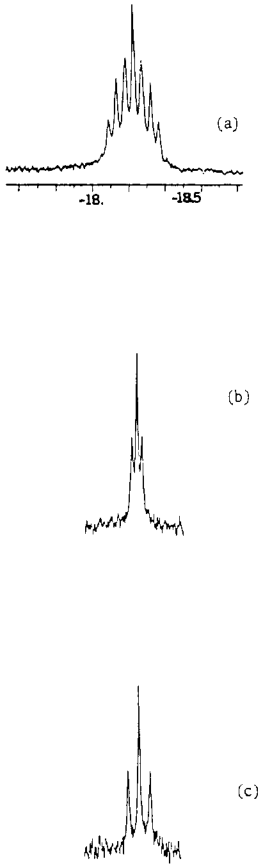

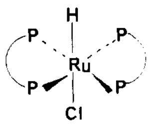

**Figure 2.** High-field hydride region of the 300-MHz $^1$H NMR spectrum of $HRuCl(TBPC)_2$: (a) normal spectrum; (b) spectrum after irradiation of the $^{31}$P peak at 27.9 ppm; (c) spectrum after irradiation of the $^{31}$P peak at 8.2 ppm.

triethylamine is added to the solution, only one chlorine atom is removed from the complex precursor and we note the formation of the monohydride $HRuCl(TBPC)_2$ (**2**). Both syntheses are variations of the synthetic method of Ikariya et al.[3c] The complexes gave satisfactory elemental analyses, and the configuration (cis or trans) was based on NMR data. Stereochemical assignments of the nonrigid molecules M(bidentate $phosphine)_2XY$ must be approached with caution,[4,8] but with complexes **1** and **2** the cyclobutane ring fixes the configuration of the ruthenium chelate ring.

For the molecule $H_2Ru(TBPC)_2$, we can envisage two chiral isomers, the cis isomer with $C_2$ symmetry or the trans isomer with $D_2$ symmetry. This differs from the situation with $H_2Ru(Me_2P(CH_2)_2PMe_2)_2$,[9] which, because of the flexibility of the ethylene bridge, gives rise to $C_{2v}$ and $D_{2h}$ symmetry for the cis and trans isomers, respectively. With complex **1**, for the trans isomer, the proton-decoupled $^{31}$P NMR spectrum should exhibit a single resonance due to the four equivalent phosphorus nuclei, whereas in the cis isomer the $^{31}P\{^1H\}$ NMR spectrum will appear as two triplets, one for each pair of cis and trans phosphorus nuclei. The data presented here are in accord with the cis isomer. This result can be unambiguously confirmed by the use of selective $^{31}$P-decoupled $^1$H NMR spectra. The cis isomer possesses magnetically nonequivalent hydrides because two different coupling constants to the $^{31}P_t$ atoms are involved. However, irradiation of the trans phosphorus nuclei ($P_t$, Figure 1) effectively removes this magnetic nonequivalence, leading to a single binominal triplet. In contrast, irradiation of the cis phosphorus nuclei ($P_c$, Figure 1) maintains their magnetic nonequivalence since each proton still possesses a cis $J_{P-H}$ and a trans $J_{P-H}$. Accordingly $P_t$ was irradiated to give spectrum b ($J_{P-H} = 26.8$ Hz) and $P_c$ to give spectrum c. Thus the assignment of **1** as the cis isomer is firmly based.

Complex **2** likewise shows two triplet resonances in the $^{31}$P spectrum. This, however, is indicative of the formation of the trans isomer (which has $C_2$ symmetry) rather than the cis molecule (which would be $C_1$, and so have four different phosphorus environments). The normal $^1$H NMR spectrum shows a 1:2:3:4:3:2:1 septet assignable as an overlapping triplet of triplets where one of the $J_{P-H}$ values is approximately double that of the other. This has been experimentally verified by selective irradiation of each of the phosphorus environments. Irradiation of the $^{31}$P peak at 27.9 ppm gives a 11.8-Hz triplet while the corresponding irradiation at 8.2 ppm produces a proton triplet with $J_{P-H} = 27$ Hz (see Figure 2). We note that the closely analogous product $HRuC(diop)_2$ has been shown crystallographically to be the trans complex.[4] The spectra reported therein and the data presented here are entirely in accord with the formation of the trans isomer.

To conclude, simple symmetry considerations and the use of selective $^{31}$P-decoupled $^1$H NMR spectra can be successfully applied to stereochemical determination of rigid chiral complexes $H_2M(P-P^*)_2$ and $HMCl(P-P^*)_2$. Utilization of the two compounds in asymmetric catalysis will be reported elsewhere.[10]

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**Registry No.** 1, 106588-05-0; 2, 106588-06-1; $(RuCl_2(COD))_n$, 50982-13-3.

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# Nature of the Lowest Energy Excited State in Vanadium(II) Polypyridine Complexes

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There is extensive literature on the photochemical and photophysical properties of $Cr(NN)_3^{3+}$ (NN = polypyridine ligand).(1) Our recent studies of the isoelectronic vanadium(II) complexes have demonstrated the initial photooxidation of $V(NN)_3^{2+}$ to $V_2(NN)_4(\mu\text{-}OH)_2^{4+}$.(2) This ion can be oxidized further to vanadium(IV), and the two redox steps can be combined in a photoinitiated two-electron process.(3) However, the efficiency of these photoredox reactions is limited by the extremely short excited-state lifetimes of $V(NN)_3^{2+}$ (less than 2 ns in solution at room temperature(2)). The photophysical experiments described herein establish that the lowest excited states in these complexes are primarily quartet MLCT (metal to ligand charge transfer) in character.

## Experimental Section

The ligands 4,7-diphenyl-1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, and 3,4,7,8-tetramethyl-1,10-phenanthroline ($Ph_2phen$, $Me_2bpy$, and $Me_4phen$, respectively) and other chemicals and solvents were reagent or spectrophotometric grade and were used as received. The method of ref 2 was used to prepare the new vanadium(II) complexes. Anal. Calcd for $C_{74}H_{48}F_6N_6O_6S_2V$ ($[V(Ph_2phen)_3](O_3SCF_3)_2$): C, 66.02; H, 3.59; F, 8.47; N, 6.24. Found: C, 66.10; H, 3.59; F, 8.34; N, 6.18. Calcd for $C_{50}H_{48}F_6N_6O_6S_2V$ ($[V(Me_4phen)_3](O_3SCF_3)_2$): C, 56.76; H, 4.57; F, 10.77; N, 7.94. Found: C, 55.41; H, 4.57; F, 10.16;

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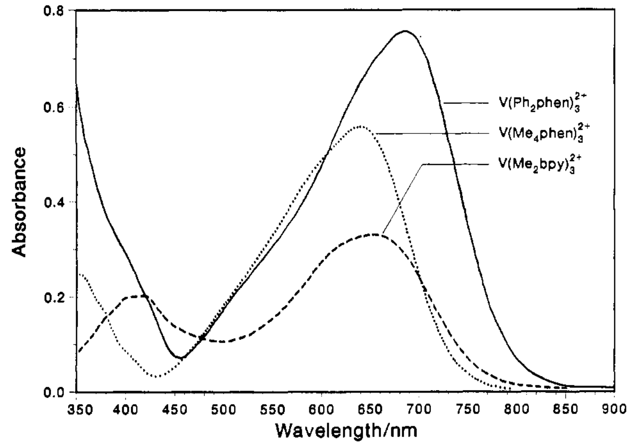

**Figure 1.** Electronic absorption spectra for vanadium(II) complexes (ca. 5 × $10^{-5}$ M) in acetone solution at room temperature: (—) V-$(Ph_2phen)_3^{2+}$; (···) $V(Me_4phen)_3^{2+}$; (- - -) $V(Me_2bpy)_3^{2+}$.

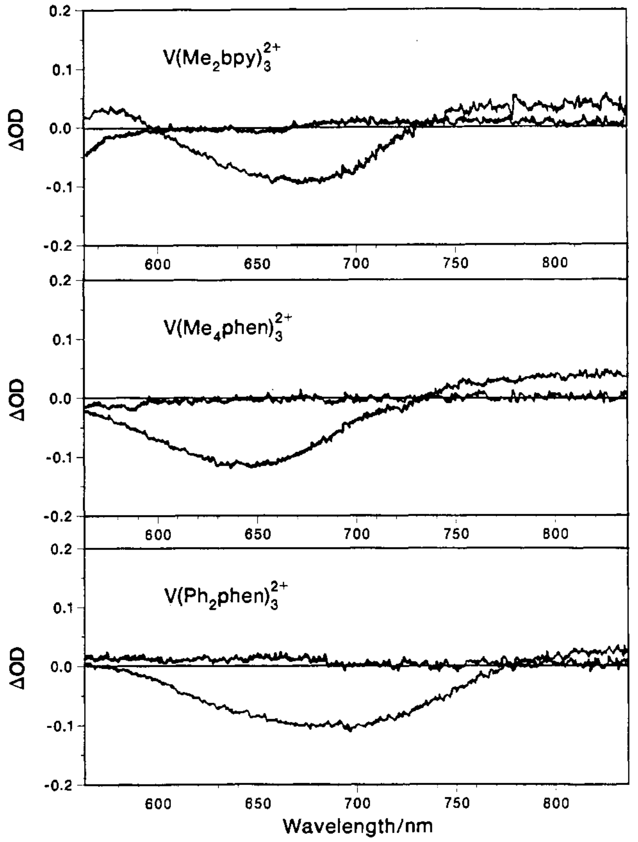

**Figure 2.** Picosecond transient difference spectra at room temperature for $V(Me_2bpy)_3^{2+}$ in ethanol, $V(Me_4phen)_3^{2+}$ in acetone, and V-$(Ph_2phen)_3^{2+}$ in acetone. Two traces are shown in each case: one 40 ps after the flash, exhibiting maximum signal intensity, and one after 5.5 ns, when the recovery of the ground-state absorption spectrum is essentially complete.

N, 8.46. Calcd for $C_{38}H_{36}F_6N_6O_6S_2V$ ($[V(Me_2bpy)_3](O_3SCF_3)_2$): C, 50.61; H, 4.02; F, 12.64; N, 9.32. Found: C, 49.72; H, 4.23; F, 13.19; N, 9.32. Room-temperature electronic absorption spectra in acetone (Figure 1): $V(Ph_2phen)_3^{2+}$, $\epsilon_{685}$ ca. 1.4 × $10^4$ $M^{-1}$ $cm^{-1}$; $V(Me_4phen)_3^{2+}$, $\epsilon_{640}$ ca. 1 × $10^4$ $M^{-1}$ $cm^{-1}$; $V(Me_2bpy)_3^{2+}$, $\epsilon_{650}$ ca. 7 × $10^3$ $M^{-1}$ $cm^{-1}$. Samples for spectroscopic and photophysical studies were prepared by freeze-pump-thaw degassing. For measurements at 5 K, samples were prepared by slow evaporation of a solution of $[V(phen)_3](O_3SCF_3)_2 \cdot H_2O$ and poly(vinyl acetate) (low molecular weight; Aldrich) in $CH_3CN$ in a drybox.

Electronic absorption spectra were recorded by using Cary 219 or Perkin-Elmer 330 spectrophotometers. For work at low temperature, samples were mounted in an Oxford Instruments cryostat (Model CF204). Picosecond flash-photolysis experiments were carried out by using an apparatus described elsewhere.[4] Sample concentrations were adjusted to give maximum absorbances (640–685 nm) of ca. 0.6 (1-mm or 2-mm path length). The samples were excited with 35-ps flashes at 532 nm, and transient difference spectra were recorded for at least eight delay times in a monitoring wavelength window of ca. 150 nm (average of 150 flashes). Since our previous work with $V(phen)_3^{2+}$ [2] gave identical lifetimes from ground-state bleaching and excited-state absorption, the lifetimes reported here were calculated from measurements of ground-state recovery. All decays were found to be exponential within experimental error. Transient spectra for two overlapping monitoring windows were combined to produce the spectra shown in Figure 2.

**Table I.** Excited-State Lifetimes (1/*e*) of $V(NN)_3^{2+}$ (NN = Polypyridine)

| NN[a] | solvent | temp, K | τ, ns |
|---|---|---|---|
| bpy | EtOH | 293 | 0.5 ± 0.1[b] |
| $Me_2bpy$ | EtOH | 293 | 0.5 ± 0.1 |
| phen | acetone | 293 | 1.6 ± 0.2 |
| | EtOH | 293 | 1.8 ± 0.2[b] |
| | EtOH/MeOH[c] | 293 | 1.7 ± 0.2 |
| | EtOH/MeOH[c] | 185 | 2.0 ± 0.2 |
| | EtOH/MeOH[c] | 117 | 3.4 ± 0.3 |
| | PVA[d] | 5 | <10[e] |
| $Ph_2phen$ | acetone | 293 | 1.0 ± 0.1 |
| $Me_4phen$ | acetone | 293 | 2.0 ± 0.2 |

[a] See text for ligand abbreviations. [b] Reference 2. [c] 4:1 (v/v). [d] Poly(vinyl acetate) film. [e] Upper limit; see Experimental Section.

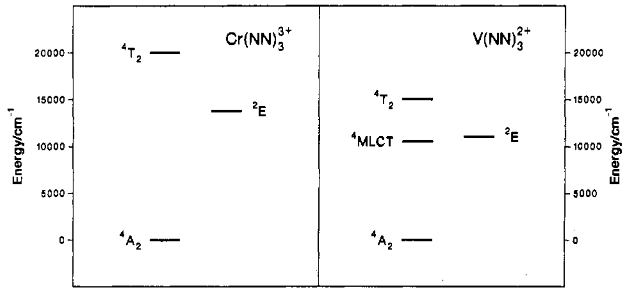

**Figure 3.** Approximate energy-level diagrams for (a) $Cr(NN)_3^{3+}$ (at left, after ref 1) and (b) $V(NN)_3^{2+}$ (at right).

Measurements at 5 K utilized excitation flashes (ca. 10 ns) at 532 nm from a Quantel Datachrom 5000 Nd:YAG laser. Data were recorded and analyzed by using Tektronix Model 7912 and 4052A electronics. The time resolution of this apparatus, determined by recording the apparent decay of scattered excitation light, was limited by the 30-ns (1/*e*) settling time of the photomultiplier-tube amplifier. For $V(phen)_3^{2+}$ at 5 K, the transient bleaching (at 650 nm) and absorption (800 nm) signals were found to decay essentially with the instrument response; thus, we estimate an upper limit of 10 ns for the excited-state lifetime under these conditions.

## Results and Discussion

Electronic absorption spectra of the vanadium(II) polypyridine complexes (Figure 1) all show broad, intense bands in the 500–800-nm region. Picosecond transient difference spectra for the $V(NN)_3^{2+}$ complexes (Figure 2) exhibit bleaching of these ground-state absorption bands and excited-state absorption at longer wavelengths (and at shorter wavelengths for $V(bpy)_3^{2+}$ and $V(Me_2bpy)_3^{2+}$). The excited-state lifetimes are given in Table I.

The photophysics of complexes such as $Cr(phen)_3^{3+}$ is dominated by the low-lying d–d excited states $^4T_2$, $^2E$, and $^2T_1$; the two doublets are commonly referred to together as "$^2E$".[1] An approximate energy diagram for $Cr(phen)_3^{3+}$ appears in Figure 3a. In this diagram, the equilibrium excited-state energies are derived from phosphorescence data (for $^2E$)[1] or from the long-wavelength "tail" of the d–d absorption band (for $^4T_2$).

The intense low-energy absorption bands in the $V(NN)_3^{2+}$ absorption spectra have been assigned primarily to MLCT transitions.[2,5] The MLCT absorption in $V(bpy)_3^{2+}$ appears at lower energy than that in $Ru(bpy)_3^{2+}$ ($\nu_{max}$ = 22 100 $cm^{-1}$; ε = 1.46 ×

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**Table II.** Electronic Spectra of Chromium(III) and Vanadium(II) Complexes

| complex[a] | absorptions ($\tilde{\nu}_{max}$, cm$^{-1}$) $^4A_2 \rightarrow {}^4T_2$ | $^4A_2 \rightarrow {}^2E$ | ref |
|---|---|---|---|
| $Al_2O_3:Cr^{3+}$ | 18 000 | 14 410 | 10 |
| $Cr(en)_3{}^{3+}$ | 21 400 | 15 000 | 11 |
| $Cr(phen)_3{}^{3+}$ | 23 400 | 13 750 | 1 |
| $MgO:V^{2+}$ | 14 300 | 11 500 | 8 |
| $V(en)_3{}^{2+}$ | 15 600 | *b* | 9 |
| $V(phen)_3{}^{2+}$ | 17 800[c] | 11 000[d] | 2, 5 |

[a] See text for ligand abbreviations. [b] Data not available. [c] Calculated;[5] obscured by MLCT absorption. [d] Predicted; see text.

$10^4$ M$^{-1}$ cm$^{-1}$ [6]), in agreement with the $M(bpy)_3{}^{2+/3+}$ electrode potentials (V, 0.09 V;[2] Ru, 0.87 V;[7] both vs. $Fc/Fc^+$ in $CH_3CN$). On the basis of the "tail" of the MLCT absorption band in $V(phen)_3{}^{2+}$ ($\epsilon_{900} \sim 10$ M$^{-1}$ cm$^{-1}$), the equilibrium energy of the lowest lying quartet MLCT excited state, "$^4$MLCT", is probably no higher than 11 000 cm$^{-1}$.

The d-d transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^2E$ in $V(NN)_3{}^{2+}$ are probably obscured by the broad, nearly featureless MLCT bands. König and Herzog have estimated that the energy of $^4T_2$ is ca. 17 800 cm$^{-1}$;[5] this is a region of intense MLCT absorption in all of these complexes. We have estimated the $^2E$ energy in $V(NN)_3{}^{2+}$ using data for other $V^{2+}$ and $Cr^{3+}$ species (Table II). Since $^2E$ lies below $^4T_2$ in $MgO:V^{2+}$,[8] the same order should hold in the stronger field environments of $V(en)_3{}^{2+}$ (en = ethylenediamine)[9] and $V(phen)_3{}^{2+}$. Also, the $^2E$ energy in $Cr(phen)_3{}^{3+}$ [1] is slightly less than that in ruby[10] and $Cr(en)_3{}^{3+}$.[11] Thus, we believe that the $^2E$ energy in $V(phen)_3{}^{2+}$ is ca. 11 000 cm$^{-1}$.

Measurement of luminescence or excited-state lifetimes should allow us to determine whether $^2E$ or $^4$MLCT is the lowest energy excited state in $V(NN)_3{}^{2+}$. (The two states might mix substantially, especially under the influence of spin-orbit coupling, but it should still be possible to evaluate their relative contributions.) We have observed no luminescence (700-1200 nm) from $V(phen)_3{}^{2+}$ or $V(bpy)_3{}^{2+}$ in the solid state or in solution, either at room temperature or at 77 K.[2] The very short excited-state lifetimes in Table I (compared to 24 ms for $^2E$ in $MgO:V^{2+}$ at room temperature[8b]) can be explained in two ways. The lowest energy excited state could be $^4$MLCT; the spin-allowed $^4$MLCT → $^4A_2$ decay should be very rapid. Alternatively, $^2E$ could be lowest lying, with the short-lived $^4$MLCT state slightly higher in energy. This latter scheme would allow for rapid decay of $^2E$ by thermally activated back intersystem crossing to $^4$MLCT. In this case, a low-temperature measurement should reveal a lifetime characteristic of $^2E$, since the thermally activated process would be inhibited. However, the lifetime we observe at 5 K, less than 10 ns, is still far too short for $^2E$. Thus, the back-intersystem-crossing model is ruled out, and the lowest energy excited state in $V(phen)_3{}^{2+}$ must be primarily $^4$MLCT in character (Figure 3b).

Fluorescence from $^4$MLCT will probably be very difficult to observe in $V(NN)_3{}^{2+}$. The breadth of the MLCT absorption band (fwhm ca. 4000 cm$^{-1}$) suggests that a large Stokes shift can be anticipated between the absorption and fluorescence maxima. Thus, even if fluorescence does occur, it will be very broad, and its maximum intensity will probably occur at wavelengths greater than 1000 nm (where the sensitivity of photomultiplier detectors is very low).

Among the $V(NN)_3{}^{2+}$ complexes in Table I, the electron-withdrawing $Ph_2phen$ gives the shortest lifetime and the electron-donating $Me_4phen$ the longest. This trend may be due to changes in the energies of the $^4$MLCT states: the intense MLCT absorption band occurs at significantly lower energy in $V(Ph_2phen)_3{}^{2+}$ than in the other complexes. Our lifetime and electronic spectral data are also consistent with the energy-gap law.[12]

The excited-state lifetime for $V(phen)_3{}^{2+}$ (EtOH/MeOH, 4:1 v/v) approximately doubles as the temperature is lowered from 293 to 117 K (Table I). An Arrhenius plot of these data gives a slope corresponding to an activation energy of ca. 100 cm$^{-1}$. This is much smaller than the values obtained for excited-state decay in other polypyridine complexes (1040 cm$^{-1}$ for $Cr(phen)_3{}^{3+}$ in $CH_3OH$;[13] 3200 cm$^{-1}$ for $Ru(phen)_3{}^{2+}$ in $CH_2Cl_2$[14]). Our small activation energy could be associated with thermal excitations to other close-lying MLCT states or with low-energy vibrations of the complex framework.[15] However, the very short $^4$MLCT lifetime we observe at 5 K shows that thermally activated processes do not play a major role in excited-state decay even at higher temperatures.

Previous studies of $Cr(NN)_3{}^{3+}$,[1,16] $Ru(NN)_3{}^{2+}$,[6] and $Os(NN)_3{}^{2+}$ [17] excited-state nonradiative decay all found larger rates for NN = bpy than for NN = phen. Our lifetimes for $V(bpy)_3{}^{2+}$ and $V(Me_2bpy)_3{}^{2+}$ (Table I) are also shorter than those for the phenanthroline derivatives. In all of these cases, then, the more flexible bpy ligands appear to permit faster excited-state decay.

Photoredox reactions of metal complexes have generally involved phosphorescent excited states. Our experiments, on the other hand, have shown that the redox-active lowest energy excited state in vanadium(II) polypyridine complexes is a MLCT state of the same spin multiplicity as the ground state.

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## Copper-Promoted Autoxidation of a Binucleating Ligand

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Hemocyanin is a copper protein that reversibly binds molecular oxygen.[2] When viewed in the light of the now well-understood and well-modeled oxygen-carrying chemistry of iron in hemoglobin,[3] this apparently simple reaction of copper might not seem

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