excitation mechanism based on electrical charging of newly created fracture surfaces. From the temperature dependence of the photoluminescence maximum the "temperature" of the TL site is estimated to be 295 K with an experimental uncertainty of 30 K.

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Registry No. KLi[Pt(CN)$_4$], 62728-87-4; KNa[Pt(CN)$_4$], 15318-78-2; Cs$_2$Ca[Pt(CN)$_4$]$_2$, 93645-96-6; Cs$_2$[Pt(CN)$_4$], 15747-35-0.

Notes

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Critical Deactivating Modes for the Metal-2,2'-Bipyridine or -1,10-Phenanthroline MLCT Excited States

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Relatively long-lived photoexcited states of transition-metal complexes have been utilized in a variety of interesting photoredox schemes.[1,2] It would clearly be of interest to understand the factors that affect excited-state properties and reactivities (lifetimes, ground- and excited-state redox potentials, absorption spectra, etc.) so that they could be systematically controlled to optimize the use of metal complexes as sensitizers. One class of chromophore that has been extensively studied consists of oxidizable metal centers bound to polypyridyl ligands like 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen).[2-4] The complexes have low-lying metal-to-ligand charge-transfer (MLCT) excited states that can be long-lived. Low-temperature emission spectra characteristically exhibit a short, poorly resolved vibrational progression with $\hbar\omega = 1350$ cm^{-1}, which has been characterized as a framework stretch of the polypyridyl ligand.[4]

Recently, we have described a series of complexes of the type Os(B)L$_4^{2+}$ (B = bpy, phen; L = py, PR$_3$, NCMe, CO, etc.) which have relatively long-lived excited states whose properties can be tuned by systematic variations in L.[5] For this series, it was found that variations in both the radiative (k_r) and nonradiative (k_{nr}) decay rate constants could be understood quantitatively.[6] In particular, variations in k_{nr} are determined largely by the excited-state energy and differences in the equilibrium geometries of the ground and excited states in accordance with the "energy gap law".[7] From the vibrational structure of the emission spectra, the most important difference in equilibrium geometry occurs in the aforementioned 1350-cm^{-1} vibrational mode and it was demonstrated that this mode functions as the critical accepting vibration. Evidence was also obtained for less important contributions from a lower frequency mode (~400 cm^{-1}), presumably arising from metal-ligand skeletal vibrations. The purpose of the present work is (1) to consider the origin of the ~1350-cm^{-1} distortion in greater detail, and (2) to provide an electronic basis for a comparison between bpy vs. phen as the chromophoric ligand.

Experimental Section

CNDO/2 calculations[8] were carried out for bpy, phen, and their diprotonated forms H$_2$bpy^{2+} and H$_2$phen^{2+}. The coordinates for bpy and phen were taken from the structures for Ru(bpy)$_6^{2+}$[9] and Fe(phen)$_3^{2+}$.[10] For the diprotonated forms, the N-H bond length was taken to be 1.05 Å and the N-H vector was taken to bisect the C-N-C angle. Where comparable, the present results agreed fairly well with previously published results for bpy[11,12] and phen.[12,13]

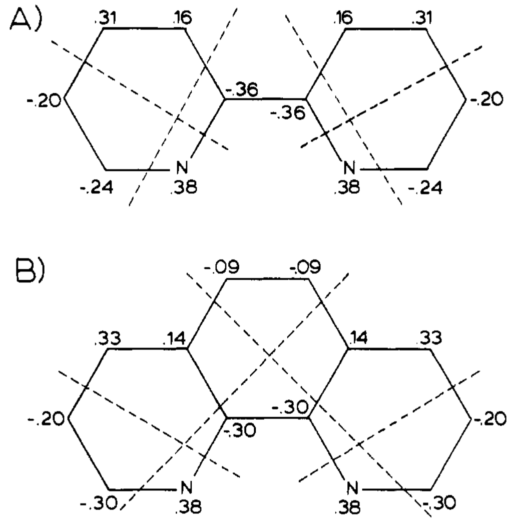

Figure 1. Calculated lowest energy π^* orbital of (A) H$_2$bpy^{2+} and (B) H$_2$phen^{2+}. The numbers indicate the contribution of the out-of-plane p orbital of the atom to the π^* orbital, and the dashed lines indicate the approximate nodal planes.

Results and Discussion

Our concern here is only with the lowest π^* orbital, and the discussion will be limited to it. Complete results are published

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Table I. Comparison of bpy Interactomic Distances (Å) for Various Species[a]

	N1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–N1	C2–C2′
bpy[d]	1.346 (2)	1.394 (2)	1.385 (2)	1.383 (3)	1.384 (2)	1.341 (2)	1.490 (2)
$ML_x(bpy)_y$[c]	1.353	1.394	1.384	1.380	1.390	1.348	1.467
$Mo(bpy)_2(O\text{-}i\text{-}Pr)_2$[b]	1.380 (10)	1.409 (2)	1.370 (3)	1.406 (3)	1.368 (2)	1.371 (2)	1.417 (3)
$Fe(\eta^6\text{-}C_7H_8)(bpy)$[d]	1.383 (2)	1.412 (7)	1.365 (7)	1.415 (5)	1.358 (4)	1.376 (5)	1.424 (4)

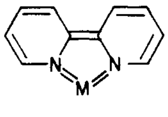
[a] Numbering scheme shown in Figure 2A. [b] Reference 15. [c] "Normal" coordinated bpy ligands.[17] [d] Reference 16.

elsewhere.[14] The diprotonated species were chosen as crude models for the metalated species. Noticeable differences were found between the results for the non- and diprotonated ligands, particularly for phen vs. H_2phen^{2+}. One calculational result for a metalated bpy ligand has been presented,[11c,d] and this agreed quite closely with the present result for H_2bpy^{2+}. For this and other reasons (vide infra),[14] we feel that diprotonation is a reasonable metalation model and only the results for the diprotonated ligands will be further discussed.

The results for the lowest π^* orbital of H_2bpy^{2+} and H_2phen^{2+} are presented in Figure 1. The two orbitals are seen to be remarkably similar, with the ethylene linkage of phen making little contribution to the lowest orbital. The HOMO and LUMO orbitals for the two protonated ligands were found to be quite similar, but the remaining orbitals show considerable differences. The differences are to be expected since phen has two more π-type orbitals than does bpy and there cannot be one-to-one correspondence of orbitals. The similarities between the HOMO and LUMO orbitals and relative energies explain the many parallels typically found between the chemistries of bpy– and phen–metal complexes.

The distortions that the ligands would undergo upon the addition of an electron to the lowest π^* orbital can be readily predicted from the results. If two neighboring atoms have the same phase contribution to the π^* orbital, there will be an increase in bonding between them and a consequent shortening of the bond. Neighbors with opposite phase contributions will feel a decrease in bonding, and the distance between them should increase. The change in bond length should reflect the contributions the two atoms of concern make to the MO. A schematic representation of the anticipated distortions are shown in Figure 2.

An alternate mechanism by which electron density can be added to the lowest π^* orbital is by metal (d) to ligand (π^*) back-bonding. Recently, the crystal structures of two compounds ($Mo(bpy)_2(O\text{-}i\text{-}Pr)_2$[15] and $Fe(\eta^6\text{-}C_7H_8)(bpy)$[16]) have been reported, where evidence for extensive back-bonding of this type is implied by the distorted structure of the bpy ligands. A comparison of pertinent bond length data is presented in Table I.[15-17] It can be seen from the data that the C–C and C–N bond lengths are significantly displaced from normal values by 0.016–0.047 Å. Further, the distortion that the bpy ligands undergo matches that predicted qualitatively in Figure 2. Previously, the distortion had been accounted for by a contribution from the resonance structure[15,16]



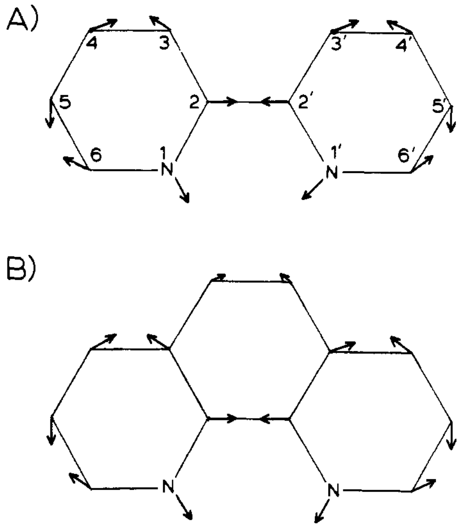


Figure 2. Predicted distortion of H_2bpy^{2+} (A) and H_2phen^{2+} (B) resulting from placing an electron in the lowest π^* orbital. The arrows indicate the general changes in the ligand framework and are only semiquantitative. The numbering scheme used for bpy in Table I is shown in A.

The present work provides a more sophisticated explanation. Analogous structures for distorted phen ligands have not yet been published. However, it can be predicted that a very similar distortion will be observed, with only very small bond length changes in the ethylene linkage because of the small contribution of those atoms to the MO.

Thus, the combination of the MO calculations and the crystal structures provides a picture of the critical molecular distortions expected in the metal-bpy MLCT excited states. From the resonance Raman spectra of $Mo(bpy)_2(O\text{-}i\text{-}Pr)_2$, it was concluded that the extent of reduction of the bpy ligand is ca. 0.5e.[15] By extrapolation, the bond length changes in the MLCT excited state might be as much as twice as large as the changes for the electron-rich, ground-state complex. It should be noted, however, that because of ground-state $d\pi$–π^* orbital mixing, less than 1e is actually transferred in the excitation $M^{n+}(bpy) \rightarrow M^{n+1}(bpy^{-}\cdot)$.[6]

The next step is to confirm that a vibrational mode or modes of bpy with $\hbar\omega$ ~1350 cm^{-1} has the equilibrium coordinate changes associated with reduction. Normal-mode analyses of both free and coordinated bpy have appeared,[18] though they may not be completely valid.[19] Detailed analyses of biphenyl[20] and substituted pyridines[21] have also appeared. We have attempted to relate the observed distortion to a combination of normal modes. A unique fit could not be obtained because there is mixing between the framework stretching modes and C–H bending modes, and the positions of the hydrogen atoms cannot be reliably estimated from available crystal structures.

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What did seem clear from the analysis is that no one mode, and in particular a mode with $\hbar\omega \approx 1350$ cm^{-1}, corresponds to the observed displacements in reduction. Rather, contributions from at least three framework stretching modes (with $\hbar\omega$ = 1000–1600 cm^{-1}) are required to approach a reasonable approximation to the displacements. The need to include more than one mode is consistent with the resonance Raman spectra associated with the MLCT absorption bands.[22,23] In the resonance Raman experiment it was found that seven modes in the region 1000–1600 cm^{-1} are reasonantly enhanced. We conclude that the observed vibrational progression of 1350 cm^{-1}, which appears in the emission spectra, probably represents an average with contributions from several progressions with frequencies in the range 1000–1600 cm^{-1}. The presence of multiple components is undoubtedly a contributing factor to the poorly resolved nature of the vibrational structure. A careful reexamination of the normal-mode analyses and an analysis of the resonance Raman enhancements would be necessary for a more detailed analysis of the problem.

Given the evidence for multiple components, a question arises as to the validity of the single-mode approximation used earlier to analyze nonradiative decay data.[6] In fact, the inclusion of multiple modes keeps the original analysis intact but changes the interpretation of the parameters derived from emission spectra. The effect of several acceptor modes with similar frequencies has been analyzed previously.[7] There it was found that multiple contributors can be treated as a single mode whose equilibrium displacement (S) can be taken as a sum of individual mode displacements ($S = \sum_i S_i$) and whose frequency is a weighted average of contributing frequencies $\hbar\omega = \sum_i \hbar\omega_i S_i / \sum_i S_i$. S is related to the true equilibrium displacement by $S = {}^1/_2(\Delta Q_e)^2(M\omega/\hbar)$ where M and ω are the reduced mass and angular frequency ($\omega = 2\pi\nu$) of the mode. The averaging procedure suggested in the ratio of sums is the same as that achieved by the relatively poor resolution obtained in the emission spectra provided that the frequencies are not drastically different and the individual peak half-widths are similar. In the relative sense that the analysis relies upon, errors will tend to cancel, so that the application of these approximations can be quite liberal. Thus, the single-mode treatment survives intact although it must be recognized that the parameters S and $\hbar\omega$ obtained from the emission spectral fits are averaged quantities for contributions from as many as seven modes.

An important point here is that C–H stretching modes do not play a detectable role in the excited-state decay process. In radiationless decay theory, it is often assumed that these modes play a dominant role because of their high frequency.[7] However, a requirement for a mode to play a major role is that there be a difference in the equilibrium normal coordinate between the ground and excited state. The π^* orbital is essentially nonbonding with respect to the C–H bond so a bond length change is not expected. This is supported both by the lack of a C–H vibrational progression in the emission spectra[4–6] and by the lack of enhancement of C–H stretching modes in the resonance Raman spectra.[22] Additional evidence comes from the lack of a drastic effect on the lifetime (less than a factor of 2) by the replacement of the hydrogen atoms with methyl groups[24] or deuterium atoms.[6a,25] The slight effects observed may be due to the mixing of the C–H bending modes with the framework stretching modes. Similar conclusions have been reached for radiationless decay from the π–π^* excited states of certain aromatic organic species.[26]

With the results of the MO calculations in hand, it is also interesting to contrast the excited-state behavior of complexes containing bpy vs. phen as the chromophoric ligand. Typically, it is observed that the phen complexes have excited-state lifetimes and quantum yields for emission that are three times as large as those for the bpy analogues.[4–6] More specifically, a state-to-state comparison of $M(B)_3^{2+}$ complexes (M = Ru, Os; B = bpy, phen) shows that k_r for analogous complexes have quite similar values, while the values for k_{nr} are three times larger for bpy than for phen.[24]

As is discussed in more detail elsewhere,[24a] k_r depends upon the transition dipole integral and the excited-state energy. Emission energies are essentially the same for analogous bpy vs. and phen complexes, suggesting that the transition dipoles are also the same for the two ligands in analogous complexes. The transition moment connects states largely metal (dπ) and ligand (π^*) in character, and so the similarities in k_r values for analogous complexes containing the two ligands are consistent with the calculated results reported here on the π^* orbitals. In addition, absorption band intensities, which are also proportional to the transition dipole integral for the first set of MLCT bands of analogous complexes, are found to be quite similar.[24] From the available evidence it seems necessary to conclude that bpy and phen are nearly equivalent in the role they play as chromophoric ligands.

On the other hand, the value of k_{nr} depends on a vibronic coupling integral and a vibrational overlap integral.[24a] Since the vibronic coupling integral involves the same metal (dπ) and ligand (π^*) orbitals, it seems likely that such integrals for bpy vs. phen complexes would remain nearly constant. The vibrational overlap integral depends in a complicated way on the excited-state energy, the frequency of the critical accepting vibrational mode, and the amount of equilibrium displacement between the ground and excited states in this mode. The value of the integral is quite sensitive to all three parameters. Typically, the excited-state energies for the phen complexes are 450 cm^{-1} higher than for the bpy analogues, and excited-state distortions for the analogous phen complexes are slightly smaller than for bpy.[25] Both of these factors would contribute to smaller values of k_{nr} for phen compared to bpy, and together they could easily account for the observed differences of ~3. Thus, the differences in excited-state properties between analogous bpy and phen complexes may not arise from electronic effects, but rather may have more subtle origins.

Conclusions

The form of the critical accepting "mode" of metal–bpy and metal–phen MLCT excited states as predicted from MO calculations is consistent with the results of crystal structures for electron-rich metal-bpy complexes. This mode actually is a composite of several modes that are framework stretching and possibly C–H bending (but not C–H stretching) in origin. The lowest π^* orbitals of bpy and phen are remarkably similar, which leads to an electronic equivalence between them in determining the photophysical properties of MLCT excited states.

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Registry No. bpy, 366-18-7; phen, 66-71-7; H_2bpy^{2+}, 20910-67-2; H_2phen^{2+}, 12088-96-9.

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