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The Low-Lying Excited State in Ligand π-Acceptor Complexes of Ruthenium(II): Mononuclear and Binuclear Species[1]

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One of the goals in our laboratories is to prepare and characterize compounds that will emulate catalytic properties of naturally occurring biochemicals containing transition metals. The particular property of interest is the ability to duplicate multielectron oxidation or reduction of substrates.[2] Potential synthetic compounds of this type could be prepared from transition metals, which exhibit multioxidation states, or multinuclear transition-metal complexes could be prepared from metal centers known to undergo at least a one-electron change. Coupling the desire to carry out the catalysis not only under normal conditions but also by photochemical means suggested that such compounds be derived from complexes having known photochemical properties.

The modeling approach taken has been to prepare multinuclear complexes derived from Ru(bpy)$_3^{2+}$, bpy = 2,2′-bipyridine, a compound with a photochemically active excited state that has been exploited in a variety of applications, including solar energy conversion.[3-11] Our initial study reported a series of compounds containing from one to four Ru(bpy)$_2$ units bound to the same bridging ligand.[12] Other investigators have prepared binuclear compounds by coupling two Ru(bpy)$_2$ units through a bridging ligand. The majority of the bridging ligands employed have been unidentate,[13-16] although a few bidentate bridging ligands have also been used.[17-19]

The types of bridging ligands employed can be separated into two major classes, those with π systems and those without. The ones with π systems can be subclassified into π-donor and π-acceptor ligands. Examples of π-donor ligands are monodentate chelates such as pyrazole[14] and bidentate ligands such as biimidazole or bibenzimidazole.[18,19] The π-acceptor ligands are represented by pyrazine[13] or 2,2′-bipyrimidine, bpyrm.[17,18] Both types give rise to different redox properties. $E_{1/2}$ values for Ru(III/II) couples are ~0.3–~0.6 V less for complexes containing π-donor ligands such as biimidazole[18] than $E_{1/2}$ for Ru(bpy)$_3^{2+}$, whereas those of complexes containing π-acceptor ligands are ~0.1–~0.3 V greater.[17,18] The visible absorption spectra of ruthenium complexes containing π-donor or π-acceptor bridging ligands also differed as to the assignment of the lowest energy transition. For complexes containing π-donor bridging ligands, the first visible transition was assigned as dπ → π*(bpy);[13] for complexes containing π-acceptor ligands, the lowest energy transition was assigned as dπ → π*(L),[14] where L represents a π-acceptor ligand.

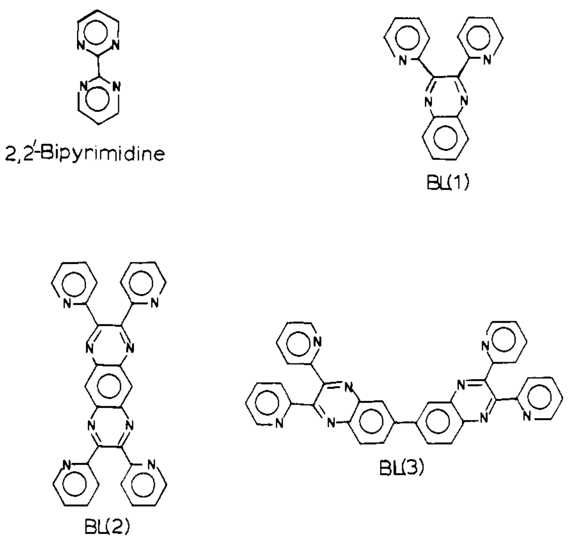

Figure 1. Ligands used in study: bpyrm = 2,2′-bipyrimidine; BL(1) = 2,3-di-2-pyridylquinoxaline; BL(2) = 2,3,7,8-tetra-2-pyridylpyrazino[2,3-*g*]quinoxaline; BL(3) = 2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline.

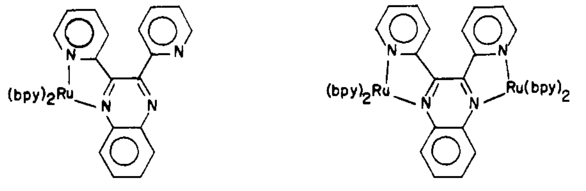

Figure 2. Mononuclear and binuclear complexes of BL(1): Ru(bpy)$_2$BL(1)$^{2+}$ and [Ru(bpy)$_2$]$_2$BL(1)$^{4+}$.

This paper describes the preparation, optical and redox properties of ruthenium(II) complexes containing the bridging ligands BL(1) and BL(2) shown in Figure 1, where BL represents a bridging ligand, and additional redox properties of ruthenium complexes containing the ligand 2,2′-bipyrimidine. Ligands with increasing aromaticity were chosen with the expectation that the resulting complexes would absorb visible light in a more accessible region of the solar spectrum. The dπ → π*(BL) transitions become well separated from the dπ → π*(bpy) absorptions, and added proof is presented that the transition assignment dπ → π*(BL) is correct.

Illustrative examples of mononuclear and binuclear complexes of bridging ligand BL(1) are given in Figure 2.

Experimental Section

Materials. Tetraethylammonium perchlorate (TEAP) was purchased as reagent grade, recrystallized three times from distilled water followed by a final recrystallization from a 1:1 methanol–acetone solution, and then dried under vacuum overnight. Acetonitrile was either spectral or pesticide grade and was dried 48 h over 4-A molecular sieves before use. Nitrogen was scrubbed by passing it through a 2.4 M HCl solution containing ~0.4 M chromous chloride generated from

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chromic chloride over zinc amalgam. Bipyrimidine was purchased from Alfa Inorganics, Inc. All other reagents were reagent grade. Elemental analyses were carried out by Integral Laboratories Inc., Raleigh, NC. These have been deposited as supplementary material and can also be obtained from the corresponding author.

Preparations. The preparation of the salt $Ru(bpy)_2Cl_2{\cdot}2H_2O$[20] was described previously. The preparation of 2,3-di-2-pyridylquinoxaline, BL(1), followed the procedure of Goodwin and Lions.[21]

Bridging Ligand 2 (BL(2)): 2,3,7,8-Tetra-2-pyridylpyrazino[2,3-*g*]quinoxaline. 1,2,4,5-Benzenetetramine tetrahydrochloride (1.0 g, 3.52 mmol) and 2,2′-bipyridyl (1.5 g, 7.04 mmol) were added to a dry 100-mL flask. Then 50 mL of anhydrous ethanol was added, and the mixture was stirred. Then triethylamine was slowly added until the suspension cleared. The solution was filtered to remove insoluble materials. The filtrate was heated under reflux for 30 min during which time a yellow precipitate formed. It was filtered, washed with small portions of cold ethanol and then ether, and dried under vacuum.

The molecular weight was determined in camphor by the freezing point depression method: predicted, 490; found, 496.

Mononuclear Complexes: $Ru(bpy)_2BL(1)(ClO_4)_2$, $Ru(bpy)_2BL(1)(PF_6)_2{\cdot}H_2O$, $Ru(bpy)_2BL(2)(PF_6)_2{\cdot}3H_2O$, $Ru(bpy)_2bpyrm(ClO_4)_2{\cdot}H_2O$. The general preparative procedure involved substitution of acetone for chloride ion in the coordination sphere of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (from 2×10^{-4} to 8×10^{-4} mol) by reaction with either $AgClO_4$ or $AgPF_6$ in ~50 mL of acetone. The AgCl formed was removed by filtration, and a two- to fourfold excess of the desired bridging ligand was added. The resulting suspension was heated under reflux and stirred under nitrogen for 24 h. The solution was allowed to cool to room temperature. The perchlorate salt of the bipyrimidine complex precipitated at this point. The remaining salts were isolated by reducing the volume of the solution to ~20 mL, filtering if necessary to remove solid impurities or excess ligand as was the case for the Bl(2) preparation, and then adding the solution to an excess of ether. The compounds precipitated and were isolated by filtration, washed with ether, and dried under vacuum.

The compounds were purified by column chromatography. The compounds were redissolved in a minimum quantity of acetonitrile and chromatographed on an alumina column developed with acetonitrile. The primary impurities were $Ru(bpy)_3^{2+}$, the μ-oxo-bridged species for solutions containing perchlorate ion, and the binuclear species for solutions containing the hexafluorophosphate salt. $Ru(bpy)_3^{2+}$ was removed from the column first with acetone at a very slow drop rate. The desired mononuclear complex was collected with use of a 1:1 methylene chloride–acetonitrile solution. The binuclear and μ-oxo-bridged species remained on the column as the middle fraction of the methylene chloride–acetonitrile solution was collected. The eluent was reduced in volume to ~20 mL and added to ether to reprecipitate the compounds. The compounds were isolated by filtration, washed with ether, and dried under vacuum.

Binuclear Compounds: $[Ru(bpy)_2]_2BL(1)(ClO_4)_4$, $[Ru(bpy)_2]_2BL(1)(PF_6)_4$, $[Ru(bpy)_2]_2BL(2)(PF_6)_4$, $[Ru(bpy)_2]_2bpyrm(ClO_4)_4{\cdot}3H_2O$. The general preparative procedure involved substitution of acetone for chloride ion in the coordination sphere of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (from 2×10^{-4} to 8×10^{-4} mol) by reaction with either $AgClO_4$ or $AgPF_6$ in ~50 mL of acetone. The AgCl formed was removed by filtration, and a stoichiometric quantity of the mononuclear complex was added. The resulting solution was heated under reflux and stirred under nitrogen for 48 h. The solutions were allowed to cool to room temperature. Perchlorate salts precipitated from the reaction solution and were isolated by filtration. Hexafluorophosphate salts were isolated by reducing the solution volume to ~20 mL and adding the concentrate to ether.

Salts were purified by column chromatography. The principal impurities were the unreacted mononuclear complex and the μ-oxo-bridged species. The compounds were dissolved in acetonitrile and added to an alumina column developed with acetonitrile. The mononuclear complexes were eluted with a 1:1 methylene chloride–acetonitrile solution. The binuclear species were removed next with acetonitrile. The middle fraction of the eluent was collected, reduced to ~20 mL, and added to an excess of ether to precipitate the compounds. The compounds were isolated by filtration, washed with ether, and dried under vacuum.

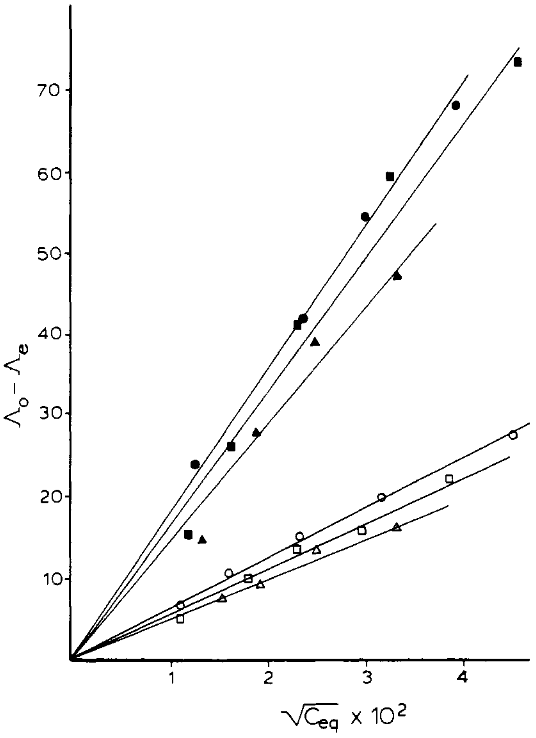

Figure 3. Dilution conductivities of ruthenium(II) mononuclear and binuclear complexes in acetonitrile at 25 °C: (●) $[Ru(bpy)_2]_2bpyrm(PF_6)_4$; (■) $[Ru(bpy)_2]_2BL(1)(PF_6)_4$; (▲) $[Ru(bpy)_2]_2BL(2)(PF_6)_4$; (○) $Ru(bpy)_2bpyrm(PF_6)_2$; (□) $Ru(bpy)_2BL(1)(PF_6)_2$; (△) $Ru(bpy)_2BL(2)(PF_6)_2$.

Physical Measurements. Visible and UV spectra were recorded with a Cary 14 instrument. Solution conductivities were obtained in acetonitrile at 25.0 ± 0.1 °C with a Beckman Model RC-18A conductivity bridge. The cell constant was determined by measuring the resistance of a 0.020 M KCl solution having a specific conductance at 25 °C of 0.002768 Ω^{-1}. Polarograms were obtained in acetonitrile solutions containing 0.1 M TEAP as the supporting electrolyte. Electrochemistry was carried out with a PAR 174 polarographic analyzer or a PAR 173 potentiostat in conjunction with a PAR 175 programmer. Polarograms were recorded with a Houston Omnigraphic X-Y recorder. Coulometry was performed with a PAR 173 potentiostat, a PAR 179 digital coulometer, and a PAR 370 cell system.

Results and Discussion

Preparations of complexes and dilution conductivity studies were carried out by procedures previously described.[12] For strong electrolytes, the equivalent conductance, Λ_e, is expected to vary linearly with the square root of the equivalent concentration, $C_{eq}^{1/2}$.[22] According to eq 1, a plot of $\Lambda_0 - \Lambda_e$, where

$$\Lambda_0 - \Lambda_e = AC_{eq}^{1/2} \qquad (1)$$

Λ_0 is the equivalent conductance at infinite dilution, vs. $C_{eq}^{1/2}$ will result in a straight line of slope A shown to be indicative of the electrolyte type.[12,23,24] Figure 3 is such a plot and supports the formulation of the compounds as mononuclear and binuclear complexes. The observed slopes fall in the 500–600 range for 2:1 electrolytes and the 1400–1700 range for 4:1 electrolytes. The slopes can also be calculated theoretically and compared to the experimental values. The observed slopes for the mononuclear complexes are less than theoretical (~700) whereas those for the binuclear species oscillate about

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Table I. Electrochemical Data for Mononuclear and Binuclear Complexes of Ruthenium(II)

	oxidations		reductions		
complex	$E_{1/2}(2)$,[a,b] V	$E_{1/2}(1)$,[a,b] V	$E_{1/2}'(1)$,[a,b] V	n[c]	$E_{1/2}'(2)$,[a,b] V
$Ru(bpy)_2BL(1)(PF_6)_2$		1.41 (58)	−0.78 (64)	1.08	−1.41 (75)
$[Ru(bpy)_2]_2BL(1)(PF_6)_4$	1.62 (61)	1.47 (72)	−0.37 (58)	0.96	−1.10 (72)
$Ru(bpy)_2BL(2)(PF_6)_2$		1.42 (67)	−0.42 (65)	1.02	−0.92 (69)
$[Ru(bpy)_2]_2BL(2)(PF_6)_4$		1.45 (100)[d]	−0.16 (65)	0.98	−0.57 (65)
$Ru(bpy)_2(bpyrm)(ClO_4)_2$		1.36[f] (61)	−1.01 (60)	1.01	−1.45[e]
$[Ru(bpy)_2]_2bpyrm(ClO_4)_4$	1.69[f] (71)	1.53[f] (63)	−0.41 (68)		−1.08 (70)

[a] Potential measurements were at a Pt electrode and referenced to a saturated sodium calomel electrode (SSCE) in 0.1 M TEAP-CH_3CN at 20 ± 1 °C. The estimated error is ±0.01 V. [b] ΔE_p values are given in parentheses and were extrapolated from the intercepts of plots of ΔE_p vs. $\upsilon^{1/2}$, where υ is the sweep rate. [c] Error of coulometric n values is ±0.05. [d] Note sweep rate dependent. Ratio of i_{max} of $E_{1/2}(1)$ to i_{max} of $E_{1/2}'(1)$ is 1.8:1. [e] On edge of an adsorption wave. [f] Values given in ref 18 were ~0.07 V more positive. The potentials were measured at a RPE in 0.1 M $NaClO_4$ vs. SCE in ref 18.

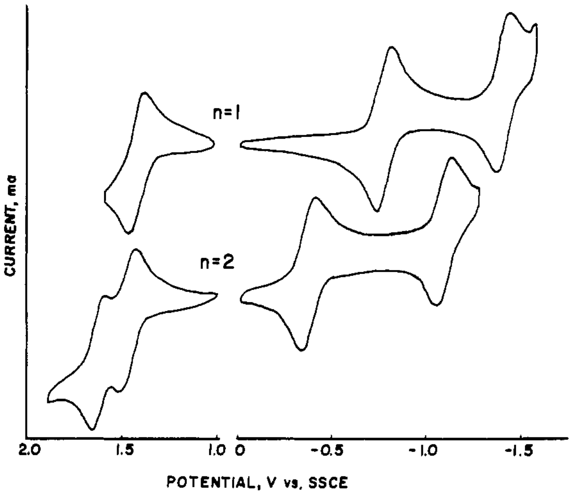

Figure 4. Cyclic voltammograms for $[Ru(bpy)_2]_nBL(1)(PF_6)_{2n}$ complexes in 0.1 M TEAP–acetonitrile solutions.

the theoretical value of ~1600. Comparison of the theoretical and experimental values for mononuclear complexes suggests ion pairing is enhanced or secondary solvent effects play a role. The mechanism may involve the remote nitrogen atoms on the bridging ligand, which are uncoordinated to a metal center. The mechanism for this interaction disappears after the sites are coordinated to a second metal center, resulting in fair agreement between experimental and theoretical conductivities.

Electrochemistry. Cyclic voltammograms for $Ru(bpy)_2BL(1)^{2+}$ and $[Ru(bpy)_2]_2BL(1)^{4+}$ are illustrated in Figure 4, and important electrochemical data are given in Table I. $E_{1/2}$ values were deduced by averaging the peak potentials for oxidation and reduction waves. The $E_{1/2}$ values determined in this way differed from those found with use of differential-pulse techniques by only ±0.02 V. For cyclic voltammetric measurements, the sweep rate was varied from 800 to 20 mV/s and ΔE_p ($\Delta E_p = E_{p(ox)} - E_{p(red)}$) varied from 90 to 65 mV for a given redox couple. Plots of ΔE_p vs. the square root of the sweep rate were linear, indicating that the electron-transfer step was reversible.[25] Limiting values of peak potential separations were extrapolated from the plots and are recorded in Table I. The values were usually larger than expected for reversible one-electron transfer ($\Delta E_p = 59/n$, where n is the number of electrons) processes. iR compensation proved to be ineffective in coorrecting the problem. ΔE_p values of 70 mV for one-electron transfers have often been reported for cyclic voltammograms in nonaqueous media and appear to be the norm rather than the exception.

Coulometric oxidations in acetonitrile solutions containing 0.1 M TEAP were attempted in order to determine n values. The oxidations were carried out at a potential ~0.2 V more positive than $E_{1/2}(1)$ for mononuclear complexes and ~0.2 V more positive than $E_{1/2}(2)$ for binuclear species. Solution color changes clearly indicated that the complexes were being oxidized, but the recorder traces failed to reach the expected base lines after the theoretical quantities of electrons were removed from the samples. Oxidized substrate was over 90% complete at this point. However, continued electroysis resulted in n values much greater than expected. For example, it was possible to obtain n values of 10 or greater from solutions originally containing $[Ru(bpy)_2]_2BL(1)^{4+}$. For binuclear complexes, cyclic voltammograms of the "oxidized" solutions after n was 2 or greater gave cyclic waves similar to those of the original complex, indicating that the complex remained intact upon oxidation and catalysis was occurring, presumably oxidation of the solvent, acetonitrile.

In contrast to the behavior of binuclear species, solutions of oxidized mononuclear complexes gave a new cyclic wave at a potential more positive than the original one. We have studied the electrochemical oxidation of $Ru(bpy)_2BL(1)^{2+}$ in more detail and plan to report the results of that study later. Some interesting preliminary observations[26] indicate rapid oxidations lead to a ruthenium(III) complex (n = 1) that undergoes disproportionation to give the original ruthenium(II) complex plus a second ruthenium(II) complex containing an oxidized ligand. The observed rate constant was determined spectrophotometrically by following absorption changes of the oxidized solution (n = 1) as a function of time. It was 1.57×10^{-3} s^{-1}.

In contrast to oxidations, it was possible to obtain n values for the first reduction $E_{1/2}'(1)$ of the complexes, and these are recorded in Table I. A direct comparison of peak currents to the $E_{1/2}'(1)$ wave indicates that the other electrochemical processes are also one-electron transfers except for $E_{1/2}(1)$ of $[Ru(bpy)_2]_2BL(2)^{4+}$. In this case the peak heights were in a ratio of 1:1.8. This is consistent both theoretically and qualitatively with two one-electron transfers. Statistically, two equivalent one-electron waves should be separated by 36 mV.[27] For $[Ru(bpy)_2]_2BL(2)^{4+}$, one would not necessarily expect the two ruthenium centers to be electrochemically equivalent after the first electron is removed, since the metals share the same bridging-ligand π system and an intervalence electron transfer of $[Ru(bpy)_2]_2BL(2)^{5+}$ generated electrochemically is observed at 1900 nm. Nevertheless, in the limit of equivalency, a peak separation of 100 mV is in accord with the near superposition of two equivalent one-electron waves. In addition, electrochemical theory leaves the peak height ratio unspecified for this situation.[28]

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Table II. Visible-UV Spectra Data for Mononuclear and Binuclear Complexes of Ruthenium(II)[a-c]

complex	$d\pi \rightarrow \pi^*$(BL)	$d\pi \rightarrow \pi^*$(bpy)	$\pi \rightarrow \pi^*$ [d]
$Ru(bpy)_2BL(1)(PF_6)_2$	515 (8.1×10^3)	427 (sh)	348 (sh), 284 (6.8×10^5), 253 (sh)
$Ru(bpy)_2BL(2)(PF_6)_2$	573 (8.0×10^3)	415 (2.3×10^4), 398 (2.3×10^4)[e]	285 (8.8×10^4), 256 (sh)
$Ru(bpy)_2bpyrm(ClO_4)_2$	422 (9.1×10^3)		284 (5.6×10^4), 236 (4.0×10^4)
$[Ru(bpy)_2]_2BL(1)(PF_6)_4$	605 (9.8×10^3)	423 (sh), 399 (1.2×10^4)	382 (sh), 283 (1.2×10^5), 243 (5.1×10^4)
$[Ru(bpy)_2]_2BL(2)(PF_6)_4$	642 (7.1×10^3), 530 (8.8×10^3)	420 (3.5×10^4), 400 (3.5×10^4)[e]	290 (1.3×10^5)
$[Ru(bpy)_2]_2bpyrm(ClO_4)_4$	594 (8.2×10^3), 545 (sh)[f]	411 (2.4×10^4)	280 (7.5×10^4), 243 (sh)

[a] λ_{max} in nm, error ±1 nm. [b] ϵ values follow in parentheses; units are M^{-1} cm^{-1}. [c] Spectra were recorded in acetonitrile solutions; $T = 20 \pm 1$ °C. ϵ values were calculated from slopes of plots of A vs. C, where A was the absorbance and C the concentration of complex in solution. [d] Transitions of $\pi \rightarrow \pi^*$ for both bridging ligands and bipyridine ligands are superimposed. [e] Could also be $\pi(BL) \rightarrow \pi(BL)^*$ transition. [f] Values reported here are in agreement with those given in ref 17 and 18.

The electrochemical processes observed in Figure 4 are typical of those found for poly(pyridyl) complexes of ruthenium. The first wave, $E_{1/2}(1)$, reportedly involves the Ru(III/II) couple[12,13,15] and is "split" into a second wave, $E_{1/2}(2)$, for binuclear complexes having metal interacting sites. This interaction has been attributed to electrostatic and electronic effects brought about by the location of the second metal center with respect to the first and the shared π system between the metal centers.[13a] The electrostatic component is thought to dominate the interaction, and it also has the effect of lowering the energy of the π^*(BL) level, giving rise to better $d\pi-\pi^*$ orbital overlap, and hence stabilizing the $d\pi$ levels as noted by an increase in $E_{1/2}(1)$ in going from mononuclear to binuclear complexes.

With the use of current symbolism, $E_{1/2}(2)$ and $E_{1/2}(1)$ are described by eq 2 and 3, respectively. The [3,2] species is

$$[3,3] + e^- \rightarrow [3,2] \tag{2}$$

$$[3,2] + e^- \rightarrow [2,2] \tag{3}$$

mixed valent, of Robin and Day classification II,[29] and intervalent electron-transfer bands are observed for the binuclear complexes reported here. This will be the topic of a subsequent paper describing this property of these compounds.

Reductions of poly(pyridyl)ruthenium complexes is ligand centered. Each bipyridine ligand of $Ru(bpy)_3^{2+}$, for example, is sequentially reduced by one electron, commencing at −1.34 V vs. SSCE. In addition, DeArmond[30] has shown that the second ligand reduction also occurs in a series at a potential 0.6–0.7 V more negative than the first. Since the π^* levels of the bipyridine and bridging ligands are not equivalent, the reductions occur independent of one another. Thus, the reductions occurring at potentials greater than −1.3 V are of the bridging ligands. For binuclear complexes and $Ru(bpy)_2BL(2)^{2+}$, $E_{1/2}'(1)$ corresponds to the first reduction of the bridging ligand and $E_{1/2}'(2)$ to the second, in keeping with DeArmond's assignment above. $E_{1/2}'(2)$ for $Ru(bpy)_2BL(1)^{2+}$ and $Ru(bpy)_2(bpyrm)^{2+}$ most likely corresponds to the reduction of one of the bipyridine ligands. Cyclic sweeps to more negative potentials led to electrode adsorption difficulties, negating the collection of additional reduction potential data.

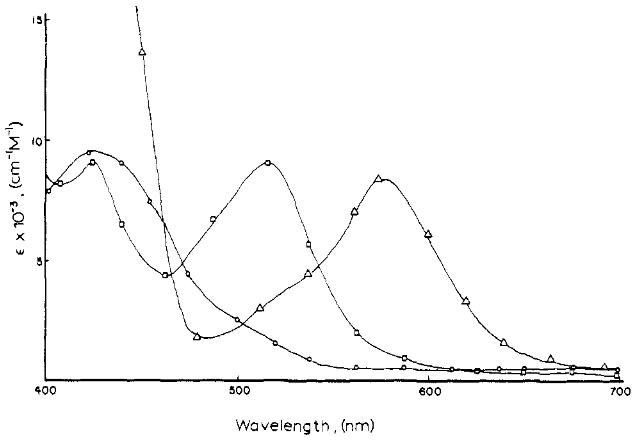
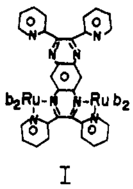
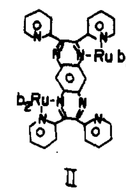


Figure 5. Visible spectra of mononuclear ruthenium(II) complexes in acetonitrile at 25 °C: (○) $Ru(bpy)_2bpyrm(PF_6)_2$; (□) $Ru(bpy)_2BL(1)(PF_6)_2$; (△) $Ru(bpy)_2BL(2)(PF_6)_2$.

The polarographic data allow one to deduce the BL(2) binding sites of ruthenium in $[Ru(bpy)_2]_2BL(2)^{2+}$. The $Ru(bpy)_2^{2+}$ units are too large, as shown with molecular models, to fit on the same side of the bridging ligand and must of necessity locate themselves on opposite sides, where there are two possible bonding sites. Either the metals could bind to the same pyrazine unit or each metal could choose its own pyrazine site. It has previously been shown that the uncoordinated nitrogen on pyrazine becomes more basic upon coordination to ruthenium in $Ru(NH_3)_5L^{3+}$, L = pyrazine.[31] If this were true in the above situation, one would expect structure I to form. Analysis of the polarographic data, however, leads to the conclusion that II is the product. If both ruthenium centers were bound to the same pyrazine ring, $E_{1/2}(1)$ and $E_{1/2}(2)$ should parallel the results found for BL(1) as the bridging ligand. This is not the case since incorporation of the second ruthenium only broadens $E_{1/2}(1)$ and does not "split" the wave to the same magnitude as in the BL(1) case. Thus, the lowest energy configuration appears to be structure II rather than I for this binuclear compound.



I



II

Visible Spectra. The visible–UV spectra of the complexes as recorded in Table II contained intense absorptions in the 240–290-nm region. Bands in this region have previously been assigned as $\pi \rightarrow \pi^*$ ligand transitions for analogous complexes.[12,13,32] Lower energy transitions were observed in the visible spectra and assigned as $d\pi \rightarrow \pi^*$ transitions. For mixed-ligand complexes containing π-acceptor ligands, the $d\pi \rightarrow \pi^*$ transitions to bipyridine fall in the 400–450-nm region.[12,13a] Lower energy transitions are observed for mononuclear and binuclear complexes reported here, as shown in Figures 5 and 6. These lower energy transitions are in accord with optical transfer of a $d\pi$ electron to the π^* level of the bridging ligand and are amplified in the discussion below.

The positions of the band maxima in Figure 5 are related to the degrees of π delocalization in the bridging ligands, analogous to the concept of increasing the mean free path and

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(29) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
(30) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.
(31) Ford, P.; Rudd, D. P.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.
(32) Bryant, G. M.; Ferguson, J. E.; Powell, H. K. *Aust. J. Chem.* **1971**, *24*, 275.

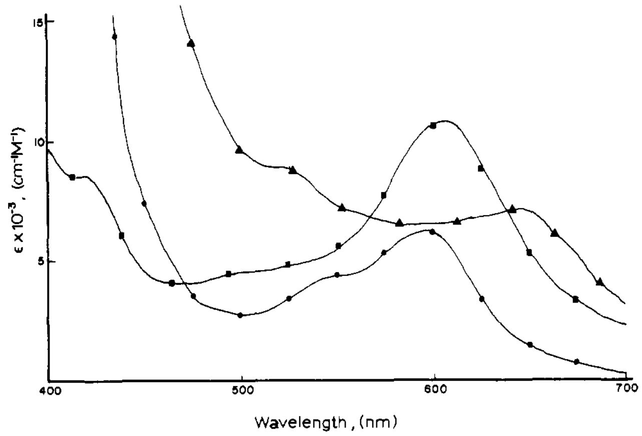

Figure 6. Visible spectra of binuclear ruthenium(II) complexes in acetonitrile at 25 °C: (●) $[Ru(bpy)_2]_2bpyrm(PF_6)_4$; (■) $[Ru(bpy)_2]_2BL(1)(PF_6)_4$; (▲) $[Ru(bpy)_2]_2BL(2)(PF_6)_4$.

hence lowering the energy for the particle in a box. Clearly, as the number of ligand π systems interacting with the metal center increases, the energy of the $d\pi \rightarrow \pi^*$ transition shifts to the red. For bipyrimidine, ruthenium(II) interacts with two pyrimidine π systems; for BL(1), there are three π systems, pyridine and pyrazine rings and the fused benzene ring bound to the pyrazine unit; and for BL(2), there are four π systems, a pyridine ring, two pyrazine rings and the fused benzene ring connecting the pyrazine components.

The position of the low-energy band as illustrated in Figures 5 and 6 shifts to the red upon formation of the binuclear complexes while the bands in the 400–450-nm region remain nearly constant. This is consistent with assigning the low-energy absorption to the $d\pi \rightarrow \pi^*(BL)$ transition. It has previously been shown that the $d\pi \rightarrow \pi^*(BL)$ transition is strongly affected by a remote metal since the transitions are directed along the metal–metal axis.[33] The π^* level of the bridging ligand is apparently stabilized by the remote positive charge of the second ruthenium center.

The difference in Table II between λ_{max} values of mononuclear and binuclear complexes for the $d\pi \rightarrow \pi^*(BL)$ absorption is greatest for the bridging-ligand bipyrimidine complexes (174 nm), intermediate for BL(1) complexes (100 nm), and smallest for BL(2) complexes (68 nm). The reason for this sequence can be qualitatively understood by considering metal-bridging ligand-bonding sites. In the case of the bipyrimidine "dimer", the metals are bound to similar pyrimidine units containing degenerate π^* orbitals. For the BL(1) "dimer", the metal centers are bound to two different pyridine rings but the same pyrazine unit. For the BL(2) binuclear complex, the metal centers interact with different pyridine rings and also different pyrazine components. In the latter case the positive charge associated with the second ruthenium is more remote than for BL(1) complexes, resulting in less stabilization of the $\pi^*(BL)$ orbitals and hence a smaller λ_{max} change. For the bipyrimidine case, both pyrimidine rings are directly affected by the positive charge of the second metal, resulting in a greater λ_{max} change than for the BL(1) case, where only the π^* level of the pyrazine bridge is shared.

The Low-Lying Excited State. The information in the preceding sections is summarized in part in Figure 7. Figure 7 is a plot of the lowest energy transition as a function of $E_{1/2}'(1)$ for data taken from Tables I and II. Also included are data for $Ru(bpy)_2BL(3)^{2+}$, $[Ru(bpy)_2]_2BL(3)^{4+}$, $[Ru(bpy)_2]_3BL(3)^{6+}$, and $[Ru(bpy)_2]_4BL(3)^{8+}$. Clearly the relationship is linear. When the energy of the absorption band is expressed in electronvolts, the correlation coefficient is 0.96 and the slope, within experimental error, is 1.

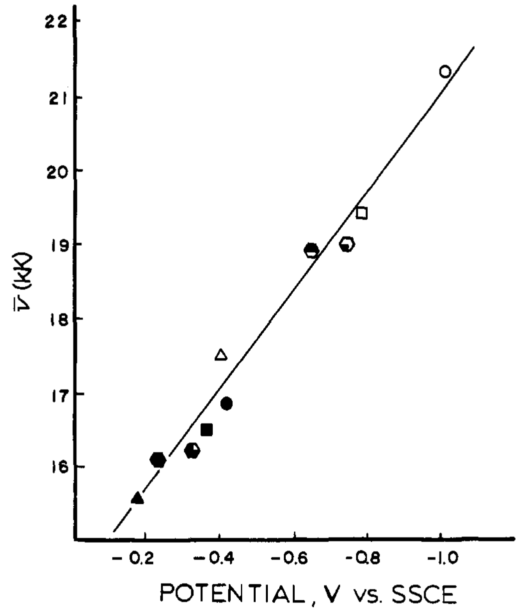

Figure 7. Correlation between the low-energy visible absorption transition and the polarographic half-wave potential of the first reduction: (○) $Ru(bpy)_2bpyrm(PF_6)_2$; (□) $Ru(bpy)_2BL(1)(PF_6)_2$; (△) $Ru(bpy)_2BL(2)(PF_6)_2$; (●) $[Ru(bpy)_2]_2bpyrm(PF_6)_4$; (■) $[Ru(bpy)_2]_2BL(1)(PF_6)_4$; (▲) $[Ru(bpy)_2]_2BL(2)(PF_6)_4$; (◓) $Ru(bpy)_2BL(3)(PF_6)_2$, from ref 12; (◒) $[Ru(bpy)_2]_2BL(3)(PF_6)_4$, from ref 12; (◑) $[Ru(bpy)_2]_3BL(3)(PF_6)_6$, from from ref 12; (◐) $[Ru(bpy)_2]_4BL(3)(PF_6)_8$, from ref 12.

The correlation indicates that both processes are physically related. The absorption process corresponds to a MLCT, which formally involves the transfer of an electron from the metal to the ligand.[32] The electrochemical $E_{1/2}'(1)$ process must correspond to the reduction of that same ligand in order for the two to correlate with each other. This is possible provided the following criteria are met. First, the reduction must be of the same energy level in all cases. The lowest energy π^* level for π-acceptor ligands has previously been assigned as $\pi^*(BL)$ for complexes having absorptions at lower energies than 450 nm.[12,13a] Second, the energy of the $d\pi$ orbitals for the compounds studied must remain fairly constant in order that the energy of the optical transition track the reduction potential of that ligand. Indeed, $E_{1/2}(1)$ does remain nearly constant in the series, $E_{1/2}(1) = 1.44 \pm 0.04$ V vs. SSCE. Third, the energy of the $\pi^*(BL)$ orbitals should be separated from the π^* orbitals of other ligands such as bipyridine. The optical absorption bands for $Ru(bpy)_3^{2+}$ assigned by Bryant, Ferguson, and Powell[32] consisted of two $d\pi \rightarrow \pi^*$ transitions due to the degeneracy of the $d\pi$ energy levels. Similarly then, two more $d\pi \rightarrow \pi^*$ bands would be expected due to the presence of the bridging ligand. A total of four $d\pi$ transitions are expected: two $d\pi \rightarrow \pi^*(bpy)$ and two $d\pi \rightarrow \pi^*(BL)$ bands based on Ferguson's model. The two transitions to the same ligand often overlap, giving rise to a single maximum and shoulder.[33] The two sets of transitions expected then can be treated independently of one another, provided the π^* levels are of different energies resulting in separated absorption bands. In this study, the π^* levels of the bridging ligands appear to be lower in energy than the π^* energy levels of the bipyridine ligand. The only possible exception is the bipyrimidine ligand complex $Ru(bpy)_2bpyrm^{2+}$ where the π^* energy level is probably comparable to that of bipyridine. Nevertheless, it does correlate with the trend found in Figure 7. Thus, Figure 7 provides much stronger evidence for assigning the lowest energy transition as $d\pi \rightarrow \pi^*(BL)$ for mixed-ligand complexes of ruthenium containing bipyridine and a π-acceptor bridging ligand. Recent Raman work is also

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(33) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

in accord with this assignment.[34] Finally, it should be mentioned that theoretically it should be possible for the bridging-ligand π^* energy level to be higher than that in bipyridine, in which case the $d\pi \rightarrow \pi^*$ assignments for mononuclear complexes would be reversed.

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Registry No. $Ru(bpy)_2BL(1)(PF_6)_2$, 82849-33-0; $[Ru(bpy)_2]_2BL(1)(PF_6)_4$, 82849-35-2; $Ru(bpy)_2BL(2)(PF_6)_2$, 82849-37-4; $[Ru(bpy)_2]_2BL(2)(PF_6)_4$, 82864-91-3; $Ru(bpy)_2(bpyrm)(ClO_4)_2$, 82864-92-4; $[Ru(bpy)_2]_2bpyrm(ClO_4)_4$, 82849-38-5; $Ru(bpy)_2BL(1)(ClO_4)_2$, 82849-40-9; $[Ru(bpy)_2]_2BL(1)(ClO_4)_4$, 82849-41-0; BL(2), 82849-31-8; $Ru(bpy)_2Cl_2$, 15746-57-3; 1,2,4,5-benzenetetramine tetrahydrochloride, 4506-66-5; 2,2′-bipyridyl, 366-18-7.

Supplementary Material Available: A listing of elemental analyses for reported compounds (1 page). Ordering information is given on any current masthead page.

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(34) Braunstein, C.; Baker, A. D.; Gafney, H. D.; Strekas, T. C. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, Aug 23–28, 1981; American Chemical Society: Washington, DC, 1981; INOR 250.

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Electron Transfer. 57. A Reverse Kinetic Salt Effect in Some Inner-Sphere Reductions by Chromium(II)[1]

Vangalur S. Srinivasan[2] and Edwin S. Gould*

Received March 15, 1982

The reactions of mono(carboxylato) derivatives of cobalt(III) with the usual metal-center reductants (bimolecular reactions between cations) should exhibit positive kinetic salt effects; i.e., they should be accelerated by addition of a nonparticipating electrolyte.[3] Past reports of such accelerations[4] have considered them mainly as sidelights subsidiary to more interesting mechanistic facets. This communication describes three such systems in which the salt effect is substantial and takes a direction opposite to that expected.

Experimental Section

Materials. Lithium perchlorate[5] and solutions of $Cr(ClO_4)_2$,[4a] $V(ClO_4)_2$,[6] and $Eu(ClO_4)_2$[7] were prepared as described. Sodium perchlorate solution was prepared by treating reagent grade $NaHCO_3$ with 70% $HClO_4$, adjusting the pH to 4, diluting to the desired volume, and then purging with N_2 to remove dissolved CO_2. Cobalt complexes were available from a previous study.[8]

Table I. Variation, with Ionic Strength, of Specific Rates for Reduction of Some (Carboxylato)cobalt(III) Complexes

			k,[a] $M^{-1}\ s^{-1}$	
reductant	$[H^+]$, M	μ, M	2-isomer	4-isomer
A. 2- and 4-Formyl-Substituted μ-Benzoato Co^{III} Dimers (I and II)				
Cr^{2+}	0.10	0.10	11.5	42
	0.10	0.25	27[c]	67,[b] 73[c]
	0.10	0.50	25,[b] 29[c]	
	0.10	0.75	31[c]	80,[b] 82[c]
	0.20	1.00		95[b]
	0.50	1.00		97[b]
	1.00	1.00	37	95
	0.10	1.50		73,[b] 71[c]
	0.10	2.00	29,[b] 26[c]	67,[b] 51[c]
	2.00	2.00	28	67
	0.10	4.00	15.0,[b] 14.6[c]	27,[b] 23[c]
	1.00	4.00	13.7,[b] 16.2[c]	23,[b] 27[c]
	4.00	4.00	12.8	29
V^{2+}	0.10	1.00	0.23[b]	0.126[b]
	1.00	1.00	0.25	0.130
	1.00	4.00		0.096[b]
	2.00	4.00	0.22[b]	
	4.00	4.00	0.25	
Eu^{2+}	0.10	1.00	0.049[b]	0.67[b]
	1.00	1.00	0.058	0.70
	2.00	4.00	0.036[b]	
	4.00	4.00	0.038	
B. 2- and 4-Formylbenzoato Complexes of $(NH_3)_5Co^{III}$ (III)				
Cr^{2+}	0.10	0.10		43
	0.10	0.25		57,[b] 48[c]
	0.10	1.00		62,[b] 66[c]
	1.00	1.00	73	
	0.10	2.50		60,[b] 60[c]
	0.10	3.50		43,[b] 44[c]
	0.10	4.00	77,[b] 73[c]	34,[b] 30[c]
	1.00	4.00	69,[b] 69[c]	
C. μ-Pyruvato Co(III) Dimer (IV)				
Cr^{2+}	0.10	0.10	10	
	0.10	1.00	37,[b] 20[c]	
	0.10	4.00	40,[b] 38[c]	
D. $HCOOCo(NH_3)_5{}^{2+}$				
Cr^{2+}	1.00	1.00	6.8	
	0.10	4.00	7.9,[b] 7.6[c]	
	1.00	4.00	7.3,[b] 7.0[c]	

[a] Specific rates at 25 °C. Values for the dimeric complexes refer to the rate of disappearance of the dimer. [b] Supporting electrolyte electrolyte $HClO_4$ + $LiClO_4$. [c] Supporting electrolyte $HClO_4$ + $NaClO_4$.

Rate Measurements. Rates were estimated from measurements of absorbance changes on a Cary Model 14 or Beckman Model 5260 recording spectrophotometer as described.[4a,7] Earlier studies[4a,8] demonstrated that reactions were first-order each in reductant and Co(III), but experiments in this series were carried out under pseudo-first-order conditions with at least a 10-fold excess of reductant and were monitored at 524 or 502 nm (the low-energy maximum of the Co^{III} complexes). Reactions were followed for at least 4 half-lives. Rate constants evaluated from successive half-life values in a single run agreed to within 5%. Specific rates obtained from replicate runs checked to better than 7%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Results and Discussion

Kinetic data appear in Table I. The few entries for the Cr(II) reductions of the μ-pyruvato dimer (IV) and for the formato monomer indicate that these reactions exhibit salt

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(1) Sponsorship of this work by the National Science Foundation is gratefully acknowledged.

(2) On leave from Vivekanada College, Mylapore, Madras, India.

(3) See, for example: (a) Weston, R. E., Jr.; Schwarz, H. A. "Chemical Kinetics"; Prentice-Hall: Englewood Cliffs, NJ, 1972; p 165. (b) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 172.

(4) See, for example: (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1320. (b) Liang, A.; Gould, E. S. *Ibid.* **1970**, *92*, 6791. (c) Gould, E. S. *Ibid.* **1970**, *92*, 6797.

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(6) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.

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