

Excited-State Absorption Spectroscopy and Spectroelectrochemistry of Tetrakis(2,2'-bipyridine)(μ -2,3-bis(2-pyridyl)pyrazine)diruthenium(II) and Its Mononuclear Counterpart: A Comparative Study

Robert M. Berger†

Received August 8, 1989

Excited-state absorption spectra of the complexes $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$ and $[Ru(bpy)_2(dpp)]^{2+}$ ($bpy = 2,2'$ -bipyridine, $dpp = 2,3$ -bis(2-pyridyl)pyrazine) in ethanol have been obtained. The excited-state spectra of both complexes exhibit bands in the near-UV region (350 nm for the binuclear complex and 370 nm for the mononuclear complex). In the visible region, a residual metal-to-ligand charge-transfer transition from the remaining Ru(II) center of the binuclear complex to the second lowest π^* orbital of the dpp ligand occurs. No comparable band appears in the spectrum of the mononuclear complex. Weak bands also occur in the 610–630-nm region in both complexes. The excited states of the binuclear and mononuclear complex decay with lifetimes of 80 ± 10 and 210 ± 20 ns, respectively, and both complexes emit in room-temperature ethanol solution ($\phi = 0.0012 \pm 0.0003$ and 0.011 ± 0.001). Spectroelectrochemistry has been used to characterize the reduced forms of the complexes. The first reduction of each complex occurs at the dpp ligand, and the spectra of these singly reduced complexes resemble the excited-state spectra. There is, however, significantly more absorption in the 450–500-nm region for the reduced complexes, consistent with the presence of one or two Ru(II) centers capable of engaging in MLCT transitions. The second reduction of the binuclear complex occurs at the dpp ligand, while the second reduction of the mononuclear complex occurs at one of the bpy ligands.

Introduction

Since the first observation¹ of luminescence from $Ru(bpy)_3^{2+}$ ($bpy = 2,2'$ -bipyridine) and the subsequent discovery of its rich photoinduced redox chemistry,²⁻⁷ this complex and related derivatives have become perhaps the most thoroughly investigated of all inorganic coordination complexes.⁸⁻¹³ Optical excitation of $Ru(bpy)_3^{2+}$ results in the population of a relatively long-lived ($\tau = 580$ ns¹⁴ in room-temperature aqueous solution) metal-to-ligand charge-transfer (MLCT) excited state,¹⁵ which is simultaneously more reducing and more oxidizing than the precursor ground state. While the long lifetime of the MLCT excited state allows a number of interesting redox processes to occur following excitation, the application of Ru(II) complexes to the problem of photochemical water splitting has been hampered by the fact that $Ru(bpy)_3^{2+}$ and its mononuclear derivatives may function only as one-electron excited-state redox reagents. Two noteworthy approaches have been used in an attempt to overcome this difficulty. The first involves the use of a relay species, a redox catalyst/electron pool, and sacrificial electron-transfer reagents. In this approach, the Ru(II) complex is used as a photosensitizer, which is oxidatively quenched by the relay species, electrons are subsequently stored at the pool for multielectron redox processes, and the sacrificial electron-transfer reagent is used to regenerate the photoactive Ru(II) species.¹⁶ A second approach hinges on the fact that binuclear and higher order oligomers containing the $Ru(bpy)_2^{2+}$ moiety may, in theory, act as multielectron excited-state redox reagents. In this context, a number of groups have reported the preparation and photophysical and photochemical characterization of both homo-¹⁷⁻³¹ and heteropolynuclear³²⁻³⁵ complexes containing the $Ru(bpy)_2^{2+}$ unit. The observation of luminescence from some of these complexes and the lack of luminescence in others have led to various hypotheses regarding the effect of metal-metal interaction on the energetics and lifetimes of the excited states.^{17,22} In order to exploit such systems, however, the relevant excited state must be sufficiently long-lived to undergo electron transfer before deactivation. Conventional (nanosecond) time-resolved luminescence and absorption spectroscopy provide a convenient probe by which the redox reactivity, energetics, and lifetime of the MLCT excited state may be characterized.

In this work, laser-flash photolysis is used to measure the lifetimes and excited-state absorption (ESA) spectra of $[Ru(bpy)_2(dpp)]^{2+}$ and $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$ ($dpp = 2,3$ -bis(2-pyridyl)pyrazine). The MLCT excited states of these complexes are further characterized by steady-state emission

spectroscopy. In addition, the electrochemically reduced forms of these complexes are characterized by cyclic voltammetry and

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† Present address: Department of Chemistry, Indiana University-Purdue University at Fort Wayne, Fort Wayne, IN 46805.

UV-visible spectroelectrochemistry. The similarities between the excited-state spectra and the spectra of the reduced complexes are discussed in the context of a single-ligand-localized excited-state/reduced species.

Experimental Section

Materials. $[\text{Ru}(\text{bpy})_2(\text{dpp})]\text{Cl}_2$ and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]\text{Cl}_4$ were prepared according to the method of Gafney et al.¹⁷ using $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (Strem) and 2,3-bis(2-pyridyl)pyrazine (Aldrich). The PF_6^- salts were obtained by metathesis of the Cl^- salt with KPF_6 in aqueous solution. Purification of the PF_6^- salt was effected by chromatography on silica gel with acetonitrile containing 0.05 M tetra-*n*-butylammonium hexafluorophosphate as the eluent or on neutral alumina with acetonitrile as the eluent. Purity was established by spectral comparison with literature data. The absence of mononuclear contaminant in the binuclear complex was verified by the lack of emission at 670 nm when the sample was excited at 425 nm.

Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by metathesis from aqueous solutions of tetra-*n*-butylammonium bromide and either potassium hexafluorophosphate or 60% aqueous hexafluorophosphoric acid (all from Aldrich). The resulting solid was collected, recrystallized twice from ethanol, and dried in vacuo at 50 °C.

Acetonitrile was obtained from Aldrich, and *N,N*-dimethylformamide (DMF) was from Burdick and Jackson. These solvents were deaerated with argon and stored over 4-Å molecular sieves. Ethanol was obtained from Midwest Solvents Co. of Illinois and methanol was spectral grade from Fisher.

Instrumentation. Routine UV-visible spectra were recorded with a Cary 219 spectrophotometer. Emission spectra were obtained by using a single-photon-counting fluorimeter (SLM 8000 series) equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. The temperature of the sample cell block was maintained at 25 °C by using a Haake constant-temperature circulator bath. Flash photolysis experiments were carried out on a Nd:YAG-based system previously described.³⁶ Electrochemical and spectroelectrochemical measurements were carried out by using a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat in conjunction with a PAR Model 175 universal programmer, a PAR 179 digital coulometer, and a Kipp and Zonen X-Y recorder. In the spectroelectrochemical work, a Perkin-Elmer 3840 diode array spectrophotometer along with a Perkin-Elmer 7700 computer was used to collect absorption spectra.

Methods. Luminescence quantum yields at 25 °C were determined as described by Demas and Crosby³⁷ by using argon-purged ethanol solutions of the complexes. The optical densities of the solutions at the excitation wavelengths were typically 0.3–0.35. Absorbance-matched, deaerated aqueous solutions of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ were used as standards. Emission spectra were corrected for instrument response with the use of correction factors supplied by the manufacturer, SLM Instruments, Inc. A correction for the difference in refractive index of the solvents was also applied.

In the laser-flash photolysis studies, argon-purged ethanol solutions of the complexes were contained in a 3 mm × 7 mm quartz cell. The binuclear complex was excited with 532.0-nm light, while the mononuclear complex was excited with 354.7-nm light. The area of the focused laser beam at the sample was determined by using a piece of photosensitive paper. The degree of excited-state saturation was determined by monitoring the change in optical density of the sample as a function of laser intensity at a wavelength of maximal ground-state bleaching as well as one of maximal transient absorption. Neutral density filters were used to attenuate the laser intensity. A double-reciprocal plot was used to determine ΔOD at saturation. The actual ΔOD 's were then used to calculate the excited-state concentration. Molar extinction coefficients were calculated from the equation³⁸

$$\Delta\text{OD}_\lambda = (\epsilon^*_\lambda - \epsilon^g_\lambda)lc^* \quad (1)$$

where ΔOD is the observed change in optical density at a particular wavelength, λ , following excitation, ϵ^g and ϵ^* are molar extinction coefficients of the ground and excited states, l is the path length of the monitoring beam through the laser-irradiated sample, and c^* is the ex-

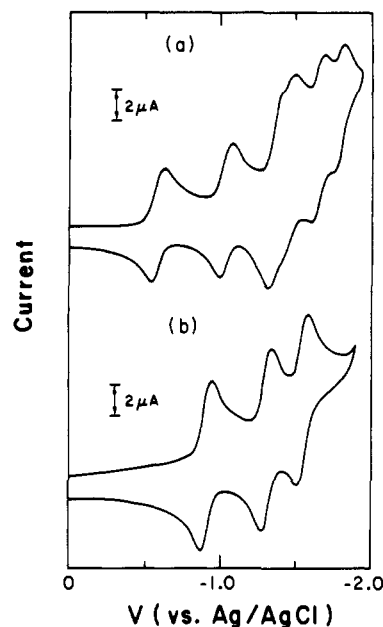


Figure 1. Cyclic voltammograms of (a) $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and (b) $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ in 0.1 M TBAH/DMF at a Pt-disk electrode. The scan rate is 200 mV s^{-1} .

cited-state concentration. Excited-state lifetimes were determined by monitoring transient absorption decay, ground-state recovery, or luminescence decay. In each case, the lifetime was determined from the slope of a natural log plot of the data.

Electrochemical and spectroelectrochemical measurements were carried out as previously described.³⁹ Solutions used in the electrochemical and spectroelectrochemical measurements were prepared in DMF or acetonitrile and were 1.0 mM in complex and 0.1 M in supporting electrolyte (TBAH). 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) and was separated from the solution with a porous Vycor plug. All potentials are recorded versus this electrode and are uncorrected for junction-potential effects. Scan rates for the cyclic voltammograms were typically 200 mV s^{-1} . For spectroelectrochemical measurements, an optically transparent thin-layer electrode (OTTLE) was fabricated as described by DeAngelis and Heineman⁴⁰ by using a 100 wire in.⁻¹ gold minigrad. The OTTLE was placed in a Plexiglas box equipped with glass windows. An Ar purge was maintained through the box during the course of the experiment in order to exclude O_2 and water vapor. Potentials corresponding to cathodic minima in the cyclic voltammograms of the complexes were applied, and the spectra were recorded once the solution had equilibrated at a given potential. The molar absorptivities for the reduced complexes were calculated by dividing the absorbance by the OTTLE path length and the concentration of the complex after subtracting the absorbance of the OTTLE containing only the solvent with supporting electrolyte.

Results

Absorption/Emission Spectra, Quantum Yields, and Lifetimes.

The absorption spectra of both complexes are characterized by intense MLCT transitions in the visible region of the spectrum. In each complex, transitions terminating in both dpp and bpy ligands may be observed. In the binuclear complex, the bands are well resolved with maxima at 525 and 425 nm in alcohol (ethanol or methanol) with extinction coefficients of 21 700 and 15 700 $\text{M}^{-1} \text{cm}^{-1}$, respectively, in good agreement with the values reported by Gafney et al.¹⁷ In DMF, the bands shift to 518 and 434 nm with extinction coefficients of 23 100 and 19 300 $\text{M}^{-1} \text{cm}^{-1}$, respectively. In the mononuclear complex, the bands are not well resolved and a low-energy shoulder appears near 470 nm along with a band at 440 nm in alcohol (444 nm in DMF). The extinction coefficient is 11 000 $\text{M}^{-1} \text{cm}^{-1}$ in both solvents.

Both complexes are luminescent in room-temperature ethanol solution, although the binuclear complex emits much less strongly

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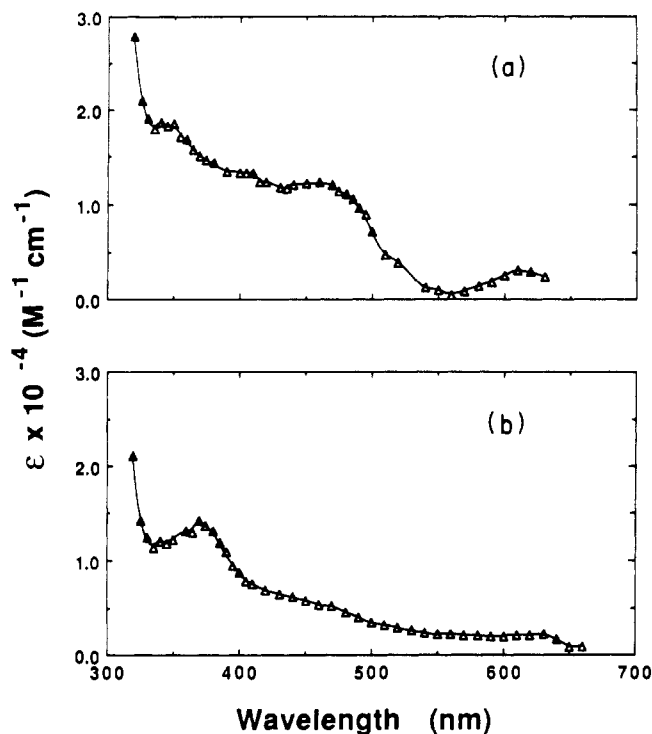


Figure 2. UV-visible absorption spectra of the excited states of (a) $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and (b) $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ as calculated from eq 1.

than its mononuclear counterpart. The corrected emission maxima for the mononuclear and binuclear complexes are 700 and 800 nm, respectively. The quantum yield of the mononuclear complex is 0.011 ± 0.001 and is independent of excitation wavelength from 436 to 475 nm. The binuclear complex has a quantum yield of 0.0012 ± 0.0003 and is similarly independent of excitation wavelength (425 or 527 nm). These quantum yields are significantly smaller than those previously reported by Gafney et al.¹⁷ The lifetime of the excited state of the mononuclear complex is 210 ± 20 ns, while that of the excited state of the binuclear complex under the same conditions is 80 ± 10 ns, as determined by luminescence decay, excited-state absorption decay, and ground-state recovery.

Cyclic Voltammetry. The cyclic voltammograms (Figure 1) of the complexes exhibit a pattern that is common to Ru(II) polypyridyl complexes. For the mononuclear complex dissolved in DMF, three reversible one-electron reductions are observed at -0.91 , -1.32 , and -1.56 V vs Ag/AgCl (3 M NaCl). A series of six one-electron waves are observed for the binuclear complex, occurring at -0.60 , -1.04 , -1.37 , -1.47 , -1.64 , and -1.77 V; however, the waves corresponding to the third and fourth reductions are not well resolved. The oxidations of these complexes in DMF are obscured by the edge of the solvent window. In acetonitrile, the mononuclear complex exhibits one reversible oxidation at $+1.45$ V, while the binuclear complex exhibits two reversible oxidations at $+1.50$ and $+1.72$ V. These values are somewhat more positive than those reported by Petersen and co-workers.²⁵ The reduction potentials of the mononuclear complex are shifted negatively by 100–120 mV in acetonitrile. The reduction potentials of the binuclear complex undergo smaller shifts (10–70 mV) in acetonitrile; however, only the first four reduction waves are well-behaved. There is evidence for the adsorption of the quadruply reduced binuclear complex to the platinum electrode. During the negative potential scan, a desorption spike is observed at -1.78 V. If the potential scan is reversed immediately after the fourth wave, a desorption spike is observed at -1.38 V.

Excited-State Absorption Spectra. The difference spectra obtained for $*[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and $*[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ are fairly typical of excited-state difference spectra of Ru(II) polypyridyl complexes and exhibit a bleaching of the ground-state

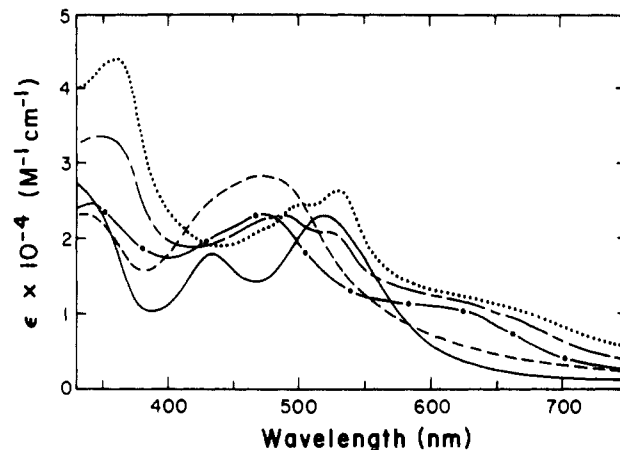


Figure 3. Near-UV-visible spectra of $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{n+}$ where $n = 4$ (—), $n = 3$ (---), $n = 2$ (-.-), $n = 1$ (- - -), and $n = 0$ (···) recorded in an OTTLE at 0.0, -0.90 , -1.24 , -1.45 , and -1.60 V vs Ag/AgCl. The solvent is DMF containing 0.1 M TBAH.

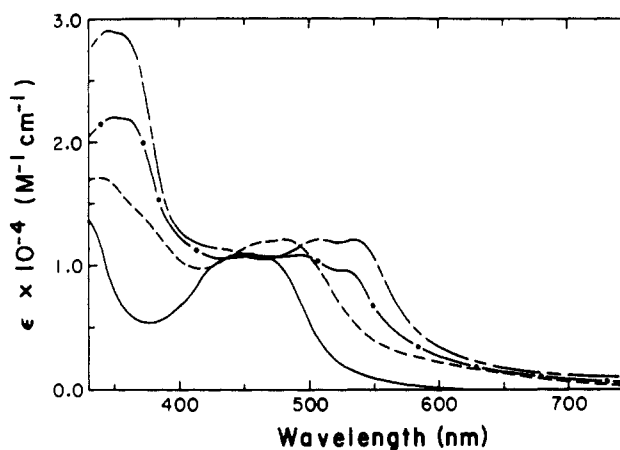


Figure 4. Near-UV-visible spectra of $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{n+}$ where $n = 2$ (—), $n = 1$ (---), $n = 0$ (-.-), and $n = -1$ (- - -) recorded in an OTTLE at 0.0, -1.20 , -1.46 , and -1.85 V vs Ag/AgCl. The solvent is DMF containing 0.1 M TBAH.

MLCT absorption band(s) along with an absorption increase in the 330–400-nm region. The difference spectra were obtained under conditions where approximately 85% saturation of the excited state was achieved. The absolute spectra of the excited states as calculated from eq 1 and the difference spectra are shown in Figure 2.

Spectroelectrochemistry. The UV-visible spectra of $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ and their reduced forms as measured in DMF solution containing 0.1 M TBAH in the OTTLE are presented in Figures 3 and 4. For the mononuclear complex the first reduction occurs at the dpp ligand while the second and third occur at the bpy ligands. In the binuclear complex, however, the first two reductions are dpp based while the third and fourth reductions involve bpy ligands.

Discussion

On the basis of detailed resonance Raman measurements, Gafney and co-workers¹⁷ have previously assigned the 525-nm band in the absorption spectrum of the binuclear species as a MLCT transition terminating in the dpp ligand, while the 425-nm band has been assigned as a Ru-to-bpy MLCT transition. Similarly, in the case of the mononuclear complex, two bands, though not well resolved, are observed. In this case as well, the lower energy transition terminates in the dpp ligand. Although they also reported emission quantum yields for both complexes, the authors acknowledged that those values were high estimates of the actual quantum yields and could only be used in a relative sense to indicate intersystem crossing efficiencies from the different excited states populated immediately after absorption. In the present study, the quantum yields of the two complexes are re-

investigated. Since the quantum yields of emission are independent of excitation wavelength within the respective MLCT manifolds, it follows that the emissive state of each complex is populated with an efficiency independent of the state initially populated.

The cyclic voltammograms of the complexes exhibit similar patterns and are consistent with one or two metal-based oxidations at positive potentials and a series of ligand-based reductions at negative potentials. This pattern is common to most d^6 polypyridyl complexes where the redox orbitals are localized on individual ligands.⁴¹ In both the mononuclear and binuclear complexes, the first reduction may be confidently assigned to the dpp ligand. Since the redox and spectroscopic orbitals in these complexes tend to be the same, the lowest energy excited state(s) also involve promotion of an electron to the dpp ligand. As can be seen in Figure 1, introduction of a second Ru(bpy)₂²⁺ moiety at the remote bidentate site of [Ru(bpy)₂(dpp)]²⁺ results in a 0.31-V shift in the reduction potential of the dpp ligand, reflecting a net stabilization of the π^* orbital of the bridging dpp ligand relative to that of a terminal dpp ligand. The second reduction of the binuclear complex occurs at a potential comparable to that of the first reduction of the mononuclear complex. Petersen et al.²⁵ and Kalyanasundaram and Nazeeruddin³⁵ have used this latter observation to suggest that the second reduction in the binuclear complex also involves the dpp ligand. However, they were only able to make a tentative assignment in the absence of spectroelectrochemical data.

The difference in the potential of the first oxidation of the mononuclear and the binuclear complex (ca. 50 mV) indicates that there is some metal-metal interaction, albeit weak, in the binuclear complex. This shift has been attributed to electrostatic effects of the second metal center and the shared π system. The overall effect involves a stabilization of the π^* level of the bridging ligand, which in turn leads to enhanced $d\pi-\pi^*$ orbital overlap and stabilization of the $d\pi$ orbitals in the binuclear complex.²⁰

The excited-state absorption spectra of these complexes are similar to the excited-state spectra of other Ru(II) polypyridyl complexes⁴²⁻⁴⁷ where single-ligand-localized transitions occur. A maximum is observed in the near-UV region in each complex, and this transient absorption decays with the same lifetime as the luminescent charge-transfer excited state. The transient absorption spectra may be confidently assigned as those of the MLCT excited states of the respective complexes. It should be noted that, at the excited-state concentrations achieved here (40–80 μ M), disproportionation of the excited state⁴⁸ or triplet-triplet annihilation^{49,50} is not likely to compete with first-order decay. In all cases, decay of the ΔOD at 370 nm or recovery of the ground-state bleach at 450 nm (mononuclear species) or 540 nm (binuclear species) was strictly first order to the preflash base line. A two-photon ionization process giving rise to solvated electrons as described by Meisel et al.⁵¹ is similarly unlikely with 532-nm excitation,⁵² but cannot be ruled out entirely, especially with 355-nm excitation. However, even in the presence of 10 mM HCl, the ΔOD decay at 370 nm and the bleach recovery at 450 nm of [Ru(bpy)₂(dpp)]²⁺ were first order to the preflash base line. Under these conditions, any electrons produced would be rapidly scavenged

by H⁺ giving rise to a nonzero ΔOD_{∞} .

The near-UV absorption in the excited-state mononuclear complex is red-shifted by about 20 nm and somewhat better resolved than that of the binuclear complex. These absorptions are attributed to intraligand transitions of the reduced dpp moiety since the dpp ligand presents the lower energy π^* orbital. Furthermore, these transitions lack the intensity to be assigned to intraligand transitions of a coordinated bpy radical anion.⁴² However, the absorptions are likely to be related to the $\pi_6 \rightarrow \pi_7$ absorption band of the bpy radical anion observed in excited-state and reduced Ru(bpy)₃²⁺.^{43,53} In the visible region, however, there is considerably more residual absorption in the case of the binuclear species. This observation can be rationalized by arguing that in the MLCT excited state of the binuclear complex, there is one Ru(II) center remaining that may be engaged in additional MLCT transitions. On the basis of the electrochemical measurements, the two lowest π^* levels of the dpp ligand are separated by approximately 2500 cm⁻¹. The band near 460 nm in the ESA spectrum of the binuclear complex may be tentatively assigned as a transition from the remaining Ru(II) center to the second lowest π^* orbital of the dpp ligand, although intraligand transitions of the reduced dpp ligand may contribute in this region as well. Only a small residual absorption is observed in the corresponding region of the ESA spectrum of the mononuclear complex. In this case, no metal-to-ligand charge-transfer transitions are expected, since the metal center is formally Ru(III). One additional feature is observed in each spectrum in the 610–630-nm region. This shoulder is reminiscent of a shoulder in the absorption spectrum of reduced terpyridyl complexes of Ru(II).³⁹ Again, the band of the mononuclear complex is red-shifted by about 20 nm relative to that of the binuclear complex.

The utility of spectroelectrochemistry in the characterization of the redox orbitals of mixed-ligand Ru(II)-polypyridyl complexes has previously been demonstrated.^{39,54} The absorption spectra of the singly reduced complexes are similar to those of the MLCT excited states in the near-UV region. This is to be expected, since the transition involved is an intraligand transition of a coordinated radical anion ligand. In each complex, the first reduction is clearly assignable to the dpp ligand. There are, however, blue shifts of ca. 20 nm in the spectra of the reduced complexes. These shifts are comparable to those observed in the $\pi_6 \rightarrow \pi_7$ band of reduced/excited-state Ru(bpy)₃²⁺^{43,53} and may have their origin in the difference in the oxidation state(s) of the coordinated metal center(s).⁵⁵ In the visible region, the shape of the absorption spectrum is similar for both the singly reduced mononuclear and singly reduced binuclear complexes, with maxima near 470 nm. The intensity in the spectrum of the binuclear complex is roughly twice that in the spectrum of the mononuclear complex. In both cases, Ru(II) \rightarrow dpp⁻ charge-transfer transitions are likely to be responsible for this absorption. To a first approximation, the intensity difference may be accounted for by the fact that two Ru(II) centers contribute in the binuclear complex with only one contributing in the mononuclear case.

Striking differences are observed in the spectra of the doubly reduced mononuclear and doubly reduced binuclear complexes. In the near-UV region, the second reduction of the mononuclear complex brings about a large increase in absorbance, while the absorbance of the binuclear complex remains virtually unchanged. The large increase in absorbance at 350 nm in the mononuclear complex is due to the presence of a reduced bpy ligand. In addition, bands at 495 and 530 nm, characteristic of the reduced bpy ligand,^{39,53} are resolved in the doubly reduced mononuclear complex.

In contrast, the visible absorption band of the singly reduced binuclear complex decreases in intensity and sharpens following the second reduction, and a shoulder appears near 630 nm. This

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band is likely related to those observed in the excited-state spectra. These results corroborate the suggestions of Petersen et al.²⁵ and Kalyanasundaram and Nazeeruddin,³⁵ and the second reduction of the binuclear complex may be unequivocally assigned as a dpp-based reduction. Only after the third reduction of the binuclear complex do the features of a reduced bpy ligand become apparent.^{39,53} These include a large increase in absorbance at 350 nm as well as resolved bands in the visible region at 495 and 525 nm. The spectrum of the triply reduced binuclear species may only be regarded as approximate because of the partial superposition of the third and fourth reduction waves. The essential point, however, is that bpy is not reduced until the third electron is added to the complex. With the third reduction of the mononuclear complex, the features of the reduced bpy moiety increase in intensity and dominate the spectrum, indicating that the third reduction of this complex is also a bpy-based reduction. Similar changes accompany the fourth reduction of the binuclear complex, and the conclusion that this reduction also occurs at a bpy ligand is obvious.

Conclusions

Ligand reduction, whether achieved via charge-transfer excitation or achieved via an outer-sphere process tends to give rise to single-ligand-localized species. The absorption spectra of the MLCT excited state and the singly reduced forms of $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ can be readily understood in this context, with the transferred or added electron residing in a π^* orbital of the dpp ligand. On the basis of spectroelectrochemical measurements, the second reduction of the binuclear complex may also be unequivocally assigned as a dpp-based reduction, while the second reduction of the mononuclear complex is bpy based.

Acknowledgment. Dr. G. Ferraudi and Dr. D. R. McMillin are gratefully acknowledged for their helpful comments and suggestions regarding the manuscript. The work described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3225 from the Notre Dame Radiation Laboratory.

Contribution from the Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, and Department of Chemistry and Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06268

Photochemistry of Semiconductor Surfaces: In Situ Photoreduction of SnS_2

R. Ken Force,[†] Mebrahtu G. Fessehaie,[‡] Robert Grosso,[‡] Skye McClain,[‡] William S. Willis,[†] and Steven L. Suib^{*,‡,§}

Received October 12, 1989

The in situ photoreduction of SnS_2 has been studied with X-ray photoelectron spectroscopy, residual gas analysis, photogravimetric analysis, and thermogravimetric analysis. Our results suggest that the photoreduction process is quite dependent on the amount of surface chloride ion that is left over during the commercial manufacture of SnS_2 from SnCl_4 . In the presence of Cl^- ions there is partial reduction of Sn^{4+} to Sn metal, which only occurs in the presence of light. Thermal treatment of impure SnS_2 does not lead to reduction to Sn. When highly pure SnS_2 is irradiated, there is no measurable reduction. The nature of the support for the SnS_2 pellet is also important since photoreduction was observed for chloride-contaminated SnS_2 mounted on Al but not when Mo was used as a holder. Surface hydroxyl groups on the Al are believed to be partially responsible for the observed photoreduction of SnS_2 . Finally, the photogravimetric analysis (PGA) method reported here is an excellent method for studies of light-sensitive materials. Our results suggest that impurity ions are responsible for the photoreduction of SnS_2 and that it may be possible to intentionally dope various semiconductors in order to initiate reduction.

Introduction

Photoprocesses in solids are important in many areas including absorption,¹ scattering,² electron-transfer,³ energy-transfer,⁴ and photocatalytic⁵ processes. Photolyses of zeolites,⁶ clays,⁷ alumina,⁸ coordination complexes,⁹ and organometallics¹⁰ have been done in order to understand and control absorption, scattering, the mode and type of electron and energy transfer, and rates of reactions. Partial or total decomposition of the solid being irradiated is of major importance in such studies. Stable solids are typically desired for such applications, although the search for systems with fast reversible absorptions or electron transfers has been intensified so that better optical storage devices may be produced. In most cases, a stable solid material would be desirable in order to achieve high efficiency or conversion.

On the other hand, the photoinstability of a solid surface is quite important in the photographic process,¹¹ in semiconductor photoresist processes,¹² and in the preparation of new materials.¹³ Photoreduction of solid surfaces or of adsorbed layers on surfaces may lead to the preparation of different isolated zerovalent clusters¹⁴ that may have properties different from those of bulk

metallic materials. Such materials might be useful in catalysis,¹⁵ semiconductor devices,¹⁶ ceramics,¹⁷ adhesion,¹⁸ and other fields.

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* To whom correspondence should be addressed.

[†] University of Rhode Island.

[‡] Department of Chemistry and Institute of Materials Science, University of Connecticut.

[§] Department of Chemical Engineering, University of Connecticut.