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Photophysics and Photochemistry of 2,2′-Bipyridine and 1,10-Phenanthroline Complexes of Vanadium(II)[1]

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The lifetimes of the lowest energy excited states of $V(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $V(phen)_3^{2+}$ (phen = 1,10-phenanthroline) are 500 ps and 1.8 ns, respectively, in ethanol at room temperature. These lifetimes are much shorter than those for the isoelectronic chromium(III) complexes. The lowest energy excited states in the vanadium systems are probably either $^2E/^2T_1$ or quartet MLCT states. Electrode potentials for the $V(NN)_3^{3+/2+}$ couples are approximately 0.09 (NN = bpy) and 0.13 V (NN = phen) in CH_3CN vs. Fc/Fc^+ (Fc = ferrocene), based on cyclic voltammetry data. Irradiation of $V(phen)_3^{2+}$ in its lowest energy electronic absorption band (λ_{max} = 640 nm) in the presence of various electron acceptors results in one-electron oxidation and ultimate formation of $(phen)_2V(\mu\text{-}OH)_2V(phen)_2^{4+}$. Similar photoredox processes are observed for $V(bpy)_3^{2+}$. The photooxidation mechanism involves oxidative quenching of the $V(NN)_3^{2+}$ excited state, followed by hydrolysis and dimerization of $V(NN)_3^{3+}$.

Introduction

During the past decade, polypyridine complexes of transition metals such as Ru, Fe, Os, Rh, Ir, and Cr have been under active investigation.[2-5] Those of Ru(II) and Cr(III) have been extensively used for experiments in photochemical energy storage because their lowest energy excited states are long-lived and capable of rapid electron-transfer reactions. Although the ruthenium and chromium complexes satisfy a number of the requirements for redox sensitizers, they suffer from two serious drawbacks. First, the lowest energy intense absorption bands for $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Cr(bpy)_3^{3+}$ lie at 450 and 427 nm, respectively; thus they can utilize only a small portion of the solar spectrum. Second, the small number of readily accessible oxidation states (II and III for Cr; I, II, and III for Ru) restricts their photoredox reactions to one-electron-transfer processes. Because the desired redox reactions usually require multiples of two electrons, additional heterogeneous[6] or homogeneous[7] catalysts have generally been necessary in order to achieve significant quantum yields for energy storage.

Our object has been to use vanadium complexes to combine the functions of sensitizer and multielectron redox agent in a single molecule. Vanadium complexes are known in all oxidation states from –I to V, and vanadium(II) (d^3) should be able to participate in photochemical redox reactions. Thus, photooxidation of vanadium(II), if followed by a second thermal electron transfer to generate vanadium(IV), would constitute a photochemically initiated overall two-electron-transfer reaction. We now report the first photochemical and photophysical examination of $V(bpy)_3^{2+}$ and $V(phen)_3^{2+}$ (phen = 1,10-phenanthroline), including their irreversible photochemical oxidation by various electron acceptors.

Experimental Section

Materials and Procedures. Methylviologen (1,1′-dimethyl-4,4′-bipyridinium, or MV^{2+}) chloride dihydrate (Sigma), ferrocene (Sigma), and 2,2′-bipyridine (Pfaltz & Bauer) were purified by recrystallization from ethanol. Aqueous trifluoromethanesulfonic acid (3 M) was distilled three times and diluted with water before use. Tetrabutylammonium trifluoromethanesulfonate was prepared by the literature procedure.[8]

Table I. Electrochemical Data from Cyclic Voltammetry Studies of $V(NN)_3^{2+}$ (NN = bpy, phen)[a]

	$V(NN)_3^{3+/2+}$			$V(NN)_3^{2+/+}$ [b]		
NN	E_{pa}/V	E_{pc}/V	i_{pa}/i_{pc}	E_{pa}/V	E_{pc}/V	i_{pa}/i_{pc}
bpy	0.57	0.47	1.7		–0.52	
phen	0.60	0.52	0.95	–0.34	–0.39	0.5

[a] In CH_3CN, 0.1 M $(Bu_4N)(O_3SCF_3)$, Ag/AgCl reference electrode. [b] The waves for $V(NN)_3^{2+/+}$ were broader than those for $V(NN)_3^{3+/2+}$ and not as well-defined. Reoxidation of $V(bpy)_3^+$ was not observed.

Europium(III) chloride hexahydrate, 1,10-phenanthroline, and acetonitrile were obtained from Aldrich (Gold Label) and used without further purification. Other chemicals and solvents were reagent grade and were used as received.

Electronic absorption spectra were recorded by using Cary 219 or Cary 14 spectrophotometers. Samples for photochemical and spectroscopic measurements were prepared by freeze–pump–thaw degassing on a high-vacuum line.

Vanadium(II) Complexes. A solution of $V(bpy)_3^{2+}$, prepared by the method of Herzog,[9] was treated with a stoichiometric quantity of ca. 3 M aqueous HO_3SCF_3 to precipitate deep blue-green $[V(bpy)_3](O_3SCF_3)_2{\cdot}H_2O$. An analogous procedure was used to prepare blue-black $[V(phen)_3](O_3SCF_3)_2{\cdot}H_2O$. The presence of water in the solid salts was verified by IR spectra. The syntheses were carried out under argon in Schlenk apparatus, and the crystalline products were dried in vacuo. Electronic absorption spectra for solutions of these $V(NN)_3^{2+}$ salts are shown in Figure 1. Extinction coefficients (NN = bpy, $\epsilon_{660} = 5.7 \times 10^3$ M^{-1} cm^{-1} in water; NN = phen, $\epsilon_{640} = 6.2 \times 10^3$ M^{-1} cm^{-1} in ethanol) are slightly lower than those reported by Bennett and Taube,[10] but close to the values of ref 11–13. The solid products can be handled briefly in air without decomposition. Their solutions are stable for extended periods when rigorously degassed but are rapidly oxidized by O_2. Anal. Calcd for $[V(bpy)_3](O_3SCF_3)_2{\cdot}H_2O$ ($C_{32}H_{26}F_6N_6O_7S_2V$): C, 45.99; H, 3.14; F, 13.64; N, 10.06. Found: C, 45.43, 45.27; H, 3.02, 2.71; F, 14.24; N, 11.44, 9.92. Calcd for $[V(phen)_3](O_3SCF_3)_2{\cdot}H_2O$ ($C_{38}H_{26}F_6N_6O_7S_2V$): C, 50.28; H, 2.89; F, 12.56; N, 9.26. Found: C, 50.61, 50.12, 50.25; H, 2.91, 2.51, 2.56; F, 11.71, 12.79; N, 8.87, 8.96, 8.86.

Electrochemistry. For cyclic voltammetry experiments, a solution of $(Bu_4N)(O_3SCF_3)$ (0.1 M) in CH_3CN was degassed by bubbling with purified argon, the appropriate solid vanadium complex added, and the voltammograms recorded immediately (PAR model 174A electronics). The electrochemical cell utilized Pt working and counter electrodes and Ag/AgCl (3 M aqueous NaCl) reference electrode. The half-wave potential for the Fc/Fc^+ (Fc = ferrocene) reference redox couple under these conditions was 0.43 V. Optimum results were obtained with high concentrations of the vanadium complexes.

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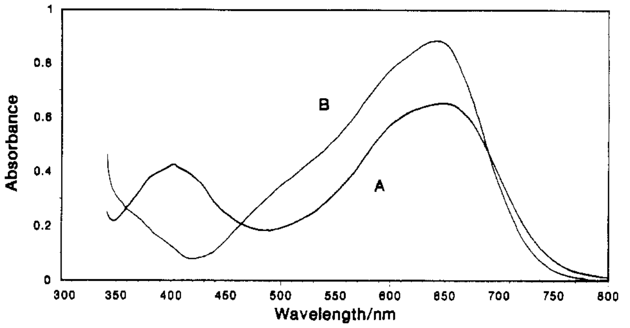

Figure 1. Electronic absorption spectra for dilute solutions of (A) [V(bpy)$_3$](O$_3$SCF$_3$)$_2$ in water and (B) [V(phen)$_3$](O$_3$SCF$_3$)$_2$ in ethanol.

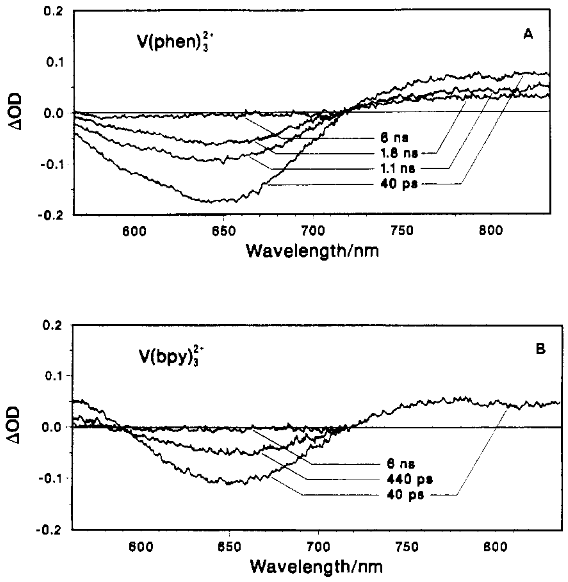

Figure 2. Picosecond transient difference spectra in ethanol solution. Delay times following the 35-ps 532-nm flash are indicated: (A) V(phen)$_3^{2+}$; (B) V(bpy)$_3^{2+}$.

Photochemistry. For steady-state photolysis experiments, tungsten (150 W, with 500-nm cutoff filter) or mercury-arc (Hanovia 450 W, with filters to isolate the 546-nm line) sources were used. Irradiated samples were kept at 26 °C by using a water bath. Reinecke's salt was used for actinometry, following the procedure of Wegner and Adamson.[14] Electron transfer was monitored by the appearance of the characteristic absorption of MV$^+$ at 395 nm.[15]

Picosecond flash-photolysis experiments were carried out by using an apparatus described elsewhere.[16] Samples having an absorbance of ca. 0.2 at 532 nm (2-mm path length) were excited with 35-ps flashes at 532 or 355 nm. Transient difference spectra were recorded at several delay times in the 550–720- and 630–800-nm regions (average of 150 flashes each), and data for the two regions overlapped to produce the spectra shown in Figure 2.

Experiments on the nanosecond and microsecond time scale utilized 10-ns 532-nm excitation flashes from a Quantel Datachrom 5000 Nd:YAG laser. Kinetic data were recorded and analyzed by using Tektronix Model 468 and 7912 waveform digitizers interfaced to a Tektronix Model 4052A computer.

Results

Electrochemistry. The results of cyclic voltammetry studies of V(bpy)$_3^{2+}$ and V(phen)$_3^{2+}$ are summarized in Table I. They show that one-electron oxidation and reduction are possible for both ions, with a greater degree of electrochemical reversibility for the phenanthroline species.[17] The trivalent species are somewhat unstable under these conditions: the V(NN)$_3^{2+/3+}$ couples approach reversible behavior only at our highest scan rates (1 V s^{-1}). Additional waves, probably due to solvent-substituted species, may be seen at slower scan rates. The V(bpy)$_3^{2+/3+}$ and V(phen)$_3^{2+/3+}$ half-wave potentials are 0.52 and 0.56 V, respectively, vs. Ag/AgCl, or 0.09 and 0.13 V, respectively, vs. Fc/Fc$^+$. Thus, the ligands phen and bpy strongly stabilize vanadium(II) (compare the electrode potential for V(H$_2$O)$_6^{2+/3+}$ in H$_2$O, −0.255 V vs. NHE[18]). Bennett and Taube estimated the V(bpy)$_3^{2+/3+}$ electrode potential to be ca. 0.8 V vs. NHE in water, based on a Marcus theory evaluation of redox reaction rates.[10] Although the two experiments were performed in different solvents and are therefore not directly comparable, the results are in qualitative agreement.

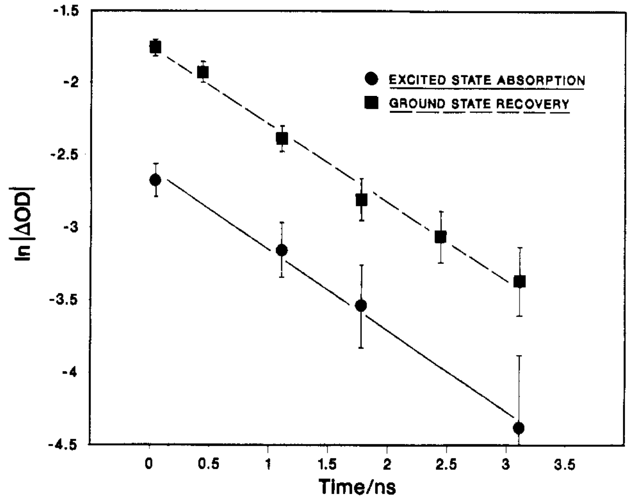

Figure 3. Logarithmic decay plots from picosecond spectra for excited-state absorption ((●) solid line, 760 nm) and ground-state bleaching ((■) dashed line, 625 nm) in V(phen)$_3^{2+}$.

Photophysics. In our microsecond and nanosecond flash-photolysis experiments, we were unable to detect any signals attributable to vanadium(II) excited states. We therefore undertook measurements on the picosecond time scale.

Transient-difference spectra recorded for V(phen)$_3^{2+}$ and V(bpy)$_3^{2+}$ in ethanol solution after excitation with 35-ps flashes at 532 nm are illustrated in Figure 2. These spectra exhibit bleaching from 550 to 690 nm and broad absorption above 700 nm. Data recorded 6 ns after the flash show almost complete restoration of the ground-state spectrum. The excited-state lifetime for V(phen)$_3^{2+}$ of 1.8 ± 0.2 ns is observed in data from both transient absorption and bleaching (see Figure 3). No evidence for any other excited states is observed. Although these experiments were conducted in the presence of excess phenanthroline, comparable spectra and lifetimes were obtained in solutions containing only V(phen)$_3^{2+}$.

Excitation of V(phen)$_3^{2+}$ with 355-nm flashes produces absorption changes similar to those described above. In these experiments, transient absorption is also observed in the 490–550-nm region, and it decays at a rate comparable to that observed for the bleaching and absorption above 550 nm.

Transient-difference spectra for V(bpy)$_3^{2+}$ (Figure 2B) show similar bleaching and absorption features. These spectra give an excited-state lifetime significantly shorter than that for V(phen)$_3^{2+}$: 500 ± 100 ps in ethanol solution at room temperature.

Steady-State Photolysis. (a) V(phen)$_3^{2+}$ + MV^{2+}. We chose to study V(phen)$_3^{2+}$ first, since it appeared to be more stable electrochemically than V(bpy)$_3^{2+}$. Nanosecond flash-photolysis experiments (532-nm irradiation) with solutions containing V(phen)$_3^{2+}$ and MV^{2+} showed small transient absorption signals attributable to MV$^+$,[15] but the formation of MV$^+$ was only partially reversible. We also discovered that these solutions slowly developed absorptions characteristic of MV$^+$ even under room

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[17] For a previous polarographic study of reduction of these V(II) complexes, see: Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *63*, 405.

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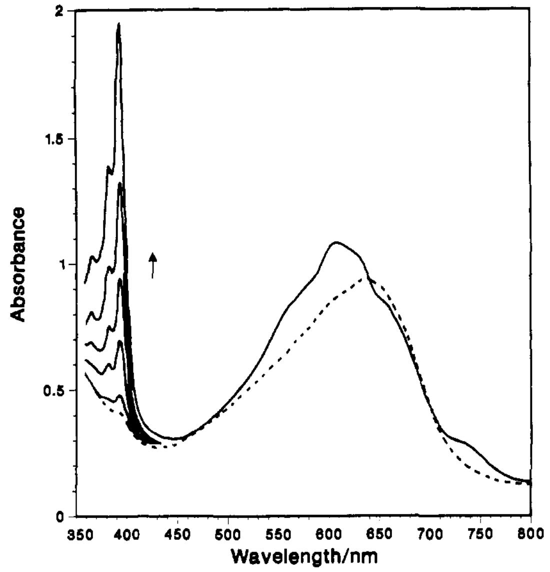

Figure 4. Electronic absorption spectra recorded during irradiation ($\lambda > 500$ nm) of an ethanol solution of $V(phen)_3^{2+}$ (1.6×10^{-4} M) and MV^{2+} (0.02 M): dashed line, spectrum before irradiation; solid lines, spectra showing increasing absorbance (shown by arrow near 395 nm) due to MV^+.

light. Thus, we decided to investigate steady-state photochemical reactions of the complexes.

The results of a typical experiment are illustrated in Figure 4. In this example (6.3×10^{-4} M $V(phen)_3^{2+}$, 1.8×10^{-2} M MV^{2+}, and 0.11 M phenanthroline in C_2H_5OH), the spectral changes reflect the irreversible formation of MV^+ during 7 h of irradiation (tungsten lamp, $\lambda > 500$ nm). After a total of ca. 14 h of irradiation, the concentration of MV^+ reached a limit corresponding to complete one-electron oxidation of $V(phen)_3^{2+}$. A similar solution irradiated at 546 nm gave an initial quantum yield for MV^+ appearance of approximately 0.04.[19]

(b) $V(phen)_3^{2+}$ + Eu^{3+}. In the above experiments with MV^{2+}, the broad absorption band at 605 nm due to MV^+ makes the identification of the vanadium-containing product difficult. We therefore also used Eu^{3+} as an electron acceptor: neither Eu^{3+} nor Eu^{2+} absorbs strongly in the visible region. An aqueous solution of $\sim 2 \times 10^{-4}$ M $V(phen)_3^{2+}$ and 2×10^{-2} M Eu^{3+}, for example, is stable in the dark. Irradiation of this sample in the lowest energy band of $V(phen)_3^{2+}$ ($\lambda > 500$ nm), however, leads to gradual spectral changes. Continued irradiation (total ca. 30 h) gives a spectrum with absorption maxima at 525 and 640 nm. These features are similar to those previously reported for the binuclear vanadium(III) complex $(phen)_2V(\mu\text{-OH})_2V(phen)_2^{4+}$.[10,20] The spectrum is illustrated in Figure 5, along with that of a separate sample prepared directly from vanadium(III) and phenanthroline.

The overall stoichiometry of the photooxidation

$$2V(phen)_3^{2+} + 2Eu^{3+} + 2H_2O \xrightarrow{h\nu} V_2(phen)_4(\mu\text{-OH})_2^{4+} + 2Eu^{2+} + 2phen + 2H^+ \quad (1)$$

requires the release of phenanthroline. We have confirmed that phen is liberated by treating the products with Fe^{2+}: addition of solid $FeSO_4 \cdot 7H_2O$ to the irradiated solution leads to rapid development of absorption ($\lambda_{max} = 510$ nm) characteristic of $Fe(phen)_3^{2+}$. The absorptions at 525 and 640 nm due to $V_2(phen)_4(\mu\text{-OH})_2^{4+}$ are unaffected by the addition of Fe^{2+}.

(c) $V(phen)_3^{2+}$ + $VO(phen)_2^{2+}$. Irradiation of aqueous solutions containing $V(phen)_3^{2+}$ and $VO(phen)_2^{2+}$ results in comproportionation to give $V_2(phen)_4(\mu\text{-OH})_2^{4+}$. Although this reaction also occurs slowly in the dark, it is markedly accelerated by light.

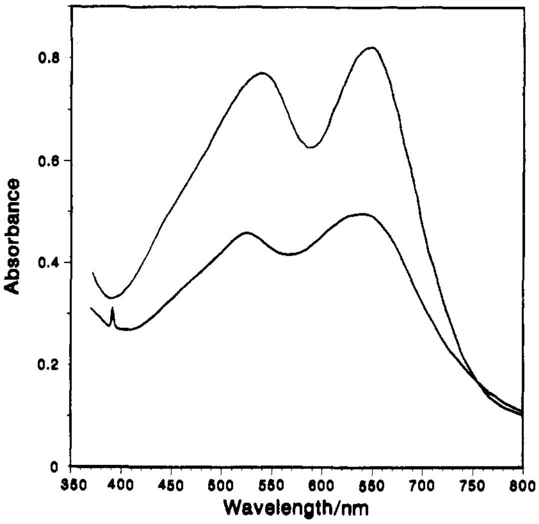

Figure 5. Electronic absorption spectra of $(phen)_2V(\mu\text{-OH})_2V(phen)_2^{4+}$ prepared photochemically from $V(phen)_3^{2+}$ and Eu^{3+} (lower spectrum; sharp spike at 390 nm is due to excess Eu^{3+}) and directly from vanadium(III) and phenanthroline (upper spectrum).

(d) $V(bpy)_3^{2+}$. Analogous photooxidation reactions occur when mixtures of $V(bpy)_3^{2+}$ with MV^{2+}, Eu^{3+}, or $VO(phen)_2^{2+}$ are irradiated. The rates for these reactions, however, are only about one-fourth as fast as those for reactions with $V(phen)_3^{2+}$ under comparable conditions.

Discussion

Excited States of $V(NN)_3^{2+}$. The lowest energy electronic absorption bands (Figure 1) for $V(NN)_3^{2+}$ are located at 640 (NN = phen) and 660 nm (NN = bpy). The high intensity of these bands suggests a strong contribution from MLCT transitions, as has been pointed out by König and Herzog.[13] These authors place the lowest energy spin-allowed d–d transition, $^4A_2 \rightarrow {}^4T_2$ (assuming octahedral microsymmetry), at about the same position. On the basis of a semiempirical calculation, they estimate that $10Dq$ in $V(bpy)_3^{2+}$ is 17 800 cm^{-1}. Comparisons with $V(en)_3^{2+}$ (en = ethylenediamine) and $Ru(bpy)_3^{2+}$ support the d–d and MLCT portions of König and Herzog's assignment, respectively. In $V(en)_3^{2+}$ the $^4A_2 \rightarrow {}^4T_2$ transition occurs at 15 600 cm^{-1},[21] and it is not obscured by charge-transfer bands. With $Ru(bpy)_3^{2+}$, the intense MLCT band ($\bar{\nu}_{max} = 22\,100$ cm^{-1}; $\epsilon = 1.46 \times 10^4$ M^{-1} cm^{-1}[22]) is found at higher energy than the intense band in vanadium(II); however, this is consistent with the electrode potentials for one-electron oxidation of the two ions (0.09 V for $V(bpy)_3^{2+}$ and 0.87 V for $Ru(bpy)_3^{2+}$,[23] both vs. Fc/Fc$^+$ in CH_3CN).

Thus, both d–d and MLCT transitions contribute to the low-energy absorptions in $V(NN)_3^{2+}$. We believe that, for two reasons, the resulting excited states do not mix extensively. First, the accepting orbitals (metal d_{z^2} and $d_{x^2-y^2}$ in $^4T_2$, and ligand π^* in MLCT) are approximately orthogonal. Second, the two excited states are likely to differ substantially in geometry: in d^3 complexes, the $^4T_2$ states show large changes in metal–ligand bond distances compared to $^4A_2$,[24] whereas distortion in MLCT states is likely to occur primarily within the polypyridine ligands.[25]

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(19) Although higher MV^{2+} concentrations appear to give larger electron-transfer yields, these experiments were limited by the solubility of MV^{2+}.

(20) The vanadium(III) complex is mentioned briefly in: Brandt, W. W.; Dwyer, F. P.; Gyarfas, E. C. *Chem. Rev.* **1954**, *54*, 959.

(21) Khamar, M. M.; Larkworthy, L. F.; Patel, K. C.; Phillips, D. J.; Beech, G. *Aust. J. Chem.* **1974**, *27*, 41.

(22) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(23) Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 229. In water the difference between the two potentials is smaller: 1.26 V for $Ru(bpy)_3^{2+}$[22] and ca. 0.8 V for $V(bpy)_3^{2+}$,[10] respectively, vs. NHE.

(24) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.

(25) For discussions of the distortions in MLCT excited states of low-spin d^6 complexes, see: Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492 and references therein.

The lowest energy excited states in complexes such as $Cr(phen)_3^{3+}$ are the d–d states ^2E and $^2T_1$ (commonly referred to together as "^2E"); we were therefore interested in the positions of doublet excited states in $V(NN)_3^{2+}$ as well. Doublet MLCT states will lie higher in energy than quartet MLCT states; therefore, the lowest energy doublet state will be ^2E in vanadium(II) just as in chromium(III). There is little direct evidence for ^2E in $V(NN)_3^{2+}$: although Sartori and co-workers claimed to observe phosphorescence at 815 nm in $V(bpy)_3^{2+}$,[26] König and Herzog[13] were unable to reproduce that result. We also find no evidence for luminescence (700–1100 nm) in either $V(bpy)_3^{2+}$ or $V(phen)_3^{2+}$ at room temperature or at 77 K, in fluid or glassy solution or in the solid state.

An accurate picture of excited-state dynamics in these complexes will probably require more detailed spectroscopic measurements, including studies at low temperature. However, the lowest lying excited state is probably either ^2E or a MLCT quartet state. Phosphorescence has been observed from ^2E in solids such as $MgO:V^{2+}$;[27,28] the equilibrium energies of ^2E and $^4T_2$ in such crystals are 11 500 and 13 200 cm^{-1}, respectively.[27] In the stronger field environment provided by the polypyridine ligands in our systems, $^4T_2$ will probably lie still farther above ^2E. The equilibrium position of the lowest excited MLCT quartet state is less certain: since this state will be distorted relative to the ground state, a substantial Stokes shift is to be expected for the transition.

If the redox-active state in our experiments is a MLCT quartet, some fluorescence would be expected. However, since this would be relatively broad and would appear at low energy, it might be very difficult to detect. On the other hand, if ^2E is lowest, its extremely short lifetime is puzzling: ^2E states in $MgO:V^{2+}$ [28] and various Cr(III) complexes[24] have lifetimes well above 1 μs. Thus, a new deactivation pathway, such as back intersystem crossing to a close-lying MLCT state, would be necessary to account for our observed data. By competition with $^2E \rightarrow {}^4A_2$ radiative decay, back intersystem crossing would reduce the intensity of phosphorescence compared to that in analogous chromium(III) derivatives.[29] Both models, then, are consistent with our failure to observe luminescence in these systems.

The excited-state lifetime for $V(bpy)_3^{2+}$ is significantly shorter than that for $V(phen)_3^{2+}$. Similar results were obtained for the corresponding Cr(III) species and attributed to the greater flexibility of the bpy ligand.[30] The same rationale applies in our systems as well, even though our decay rates are considerably larger.

Nature of the Photooxidation Product. The formulation $V_2(phen)_4(\mu\text{-}OH)_2^{4+}$, for the violet complex we obtain on photooxidation of $V(phen)_3^{2+}$, was first discussed by Bennett and Taube.[10] Their conclusion was based on pH changes during thermal oxidation of $V(phen)_3^{2+}$. Additional evidence in favor of this formula is provided by our own experiments with added Fe^{2+}, which show that phenanthroline is liberated during the photooxidation.

This species was also studied by Murray and Sheahan, who proposed a mixed-valence $V^{II/III}$ description.[31] In order to investigate further the oxidation state of the material, we irradiated various mixtures of $V(phen)_3^{2+}$ and $VO(phen)_2^{2+}$. We obtained the highest yield of product with equimolar quantities of the two reactants. If the mixed-valence assignment were correct, the yield should be highest for a 3:1 mixture of $V(phen)_3^{2+}$ and $VO(phen)_2^{2+}$. Solutions of the product also do not exhibit intervalence charge-transfer absorption in the 800–2600-nm region.[32] Finally, the quantity of MV^+ formed on exhaustive irradiation of $V(phen)_3^{2+}$ solutions containing excess MV^{2+} corresponds to complete one-electron oxidation of $V(phen)_3^{2+}$. Our results, therefore, clearly support the vanadium(III) oxidation state assignment for the violet product.

Mechanism of the Photooxidation. The occurrence of both oxidation and ligand substitution in our photoredox reactions raises a mechanistic question: Does electron transfer occur before or after substitution? Two types of evidence argue in favor of initial electron transfer. First, $V(phen)_3^{2+}$ solutions are stable under irradiation ($\lambda > 500$ nm) even in the absence of excess phen, so that photosubstitution is not an important process for the vanadium(II) complexes. Second, neither $V(H_2O)_6^{2+}$ nor $V(phen)_3^{2+}$ is a strong enough reductant to react with MV^{2+}.[33] Even if a partially substituted species, such as $V(phen)_2(H_2O)_2^{2+}$, formed photochemically, it would probably have a reducing strength intermediate between those of $V(H_2O)_6^{2+}$ and $V(phen)_3^{2+}$ and therefore also would be incapable of thermal reaction with MV^{2+}.

These reactions, then, represent the first oxidative quenching processes for a d^3 excited state.[34] Our lifetime data, and the quantum yield for steady-state photolysis with MV^{2+} as illustrated in Figure 4 (see above), require a rate constant k_q for the reaction

$$V(phen)_3^{2+*} + MV^{2+} \rightarrow V(phen)_3^{3+} + MV^+ \qquad (2)$$

of approximately 1.2×10^9 M^{-1} s^{-1}. A somewhat larger value for k_q would account for the partially reversible electron transfer to MV^{2+} that we have observed in nanosecond flash photolysis. Thus, the initial excited-state-quenching reaction (eq 2) is essentially diffusion-controlled.

Summary

Our photoredox experiments with MV^{2+} and Eu^{3+} lead to the following overall mechanism:

$$V(phen)_3^{2+}\ (^4A_2) \xrightarrow[<35\ ps]{h\nu} V(phen)_3^{2+*}\ (^2E \text{ or MLCT}) \qquad (3)$$

$$V(phen)_3^{2+*} + A \rightarrow V(phen)_3^{3+} + A^- \qquad (4)$$

$$2V(phen)_3^{3+} + 2H_2O \rightarrow (phen)_2V^{III}(\mu\text{-}OH)_2V^{III}(phen)_2^{4+} + 2phen + 2H^+ \qquad (5)$$

With $VO(phen)_2^{2+}$ as oxidant a slightly different sequence occurs:

$$V(phen)_3^{2+*} + VO(phen)_2^{2+} \rightarrow V(phen)_3^{3+} + VO(phen)_2^{+} \qquad (6)$$

$$V(phen)_3^{3+} + VO(phen)_2^{+} + H_2O \rightarrow (phen)_2V^{III}(\mu\text{-}OH)_2V^{III}(phen)_2^{4+} + phen \qquad (7)$$

Analogous reactions occur with $V(bpy)_3^{2+}$.

The short lifetime of the lowest energy excited state in these systems makes photoinduced electron transfer relatively inefficient. However, because $V(NN)_3^{3+}$ is subject to hydrolytic dimerization, the photoredox reactions are irreversible. These reactions, therefore, present convenient methods for permanent photochemical generation of powerful reductants such as MV^+ and Eu^{2+}.

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We are currently examining two aspects of these new photoredox reactions: the barrier toward regeneration of $V(NN)_3^{2+}$ from the vanadium(III) solutions[35] and the photochemical properties of vanadium(II) complexes of strong field ligands such as isocyanides[36] and phosphines.[37] In these complexes both MLCT and d–d quartet excited states should be well above ^2E, so that their excited-state lifetimes should be significantly longer than those observed here.

Another area we are now exploring is the capacity of $V_2(NN)_4(\mu\text{-}OH)_2^{4+}$ for additional electron transfer. Bennett and Taube observed disproportionation following one-electron thermal oxidation of V(2,2′:6′,2″-terpyridine)$_2^{2+}$;[10] thus, we are studying both disproportionation (reaction 8) and thermal electron transfer to A (reaction 9) as second steps in photoinitiated overall two-electron-transfer schemes based on these vanadium complexes.

$$V_2(NN)_4(\mu\text{-}OH)_2^{4+} + NN \rightarrow VO(NN)_2^{2+} + V(NN)_3^{2+} + H_2O \quad (8)$$

$$V_2(NN)_4(\mu\text{-}OH)_2^{4+} + 2A \rightarrow 2VO(NN)_2^{2+} + 2A^- + 2H^+ \quad (9)$$

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Exact Results for EPR g and A Tensors in the $S_1 = 1, {}^3/_2, 2, {}^5/_2$ and $S_2 = {}^1/_2$ Spin-Coupled Systems. The Effect When S Is Not a Good Quantum Number

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Exact expressions for the EPR **g** and **A** tensors in spin-coupled systems are given in terms of the parameters from the isolated spins for $S_1 = 1, {}^3/_2, 2, {}^5/_2$ and $S_2 = {}^1/_2$. These results include the effect of interactions between different spin manifolds, i.e. when S is not a good quantum number. The **g** tensor and the hyperfine tensors are rather sensitive measures of the intermanifold coupling, thus making EPR an excellent probe of spin-coupling parameters. The resonance positions for selected spin states are given in terms of observed g values. In the presence of significant intermanifold interaction the observed g values along the major axes do not simply correspond to the principal components of the molecular **g** tensor.

Introduction

The study of binuclear spin-coupled systems has been of longstanding interest.[1] Primary interest has been in homobinuclear systems where $S_1 = S_2$, the classic example being the work of Bleaney and Bowers on the copper acetate dimer.[2] However, heterobinuclear systems have been increasingly studied both because the magnetic properties for $S_1 \neq S_2$ systems are of fundamental interest[3–8] and because a number of biological systems have different spin-coupled metal ions associated with the active site.[9–13]

Electron paramagnetic resonance (EPR) spectroscopy has been an important tool for elucidating the properties of spin-coupled systems.[3,4,14–16] This technique conveniently probes the ground state and, in favorable cases, the first excited spin manifold. The data derived from the EPR spectrum are the **g** tensor and, if one (or both) of the nuclei have spin, the hyperfine coupling tensor(s), **A**. The interaction between the spins can substantially alter the magnitude of the components of the **g** and **A** tensors relative to the single-spin values, and the relationship between the parameters in the coupled state and the parameters of the single uncoupled spins is of fundamental interest.[17] This relationship has been studied in the past, but the equations presented always include the assumption that coupling between various spin manifolds is negligible, i.e., the total spin S has been assumed to be a good quantum number. The existence of matrix elements that connect different spin states has been recognized,[7,12,17,19] but the explicit

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