remote Pt site. This should give rise to spectroscopy that is dominated by the chromophoric metal but experiences perturbations associated with the electronic influence of the remote Pt site. The M → BL CT bands occur at 582 (dpq) and 630 (dpb) nm for the ruthenium systems and at 598 (dpq) and 638 (dpb) nm for the osmium systems, consistent with the expected trends. These systems also exhibit transitions in the 410–420 nm region, assigned as M → bpy CT transitions.[6,7,10,13] The transitions in the UV are typical of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in mixed-ligand polyazine systems with bpy-based bands at ca. 290 nm and BL-based transitions at 340–350 nm for the dpq systems and 380–390 nm for the dpb-based systems. No emission is observed for any of the title bimetallics. Given the low energy of their MLCT absorbances, the emission may be beyond the detection limit of our R666-S red-sensitive PMT.

The electrochemical properties of these new bimetallic complexes are summarized in Table 1. Each complex exhibits one reversible oxidation and four reductions within the window of +2.0 to −2.0 V vs Ag/AgCl. The ruthenium-based systems also display an irreversible oxidation that appears as a shoulder, just prior to the reversible oxidative process.

The electrochemical properties of the monometallic synthons $[(bpy)_2M(BL)]^{2+}$ have been previously studied.[7,10,13] The ruthenium systems possess $Ru^{II/III}$ oxidations at 1.47 and 1.48 V vs Ag/AgCl for the dpq and dpb systems, respectively.[7,13] The osmium-based systems oxidize at much less positive potentials, 0.99 and 1.00 V vs Ag/AgCl for the dpq and dpb systems, respectively.[10,13] Within each metal-based series, the dpb-based systems undergo reduction at less negative potentials that the dpq systems with $E_{1/2}^{red} = -0.72$ (dpq) and −0.62 (dpb) V for the Ru-based systems and −0.76 (dpq) and −0.61 (dpb) V for the Os-based systems.[7,10,13]

Yam et al. reported the electrochemical properties of $[(bpy)_2Ru(dpp)PtCl_2]^{2+}$ in a recent communication.[16] In acetonitrile, they observe a $Ru^{II/III}$ couple at 1.57 V and a dpp/dpp$^-$ couple at −0.54 V vs SCE. They report an irreversible oxidation at 1.47 V vs SCE, although the nature of this process is not discussed. Our data indicate that this irreversible wave in their system represents a platinum-based process.

The reversible oxidation in our mixed-metal bimetallics is assigned as a metal-based $Os^{II/III}$ or $Ru^{II/III}$ couple. The irreversible oxidative process that occurs just prior to the $Ru^{II/III}$ couple represents the oxidation of the platinum center. This Pt-based oxidation occurs just prior to onset of solvent oxidation in the osmium-based bimetallics. It is interesting to note that, in both series, the Ru- and Os-based bimetallics, the dpb bimetallics are easier to oxidize than the analogous dpq systems. This is not seen in the homobimetallic complexes of the form $[(bpy)_2M(BL)M(bpy)_2]^{4+}$ discussed above.[6,7,10,13] This trend in metal oxidation potentials would indicate that these ligands function to a certain degree as π donors to the M^{II} site within this molecular architecture. The higher energy filled π orbitals on the dpb would make it a better π donor than the dpq and give rise to the observed trend in oxidation potentials.

All the bimetallics studied exhibit a BL/BL^- reduction that occurs at substantially more positive potentials than the monometallic synthon, $[(bpy)_2M(BL)]^{2+}$. Component modification establishes the role of the BL in this reductive process. The second reductions are reversible and are assigned the BL^-/BL^{2-} couple. The presence of two one-electron reductions at low potential is indicative of bimetallic formation when the dpq or dpb ligand is bridging.[6−13] Subsequent reductions are not as well behaved, due to the formation of a neutral complex by the first two BL-based reductions, $[(bpy)_2M(BL^{2-})PtCl_2]$, which adsorbs to the electrode surface. A third and a fourth reduction are observed which represent the sequential reduction of the coordinated bpy ligands; however, resolution of these waves is difficult.

The electrochemical properties of the $[(bpy)_2Os(BL)PtCl_2]^{2+}$ complexes are consistent with an Os-based HOMO (highest occupied molecular orbital) and a BL-based LUMO (lowest unoccupied molecular orbital), consistent with a lowest lying electronic absorption that is $Os(d\pi) \rightarrow BL(\pi^*)$ charge transfer in nature. In the $[(bpy)_2Ru(BL)PtCl_2]^{2+}$ systems, the $Ru(d\pi)$ and $Pt(d\pi)$ orbitals appear to be similar in energy but the light-absorbing properties of these systems are dominated by the ruthenium chromophore. This is not surprising since $Pt(bpy)Cl_2$ has a higher energy, less intense MLCT than $[Ru(bpy)_3]^{2+}$.[1−3,22−24]

The coupling of a good light-absorbing metal with directed charge transfer to the remote platinum site could impart some interesting photochemical properties to these complexes. Studies are currently underway to probe the photochemical behavior of these complexes in detail. Studies aimed at probing the interaction of these new systems with DNA are in progress.[25]

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Supporting Information Available: Electronic spectra for $[(bpy)_2Ru(dpq)PtCl_2](PF_6)_2$ and $[(bpy)_2Os(dpq)PtCl_2](PF_6)_2$ (1 page). Ordering information is given on any current masthead page.

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