

boron centers are thermodynamically weak but may be short (1.632–1.697 Å), indicating possible kinetic stability.

In the case of reactive boron hydrides (BH_3 , B_3H_7 , and B_4H_8) the complex is more stable than the boron hydride plus NH_3 , while in the case of the observed carboranes ($\text{C}_2\text{B}_3\text{H}_5$, $\text{C}_2\text{B}_3\text{H}_7$) and B_5H_9 the complex is less stable than the observed free species plus NH_3 .

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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Localized States in Reduced and Excited-State Ruthenium(II) Terpyridyls

Robert M. Berger and David R. McMillin*

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Spectroelectrochemical studies of $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+}$ and $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^{2+}$ ($\text{trpy} = 2,2':6',2''\text{-terpyridine}$, $\text{bpy} = 2,2'\text{-bipyridine}$, $4,4'\text{-dph-bpy} = 4,4'\text{-diphenyl-2,2'\text{-bipyridine}$, $\text{py} = \text{pyridine}$) as well as the corresponding homoleptic polypyridyl complexes have been carried out. The results show that one-electron reduction of the mixed-ligand complexes involves introducing an electron into a π^* orbital that is essentially localized on the trpy ligand system. Low-temperature EPR spectra support this interpretation and together with the other data suggest that the electron is localized on a single trpy ligand in $\text{Ru}(\text{trpy})_2^+$ as well. Finally, the linear correlation between the energy of the MLCT emission maximum and the difference in potential between the first oxidation and reduction waves of these complexes indicates that the same ligand orbital is populated in the lowest energy metal-to-ligand charge-transfer excited state.

Introduction

Since the first report¹ of luminescence from $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$), the photophysical and photochemical properties of this and related d^6 polypyridyl complexes have been the subject of intense interest.²⁻¹⁸ Two models of the emitting metal-to-ligand

charge-transfer (MLCT) excited states of $\text{Ru}(\text{bpy})_3^{2+}$ have been proposed. One of these involves the symmetric delocalization of the transferred electron density over all three bipyridine ligands (delocalized model).² In the other, so-called localized model, the transferred electron density tends to be found on only one of the bipyridines, but it can "hop" from ligand to ligand. Excited-state absorption⁵ and transient circular dichroism measurements⁶ as well as steady-state¹¹ and time-resolved¹² photoselection measurements are consistent with localization. Perhaps the strongest evidence for a localized excited state, however, comes from the time-resolved resonance Raman (TR^3) spectrum of the excited state at room temperature¹³ or in a rigid ethanol/methanol glass.¹⁴ These experiments clearly establish that localization occurs on at least a nanosecond and even a picosecond^{14a} time scale. The photophysics and photochemistry of the related $2,2':6',2''\text{-terpyridine}$ (trpy) complexes have received far less attention, although these species are interesting in their own right.¹⁹⁻²² It has, however, been argued that charge localization can occur in these systems, too.²³ In the excited states of mixed-ligand complexes containing both tridentate and bidentate polypyridine ligands, charge localization is certainly expected; however, the questions remain as to which ligand is favored and to what extent substituents influence the localization. A priori, trpy , with a more extended π -system than bpy , would be expected to present a more energetically accessible π^* orbital and hence a lower energy excited state. In an attempt to answer this question for $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+}$ ($\text{py} = \text{pyridine}$) and related systems, we have at-

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tempted TR³ measurements, but we have found it difficult to identify the Raman scattering in an unambiguous way. Consequently, we have carried out a series of spectroscopic and electrochemical measurements in order to answer the question.

This approach hinges on the fact that spectroscopic studies¹⁶⁻¹⁸ have shown that localization also occurs in (ground-state) reduced species such as Ru(bpy)₃²⁺ and Ru(bpy)₃. If it can be shown that the same ligand orbital is involved in the d-π* excited state (spectroscopic orbital) and the first electrochemical reduction (redox orbital),²⁴⁻²⁶ then it is possible to identify the spectroscopic orbital by electrochemical means. In the following we report the results of our studies of Ru(trpy)(bpy)(py)²⁺ and Ru(trpy)(4,4'-dph-bpy)(py)²⁺, where 4,4'-dph-bpy denotes 4,4'-diphenyl-2,2'-bipyridine, as well as results pertaining to the related homoleptic complexes. DeArmond and co-workers have already presented evidence for localization of the redox orbitals in the Ru(trpy)₂²⁺ system.^{23b}

Experimental Section

Materials. [Ru(trpy)₂]Cl₂²⁷, [Ru(trpy)(bpy)(py)]Cl₂²⁸, [Ru(trpy)(4,4'-dph-bpy)(py)]Cl₂²⁸ and [Ru(4,4'-dph-bpy)₃]Cl₂²⁹ were prepared by literature methods. [Os(trpy)₂]Cl₂ was prepared by a modification of the method used for [Ru(trpy)₂]Cl₂. [Ru(bpy)₃]Cl₂ was obtained from G. F. Smith. The Cl⁻ salts of all the complexes were converted to the PF₆⁻ salts by metathesis with either saturated aqueous NH₄PF₆ or 60% aqueous HPF₆ (both from Aldrich). Purification was carried out by chromatography on basic alumina with 2:1 (v/v) toluene/acetonitrile as the eluent or on Sephadex LH-20 (Pharmacia) with methanol as the eluent. Purity was established by microanalysis or by spectral comparisons with literature data.

Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by metathesis from tetra-*n*-butylammonium iodide and NH₄PF₆. The resulting solid was isolated, recrystallized twice from ethanol, and dried under vacuum at 60 °C. The solvent, *N,N*-dimethylformamide (DMF), was obtained from Burdick and Jackson, deoxygenated by a N₂ stream, and stored over 4-Å molecular sieves (Mallinckrodt) in an inert-atmosphere box.

Instrumentation. UV-visible spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer controlled by a Perkin-Elmer 7300 series computer. Emission spectra were recorded by using an SLM-Aminco SPF-500C fluorometer. Cyclic voltammograms were obtained with a BAS CV-1A potentiostat and a Hewlett-Packard 7015B X-Y recorder. Potentials were monitored with a Beckman TECH 300 digital multimeter. Thin-layer coulometry was carried out with a PAR 173 potentiostat equipped with a PAR 179 digital coulometer. EPR spectra were recorded by using a Varian E-109 spectrometer and Hewlett-Packard 935 computer.

Methods. Solutions used for luminescence measurements were absorbance-matched at 460 nm (*A*₄₆₀ = 0.4) and were 0.5 M in TBAH. The solvent was DMF. Correction factors for the emission spectra were supplied by the manufacturer, SLM Instruments, Inc. Solutions used in the electrochemical and spectroelectrochemical measurements were prepared in DMF and were 1.0 mM in complex and 0.5 M in supporting electrolyte. An optically transparent thin-layer electrode (OTTLE) was prepared as described in the literature³⁰ by using a 100 wire/in. gold minigrad. The OTTLE was used for the thin-layer cyclic voltammetry (TLCV) measurements, as well as all other thin-layer measurements. Conventional cyclic voltammetry was carried out with a Pt-disk working electrode (BAS PTE). A Pt wire was used as the auxiliary electrode in all electrochemical measurements. The reference electrode was an aqueous Ag/AgCl (3 M NaCl) electrode (BAS RE-1), which was joined to the solution with a porous Vycor plug. All potentials are reported versus this electrode and are uncorrected for junction-potential effects. Electrochemical operations were carried out in the inert-atmosphere box. Scan rates were 190 mV s⁻¹ for conventional CV measurements and 1.9 mV s⁻¹ for TLCV measurements.

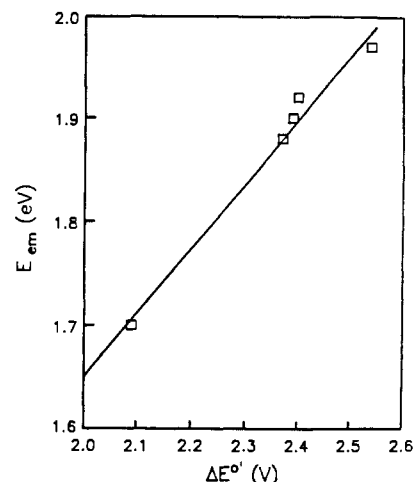


Figure 1. Linear correlation between E_{em} and $\Delta E^{\circ'}$ for Os(trpy)₂²⁺ and the ruthenium(II) polypyridyl complexes. See text for definition of symbols. In order of decreasing energy of emission, the complexes are Ru(bpy)₃²⁺, Ru(4,4'-dph-bpy)₃²⁺, Ru(trpy)(bpy)(py)²⁺, Ru(trpy)(4,4'-dph-bpy)(py)²⁺, and Os(trpy)₂²⁺.

Table I. UV-Visible Absorption Bands in Ruthenium(II) Polypyridyl Complexes

	λ , nm (ϵ , M ⁻¹ cm ⁻¹)		
	$n = 2$	$n = 1$	$n = 0$
Ru(trpy) ₂ ²⁺	478 (14 300)	626 (sh) 521 (11 100) 418 (8050) 365 (sh)	665 (sh) 549 (13 400) 450 (11 600) 350 (34 800)
Ru(bpy) ₃ ²⁺	453 (14 300)	524 (15 000) 498 (15 400) 337 (21 300)	537 (17 400) 504 (15 600) 340 (33 900)
Ru(4,4'-dph-bpy) ₃ ²⁺	477 (28 100) 450 (sh) 353 (27 100)	601 (12 300) 532 (23 500) 483 (sh)	608 (22 100) 577 (22 800) 429 (26 200)
Os(trpy) ₂ ²⁺	660 (3360) 540 (sh) 478 (12 800)	620 (sh) 505 (12 100) 420 (13 300)	344 (54 100) 449 (25 300) 342 (33 800)
Ru(trpy)(bpy)(py) ²⁺	473 (9550) 416 (sh)	625 (sh) 513 (9930) 431 (8610) 368 (sh)	577 (22 800) 449 (25 300) 342 (33 800)
Ru(trpy)(4,4'-dph-bpy)(py) ²⁺	484 (16 000) 424 (sh) 353 (sh)	625 (sh) 531 (14 900) 400 (sh) 372 (sh) 351 (20 900)	

For spectroelectrochemical measurements, the OTTLE was placed in a plexiglass box with glass windows. An inert-gas purge (Ar or N₂) was maintained through the box during the experiment in order to exclude O₂ and water vapor. After application of a potential corresponding to the cathodic peak potential, a period of at least 5 min was allowed for equilibration of the electroactive species. Due to the large (ca. 160 mV) peak-to-peak separation between the cathodic and anodic waves, the cathodic peak potential was typically 70–80 mV negative of $E^{\circ'}$. Once the current had stopped, the applied potential could be substituted into the Nernst equation, which indicated about 95% conversion to the reduced form. The molar absorptivities in Figures 4 and 5 represent the apparent values calculated by dividing the absorbance by the OTTLE pathlength and the concentration of the complex.

In the EPR experiment a thin-layer bulk electrolysis was performed, and the electrolyzed solution was flushed into an EPR tube and diluted to approximately 10⁻⁴ M with 0.5 M TBAH/DMF. The tubes were sealed immediately and frozen in liquid nitrogen. EPR spectra were recorded at -150 °C. In order to determine the components in the mixed-ligand spectra, the first derivative spectra of the reduced complexes were integrated by using the HP 935 software package. Since the coordinated bpy-type anions exhibited no signal at 0.331 T, the contribution from the trpy radical could be zeroed out by subtracting the appropriately scaled spectrum of Ru(trpy)₂⁺. In each case, the ratio of the area of the resulting difference spectrum to the total area of the original mixed-ligand spectrum gave the fractional contribution from the bpy anion.

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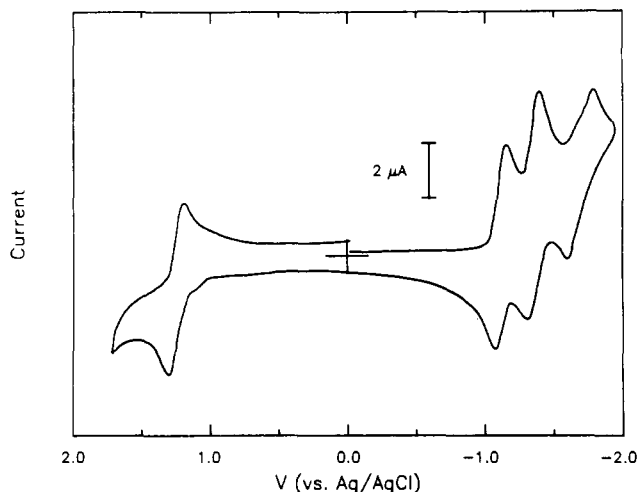


Figure 2. Cyclic voltammogram of a 1.0 mM solution of $[\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})](\text{PF}_6)_2$ in 0.5 M TBAH/DMF at a Pt-disk electrode. The scan rate was 190 mV/s, and the temperature was 22 °C.

Table II. Formal Potentials for Serial Redox Processes of Ruthenium(II) Polypyridyl Complexes in 0.5 M TBAH/DMF^a

complex	$E^{\circ}, {}^b \text{V}$			
	3/2	2/1	1/0	0/-1
$\text{Ru}(\text{trpy})_2^{2+}$	+1.32	-1.15	-1.36	-1.81
$\text{Ru}(\text{bpy})_3^{2+}$	+1.32	-1.22	-1.38	-1.64
$\text{Ru}(4,4'\text{-dph-bpy})_3^{2+}$	+1.25	-1.15	-1.30	-1.52
$\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+}$	+1.27	-1.12	-1.40	-1.72
$\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^{2+}$	+1.25	-1.12	-1.36	-1.70
$\text{Os}(\text{trpy})_2^{2+}$	+1.00	-1.09	-1.34	-1.77

^a E° vs Ag/AgCl (3 M NaCl). ^b $E^{\circ} = (E_{pc} + E_{pa})/2$ from cyclic voltammetry for the $n/(n-1)$ process at a Pt-disk electrode. Scan rate = 190 mV s⁻¹.

Results

Absorption and Emission Spectra. With the exception of $\text{Ru}(\text{trpy})_2^{2+}$, all of the complexes studied are luminescent at room temperature in DMF solution containing 0.5 M TBAH, although the emission intensities from the mixed-ligand complexes are quite weak. The ratios of the emission yields in the series $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^{2+}$, and $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+}$ are, in order, 100:4:1. The corrected emission maxima are indicated in Figure 1, and the absorption data are summarized in Table I.

Electrochemistry and TLCV. All of the complexes exhibit a reversible oxidation near +1.3 V vs Ag/AgCl (+1.00 V in the case of $\text{Os}(\text{trpy})_2^{2+}$) and several reversible one-electron reductions commencing at potentials more negative than -1.1 V. The cyclic voltammogram of a representative case, $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^{2+}$, is shown in Figure 2, and the electrochemical data are summarized in Table II. In the longer time scale TLCV experiment, the reductions of the homoleptic complexes are well-behaved, but in the case of the mixed-ligand complexes, only the first reduction is chemically reversible (Figure 3).

Spectroelectrochemistry. The UV-visible spectra of $\text{Ru}(\text{trpy})_2^{2+}$, $\text{Ru}(\text{bpy})_3^{2+}$, and $\text{Ru}(4,4'\text{-dph-bpy})_3^{2+}$ species as well as the singly reduced mixed-ligand complexes have been measured in the thin-layer cell, and the absorption maxima are compiled in Table I. The spectra of $\text{Ru}(\text{bpy})_3^{n+}$ ($n = 2, 1, 0$) are in good agreement with those previously reported.¹⁸ Representative spectra, obtained for the $\text{Ru}(\text{trpy})_2^{n+}$ series, are shown in Figure 4. The spectra of $\text{Ru}(\text{trpy})_2^+$, $\text{Ru}(\text{bpy})_3^+$, and $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^+$ are compared in Figure 5.

EPR Measurements. The EPR spectrum of $\text{Ru}(\text{trpy})_2^+$ exhibits $g_{\perp} = 1.991$ and $g_{\parallel} = 1.960$, in good agreement with a previous report,^{23b} while the corresponding bpy and 4,4'-dph-bpy complexes give $g_{\perp} = 2.001$ and $g_{\parallel} = 1.98$. As discussed below, the EPR spectra of the mixed-ligand complexes reflect contributions from both the coordinated trpy and the coordinated bipyridine radical anions. Integrations reveal relative contributions of 18% and 26%

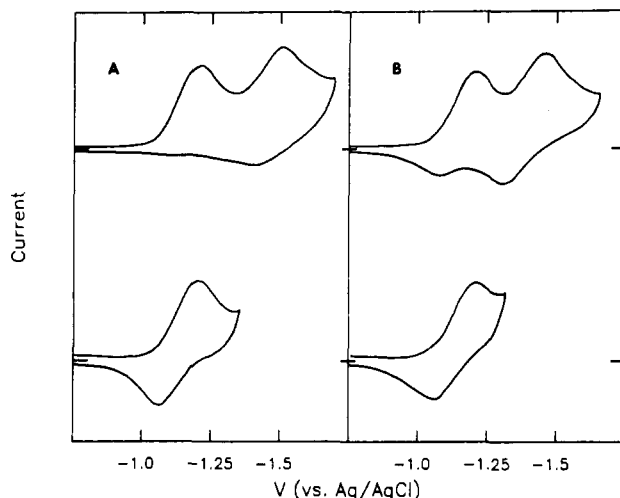


Figure 3. Thin-layer cyclic voltammograms of 1.0 mM solutions of $[\text{Ru}(\text{trpy})(\text{bpy})(\text{py})](\text{PF}_6)_2$ (A) and $[\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})](\text{PF}_6)_2$ (B) in 0.5 M TBAH/DMF at a gold minigrad in an OTTLE. The scan rate was 1.9 mV/s, and the temperature was 22 °C. The lower trace in each case shows the effect of reversing the scan prior to the second reduction wave.

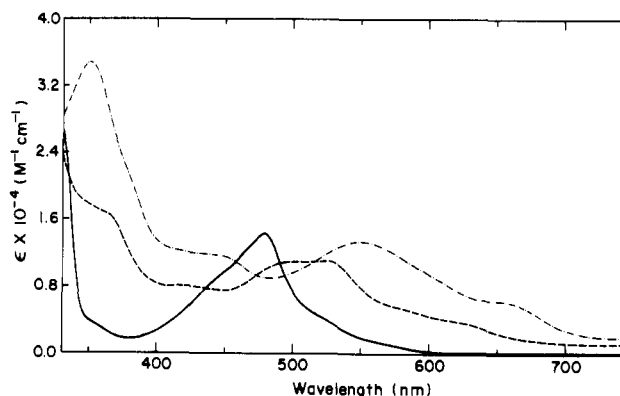


Figure 4. Near-UV-visible spectra of $\text{Ru}(\text{trpy})_2^{2+}$ (—), $\text{Ru}(\text{trpy})_2^+$ (---), and $\text{Ru}(\text{trpy})_2$ (-·-) recorded at -0.8, -1.24, and -1.49 V, respectively, vs Ag/AgCl in an OTTLE at 32 °C. The solvent was DMF containing 0.5 M TBAH.

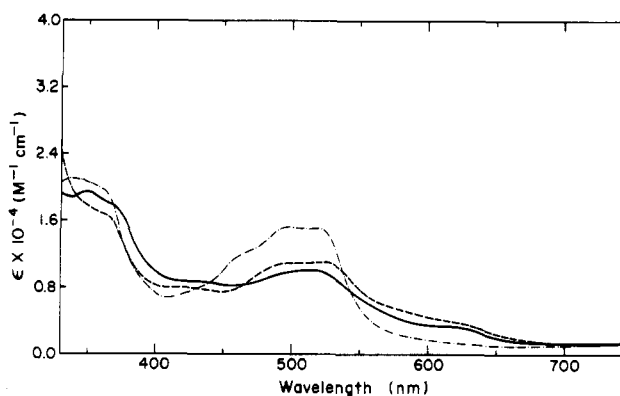


Figure 5. Near-UV-visible spectra of $\text{Ru}(\text{bpy})_3^{3+}$ (-·-), $\text{Ru}(\text{trpy})_2^+$ (---), and $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^+$ (—) recorded at -1.31, -1.24, and -1.21 V vs Ag/AgCl, respectively, in an OTTLE at 32 °C. The solvent was DMF containing 0.5 M TBAH.

in the mixed-ligand complexes containing bpy and 4,4'-dph-bpy, respectively. No nitrogen hyperfine splitting is resolved.

Discussion

Correlation between ΔE° and E_{em} . The cyclic voltammograms of the homoleptic and mixed-ligand complexes exhibit similar patterns and are consistent with a single metal-based oxidation and a series of ligand-based reductions. This pattern is a familiar one for d^6 polypyridyl complexes where orbitals tend to be localized

on individual ligands.^{18,31} If the redox and spectroscopic orbitals are the same, a linear correlation between the MLCT emission maximum^{26,32,33} or the MLCT absorption maximum^{26,34-37} and the quantity $\Delta E^{o'} = E^{o'}(\text{RuL}_3^{3+/2+}) - E^{o'}(\text{RuL}_3^{2+/+})$ results in which case the spectroscopic orbital of a mixed-ligand complex may be identified from the electrochemical properties of the corresponding homoleptic complexes.³⁸⁻⁴⁰ Figure 1 shows that just such a linear correlation is obtained for our systems; however, as can be seen from Table II, the reduction potentials in the trpy/bpy systems are so similar that clear orbital assignments cannot be made solely on the basis of $E^{o'}$ values. Therefore, we sought to characterize the reduced forms by spectral means.

Spectroelectrochemical Measurements. The utility of spectroelectrochemistry in the study of electrochemically generated reduction products of d⁶ polypyridyl complexes has previously been demonstrated.^{18,41-43} As a rule of thumb, the UV-visible spectrum of the reduced form of the appropriate homoleptic complex provides a model spectrum for a particular ligand anion in a mixed-ligand complex. In the case of $\text{Ru}(\text{bpy})_3^{2+}$, we find that two strong absorption bands grow in when an electron is added, in accord with a previous report.¹⁸ One maximizes at around 340 nm, and it has been assigned as a $\pi-\pi^*$ transition from the highest completely filled MO (π_6) to the half-filled HOMO (π_7) of the bpy anion.^{18,44,45} This band corresponds to a resonance-Raman-active band found in the excited-state absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$.⁴⁶ Another, more structured absorption appears near 525 nm and has been assigned as a $\pi^*-\pi^*$ transition ($\pi_7-\pi_{10}$)^{18,44,45} of bpy^- . The spectrum of $\text{Ru}(\text{trpy})_2^+$ is qualitatively similar, but two additional absorption bands are resolved. One appears as a pronounced shoulder at 625 nm in the spectrum of $\text{Ru}(\text{trpy})_2^+$, and it shifts to 665 nm on further reduction. A second, barely resolved band is observed between 420 and 450 nm in the $\text{Ru}(\text{trpy})_2^+$ and the $\text{Ru}(\text{trpy})_2$ spectra (Figure 4). Two similar features are observed in the spectrum of singly and doubly reduced $\text{Os}(\text{trpy})_2^{2+}$.

The spectrum of $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^+$ is fairly easy to interpret since it virtually tracks the spectrum of $\text{Ru}(\text{trpy})_2^+$ (Figure 5). In particular, two weak absorptions are resolved, maximizing near 430 nm and 625 nm. Therefore, we conclude that the trpy ligand is reduced first. The spectral analysis is, however, slightly less clear-cut in the complexes containing the 4,4'-dph-bpy ligand. One complication is that unreduced $\text{Ru}(4,4'\text{-dph-bpy})_3^{2+}$ exhibits a band at 350 nm that presumably represents a MLCT transition terminating in the so-called χ -type π^* orbital of 4,4'-dph-bpy.⁴⁷ Upon reduction of the complex, the absorption in this region is broadened and intensified so that it tails into the visible region such that transitions in the neighborhood of 420-450 nm are not well resolved. In addition the spectrum of $\text{Ru}(4,4'\text{-dph-bpy})_3^+$ exhibits a distinctive maximum at 600 nm very near the low-energy

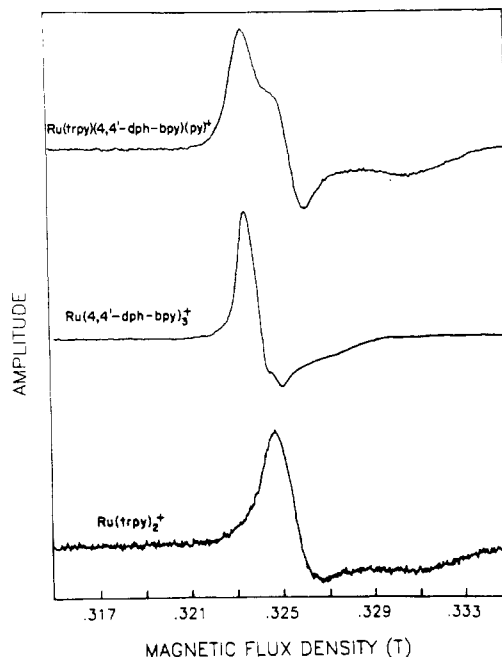


Figure 6. EPR spectra of $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^+$, $\text{Ru}(4,4'\text{-dph-bpy})_3^+$, and $\text{Ru}(\text{trpy})_2^+$ in 0.5 M TBAH/DMF at -150°C . The complexes were reduced at -1.30 , -1.24 , and -1.30 V vs Ag/AgCl, respectively, in an OTTLE.

band previously identified in the spectrum of $\text{Ru}(\text{trpy})_2^+$. Nevertheless, preferential reduction of trpy is indicated as the absorption spectrum of $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^+$ does exhibit a band at 625 nm (Table I). The EPR results discussed below also support this interpretation.

EPR Measurements. As noted above, the EPR spectra of $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(4,4'\text{-dph-bpy})_3^+$ are virtually identical and evidence less anisotropy than that of $\text{Ru}(\text{trpy})_2^+$. On the other hand, the EPR spectra of solutions of the reduced mixed-ligand complexes exhibit three distinct g values (Figure 6). However, careful spectral analysis reveals that the resolved g values are virtually identical with those observed in the spectra of the homoleptic systems, which implies that the mixed-ligand spectra actually reflect contributions from both types of polypyridyl anions. Thermal population of higher energy states may explain part of the effect; however, in order to obtain reasonable intensities the mixed-ligand complexes were reduced at -1.30 V vs Ag/AgCl, ca. 100 mV negative of the cathodic peak. Therefore, some formation of the doubly reduced forms also occurs, and for the reasons described above, a quantitative interpretation of the EPR results is precluded. For our purposes, the salient result is that the signal from the coordinated trpy anion is dominant for both of the singly reduced mixed-ligand complexes. Thus, the electronic spectra and the EPR data both indicate that the first reduction takes place at the trpy ligand.

Excited-State Considerations. From the correlation between $\Delta E^{o'}$ and E_{em} , it follows that a π^* orbital of the trpy moiety is likely to be populated in the thermally equilibrated excited-state manifolds of the trpy-containing complexes that show emission. Excited-state absorption measurements have confirmed this for the case of $\text{Ru}(\text{trpy})_2^{2+}$ as well.⁴⁸ Despite a similar $d^5\pi^*$ percentage in the excited state, $\text{Ru}(\text{trpy})_2^{2+}$ is unique in the series in that it is nonemissive at room temperature. The reason is that trpy is a relatively weak-field polypyridyl ligand due to intrinsic geometric limitations. A recent crystal structure of a bis(terpyridine) complex of Ru(II) with an annelated derivative of trpy has shown that the coordination about the metal center deviates substantially from octahedral such that the N-Ru-N'' bite angle is only about 160° .⁴⁹ As a result of this strain, low-lying ligand

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field states occur that provide for rapid nonradiative decay.^{21,22b} Consistent with this hypothesis, the emission yield increases in the series $\text{Ru}(\text{trpy})_2^{2+} < \text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+} < \text{Ru}(\text{bpy})_3^{2+}$ in line with the anticipated increase in ligand field strength. It should be noted, however, that low-symmetry effects could also be important. Thus, in the case of $\text{Ru}(\text{trpy})_2^{2+}$, the dominant low-symmetry component of the ligand field is expected to reflect a tetragonal compression, whereas in the mixed-ligand systems, the low symmetry distortion is more likely to be described in terms of a tetragonal elongation. Unfortunately, the influence that the low-symmetry field has on the energies of the various d-d excited states is difficult to assess even in a qualitative sense.

Conclusions

Ligand reduction, whether achieved via an outer-sphere process or via charge-transfer excitation, tends to be single-ligand-localized in polypyridine complexes. Here the techniques of cyclic voltammetry, spectroelectrochemistry, and EPR spectroscopy have been applied to the problem of discerning the site of electrochemical reduction in mixed-ligand polypyridyl complexes of Ru(II). The results clearly demonstrate that the first reduction in $\text{Ru}(\text{trpy})(\text{bpy})(\text{py})^{2+}$, as well as $\text{Ru}(\text{trpy})(4,4'\text{-dph-bpy})(\text{py})^{2+}$, is primarily localized on the trpy ligand. Due to the correlation

of the emission energies with the electrochemical data, we conclude that the transferred electron density is localized primarily on the trpy ligand in the lowest energy MLCT excited state as well. It seems reasonable that trpy is reduced before bpy because the former presents a more extended π system and presumably more stable π -antibonding orbitals. The 4,4'-dph-bpy ligand may present an even more extended π system; however, there would be considerable steric strain in the fully planar conformation. The presence of an additional nitrogen atom (more electronegative than carbon) in the trpy ligand and a potentially smaller average charge separation in $\text{Ru}^{\text{II}}(\text{trpy})$ versus $\text{Ru}^{\text{II}}(4,4'\text{-dph-bpy})$ may also favor trpy reduction. Solvation effects may also be important. Finally, the similarities among the g values and the absorption spectra of the singly reduced forms of the mixed-ligand complexes and $\text{Ru}(\text{trpy})_2^+$ suggest that localized trpy⁻ states occur in the latter system as well, in accord with the conclusions of DeArmond and co-workers.^{23b}

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Contribution from the Department of Chemistry,
College of General Education, Nagoya University, Nagoya 464-01, Japan

XANES Study at the Co K Absorption Edge in a Series of Cobalt(III) Complexes

Mitsuru Sano

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Systematic measurements of Co K-edge spectra have been carried out for a series of cobalt(III) complexes. A counterion effect has been observed in the higher energy region of the XANES. The energy of the 1s-3d transition increased in the following order: $\text{dtc}^- < \text{ox}^{2-} < \text{NO}_2^- < \text{phen} < \text{NH}_3, \text{en} < \text{CN}^-$ (dtc^- = diethyldithiocarbamate ion, ox^{2-} = oxalate ion, phen = 1,10-phenanthroline, en = 1,2-diaminoethane). This order is correlated with the energy of the 3d antibonding orbital. One-electron interpretation has been done for $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$ spectra with DV-X α MO calculations and relates the main absorption bands to transitions from the Co 1s orbital to MO's that result from the interaction of the Co 4p and antibonding ligand orbitals. The XANES feature also reflects the symmetry of the complex. Comparisons of XANES spectra have been made between geometrical isomers of $[\text{CoCl}_2(\text{en})_2]^+$, $[\text{Co}(\text{gly})_3]$ (gly⁻ = glycinate ion), and $[\text{Co}(\text{methio})_2]^+$ (methio⁻ = methionate ion).

Introduction

The EXAFS contains structural information on atoms surrounding an X-ray absorbing atom and is now widely used as a powerful tool for structural studies.¹ The analysis of EXAFS is usually made by using parameters whose values may be determined from EXAFS spectra of model compounds or from theoretical considerations. The information derived from EXAFS is only the one-dimensional radial distribution function about an absorbing atom. XANES may give information complementary to that extracted from EXAFS and may reflect the coordination geometry and the electronic structure of the absorbing atom; so this is particularly important in the study of systems for which EXAFS is of limited usefulness. In fact, interests in the determination of the local structure of complex systems like proteins, surfaces, and amorphous materials have renewed attention to XANES.

Although X-ray absorption spectra have been measured for many years,² the relations between the intensity, shape, and location of edge features on one hand and the ligand field geometry and electronic structure of the absorbing atom on the other still remain for further systematic studies. Cobalt(III) compounds are suitable for the studies because a wide variety of complexes are easily prepared and are fairly stable.

In the present work, we measured the Co K-edge spectra of a series of cobalt(III) complexes and investigated the relation between the feature of XANES and the nature of the cobalt complex.

Experimental Section

The cobalt(III) complexes except for $\text{K}_3[\text{Co}(\text{CN})_6]$ were prepared according to standard methods.³ A small amount of each sample was ground and diluted with boron nitride (ca. 25 mg/140 mg)⁴ and contained in a plastic cell between polypropylene windows spaced 1.0 mm apart.

The Co K-edge spectrum was measured by using the EXAFS facilities at Beam Line 10B of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF). Synchrotron radiation from the electron storage ring (2.5 GeV, average 150 mA) was monochromatized with a channel-cut Si(311) monochromator.⁵ The absorption spectrum of a piece of Cu foil was measured simultaneously with acquisition of data on the cobalt complexes, and relative energies were calibrated with respect to the first inflection point of the Cu metal absorption edge, defined to be 8978.8 eV. The incident and transmitted beam intensities were measured with N_2 - and Ar(15%)- N_2 -filled ionization chambers, respectively. Other instrumental details are given in ref 5. The XANES spectra were obtained from transmission data at room temperature in the

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