which was assigned an estimated occupancy of 0.25 on the basis of its intensity in a difference Fourier map. Full-matrix least-squares refinement of all non-hydrogen atoms using isotropic thermal parameters yielded an R of 0.060. The final stage of refinement made use of the blocked-cascade least-squares method and a riding model for hydrogen atoms in which a hydrogen atom was given a computed position and assigned a thermal parameter 1.2 times that of the carbon atom to which it was bonded. In addition, the atoms Ru, Pd, Cl(1), Cl(2), P(1), P(2), C(1), C(2), O(1), and O(2) of the title compound, as well as the fully occupied molecule of dichloromethane, were given anisotropic thermal parameters. This brought the number of parameters to 274, yielding R of 0.043, $R_w = 0.049$, by using 4605 reflections ($I > 3\sigma(I)$). Neutral-atom scattering factors and corrections for anomalous dispersion for Pd, Ru, Cl, and P were from ref 40. Positional and isotropic thermal parameters, hydrogen atom coordinates, anisotropic thermal parameters, and structure factor tables are available as supplementary material.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 7924575) for support. A.M. was supported by a USA/France NSF/CNRS Exchange Postdoctoral Award and J.P.F. was an Earl C. Anthony and University of California Regents Follow. We thank Professor H. Hope for useful discussions.

Registry No. A, 78055-58-0; B, 78790-90-6; C, 78790-91-7; D, 82648-72-4; E, 82690-70-8; $[Ru(CO)_3(Ph_2Ppy)]_3$, 82690-69-5; $(Ph_2Ppy)_2Ru(CO)_3$, 82648-71-3; $Pd(Ph_2Ppy)_2Cl_2$, 78088-45-6; $Ru_3(CO)_{12}$, 15243-33-1; $(1,5\text{-COD})PdCl_2$, 12107-56-1; $Pd(PhCN)_2Cl_2$, 14220-64-5; $Pd_2(dba)_3$, 51364-51-3; Ru, 7440-18-8; Pd, 7440-05-3.

Supplementary Material Available: Anisotropic temperature factors (Table V), hydrogen coordinates (Table VI), a stereoscopic view of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E (Figure 4), and a table of structure factors for $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ (31 pages). Ordering information is given on any current masthead page.

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Concerning the Absorption Spectra of the Ions $M(bpy)_3^{2+}$ (M = Fe, Ru, Os; bpy = 2,2′-Bipyridine)

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An electronic structural model, which includes spin–orbit coupling, is developed for the absorption spectra of the ions $M(bpy)_3^{2+}$ (M = Fe, Ru, Os; bpy = 2,2′-bipyridine). It is found that, even for Os, the excited states can be classified as "singlets" and "triplets" although there is considerable mixing between the pure spin states. Consequently, the luminescent excited states of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ are assigned as being states largely "triplet" in character. Explicit assignments of the absorption spectra for the complexes are proposed. The implications of the present treatment relative to other theoretical analyses are discussed.

Introduction

Polypyridyl complexes of the type $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) have been studied intensively[1] in part because of possible applications of their metal to ligand charge transfer (MLCT) excited states in energy conversion processes.[2] Despite their importance, the electronic structures of the MLCT excited states have not been clearly delineated. In particular, three rather fundamental questions have not been totally resolved: (1) Is the promoted electron localized in the π^* levels of a single bpy ligand or is it delocalized over the π^* orbitals of all three bpy ligands?[3–5] (2) Can the lower lying excited states be characterized as being triplet states or is such a description meaningless?[5,6] (3) Why is the excited-state lifetime of $Os(bpy)_3^{2+}$ so much shorter than that of $Ru(bpy)_3^{2+}$?[5,7,8]

Pertinent information concerning each of the three questions is obtainable from an analysis of electronic absorption spectra. Recently, the polarized absorption spectra (at 8 K) of the $M(bpy)_3^{2+}$ ions (M = Fe, Ru, Os) doped into single crystals of $Zn(bpy)_3^{2+}$ salts have been reported.[6] It was noted that the intensity of the lowest lying MLCT transitions relative to the strongest MLCT transitions increased dramatically in the series Fe < Ru < Os. The increase was found to be proportional to λ^2, where λ is the spin–orbit coupling constant of the metal, and it was inferred that lowest energy bands were transitions to "triplet" states into which appreciable singlet character was mixed via spin–orbit coupling. It was also found that the absorption spectrum of $Os(bpy)_3^{2+}$ was much more complex than that of the other ions, and it has been suggested that spin–orbit coupling could be responsible for the increased complexity as well.[6,9] Neither of these latter two points was

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substantiated by an explicit model. Several other workers have since proposed different assignments of the absorption spectra.[9-11] Any differences between the earlier and later work were limited to explicit band assignments, and there was no disputation of the assignment of the lower energy bands as being "triplet" transitions.

Crosby and co-workers have suggested an entirely different interpretation of the spectra.[5,12] They had developed a mathematical model for the excited states based upon the coupling of the promoted electron in the bpy π^* orbitals to the metal $(d\pi)^5$ core electrons. The effect of spin–orbit coupling upon the metal $(d\pi)^5$ core states was included in the treatment. With use of the model, the weaker, lower energy transitions were assigned as arising from a particular $(d\pi)^5(\pi^*)^1$ configuration, which gives rise to a singlet and three triplet states. As such it was concluded that the designation of states as being "singlet" or "triplet" was meaningless. The model presented could not account for the marked increase in intensity of the bands in the series Fe < Ru < Os.

Models for evaluating the effects of spin–orbit coupling on the MLCT spectra of various square-planar complexes have been developed by several authors.[13-15] The work on square-planar complexes clearly showed that the weaker, lower energy bands present in the various complexes could be assigned as being "triplet" transitions. Further, it was found that the relative intensities and energies of the several transitions could be reasonably well accounted for by simply including the effects of spin–orbit coupling upon the pure singlet and triplet states whose energies were determined from a simple one-electron molecular orbital scheme (i.e., without including extensive configuration interaction). An important feature of the analyses was that the spin–orbit coupling between the excited-state wave functions themselves must be calculated and not just that between the metal $(d)^n$ core states. Thus, the method used by Crosby et al.[5] for introducing spin–orbit coupling could well be in error.

Here, an electronic structural model that includes spin–orbit coupling is presented for the $M(bpy)_3^{2+}$ ions. In the interest of simplicity, only a simple one-electron molecular orbital scheme is used. The primary emphasis is to determine what the effects of spin–orbit coupling are on the observed spectra. Secondarily, an explicit assignment of the several bands observed in the spectra will be suggested. Several workers have attempted to include the effects of configuration interaction in various models for the absorption spectra with varying results.[10,16-18] Here, such terms will not be explicitly included in the treatment, though some of their effects may be implicitly included in the parametric model. Because of the approximations involved, the explicit band assignments proposed here are tenuously made. The purpose in attempting a complete assignment is to delineate certain trends and suggest areas where a more sophisticated analysis should lead to improvement.

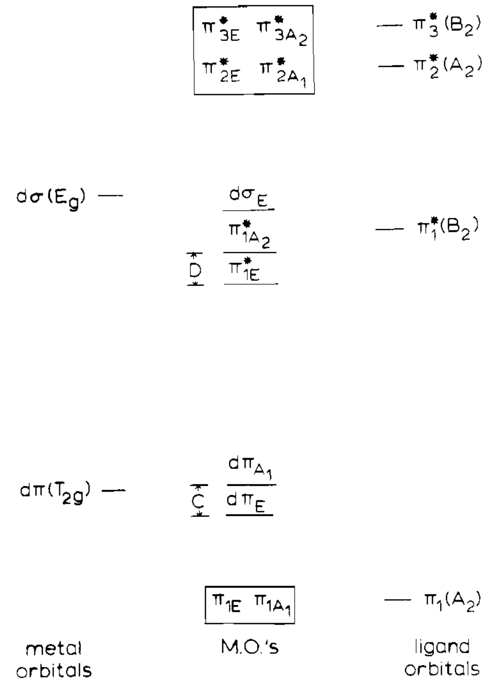

Figure 1. Molecular orbital scheme for $M(bpy)_3^{2+}$. Orbitals through the $d\pi$ are filled. Δ is positive and Γ is negative as shown.

Description of the Model

The development of the model proceeds in three discrete steps: (1) A molecular orbital (MO) scheme is presented to obtain the relative energies of the various excited-state configurations in the absence of spin–spin and spin–orbit coupling. (2) Spin–spin coupling is introduced to resolve the excited-state configurations into singlet and triplet states. (3) The spin–orbit coupling in the excited states due to the presence of the transition metal is calculated. The result is an electronic structural model that depends on four parameters, which must be evaluated to model the spectra.

The MO scheme is presented in Figure 1. The π and π^* orbitals of bpy (in the cis configuration) transform as either B_2 or A_2 in the C_{2v} point group depending upon whether they are antisymmetric or symmetric with respect to the C_2 rotation. (The xz plane is taken as the molecular plane. B_2 and A_2 correspond to the ψ and χ notation, respectively, of Orgel.[19]) Combining three B_2 bpy orbitals gives rise to molecular orbitals of A_2 and E symmetries, in the molecular D_3 point group, while the combination of three A_2 bpy orbitals gives MO's of A_1 and E symmetries. The metal $d\pi$ (T_{2g}) orbitals transform as A_1 and E in the D_3 point group.

The results of several different types of MO calculations for *cis*-bpy have been reported.[11,16-18,20,21] They all agree that the highest energy π orbital (π_1) has A_2 symmetry and the lowest energy π^* orbital (π^*_1) has B_2 symmetry. Further it is found that π^*_1 occurs at least 6000 cm^{-1} lower in energy than the next lowest π^* orbitals (π^*_2 and π^*_3 which have A_2 and B_2 symmetries, respectively). Thus, it is quite clear that the lowest energy MLCT manifold arising from $d\pi \rightarrow \pi^*_1$ transitions should be reasonably well separated from higher energy transitions. This assessment has been previously made

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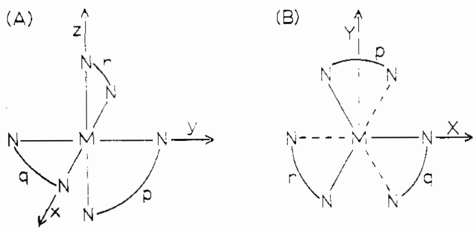

Figure 2. (A) Octahedral coordinate system for $M(bpy)_3^{2+}$. (B) Symmetry coordinate system for $M(bpy)_3^{2+}$. The *Z* axis is normal to the plane of the page.

on both theoretical[11,16–18,21] and experimental[22] grounds. Only the $d\pi \rightarrow \pi^*_1$ transitions will be considered in the present model.

As mentioned above, the degeneracy of the metal $d\pi$ (T_{2g}) orbitals is partially lifted to give orbitals that are labeled $d\pi_E$ and $d\pi_{A_1}$. The energy difference between them is given by the quantity Δ, which is defined as positive if the $d\pi_{A_1}$ orbital occurs higher in energy than $d\pi_E$. Similarly the π^*_1 orbitals are split into $\pi^*_{1A_2}$ and π^*_{1E}. The energy difference between them is given by the quantity Γ, which is defined as positive if the π^*_{1E} orbitals occur higher in energy than $\pi^*_{1A_2}$. In Figure 1 as drawn, Δ is positive and Γ is negative. This is the ordering suggested by the spectral fits (vide infra).

There are four different possible excited-state configurations whose relative energies are determined by Δ and Γ. With the $d\pi_{A_1} \rightarrow \pi^*_{1A_2}$ transition arbitrarily being selected as the reference, the $d\pi_{A_1} \rightarrow \pi^*_{1E}$ transition occurs at energy Γ, $d\pi_E \rightarrow \pi^*_{1A_2}$ occurs at Δ, and $d\pi_E \rightarrow \pi^*_{1E}$ occurs at $\Gamma + \Delta$.

So that the molecular orbitals can be written in terms of localized orbitals, the coordinate system and labeling scheme presented in Figure 2 are used. The lower case letters *x*, *y*, and *z* designate the octahedral axes, the upper case letters *X*, *Y*, and *Z* designate the symmetry axes in point group D_3, and the bipyridine ligands are labeled p, q, and r. The metal is at the origin, and the *Z* (C_3) symmetry axis passes through the origin and the point (1, 1, 1) in the octahedral axis system. The *Y* axis is selected as the C_2 axis of bipyridine p, which passes through the origin and the point (0, 1, −1). Unless explicitly stated otherwise, all further references will be to these symmetry axes.

The bases for the $d\pi$ orbitals are defined in eq 1 by following

$$d\pi_{A_1} = |20\rangle \qquad d\pi_{E+} = -\frac{1}{3^{1/2}}(2^{1/2}|2{-2}\rangle + |21\rangle)$$
$$d\pi_{E-} = \frac{1}{3^{1/2}}(2^{1/2}|22\rangle - |2{-1}\rangle) \qquad (1)$$

the work of Sugano[23] and using ket notation. They are defined with respect to the octahedral bases in eq 2. These bases are

$$d\pi_{A_1} = \frac{1}{3^{1/2}}(d_{xy} + d_{xz} + d_{yz})$$
$$d\pi_{E+} = -\frac{1}{3^{1/2}}(d_{xy} + e^{-2\pi i/3}d_{xz} + e^{2\pi i/3}d_{yz}) \qquad (2)$$
$$d\pi_{E-} = \frac{1}{3^{1/2}}(d_{xy} + e^{2\pi i/3}d_{xz} + e^{-2\pi i/3}d_{yz})$$

chosen, rather than those originally selected by Orgel,[19] because the spin–orbit coupling matrix elements and other integrals are easier to calculate. The basis sets for the π and π^* orbitals are similarly defined in eq 3, where the subscript indicates which bipyridine the particular π or π^* orbital is from.

Table I. Symmetry Labels and Relative Energies of $d\pi \rightarrow \pi^*_1$ Excited States Prior to Spin-Orbit Coupling

confign	resulting states	energies
$d\pi_E \rightarrow \pi^*_{1A_2}$	^1E: 1E	$K + \Delta$
	^3E: 2E, 3E, $1A_1$, $1A_2$	$-K + \Delta$
$d\pi_{A_1} \rightarrow \pi^*_{1A_2}$	$^1A_2$: $2A_2$	K
	$^3A_2$: $2A_1$, 4E	$-K$
$d\pi_E \rightarrow \pi^*_{1E}$	^1E: 5E	$K + \Gamma + \Delta$
	$^1A_1$: $3A_1$	
	$^1A_2$: $3A_2$	
	^3E: 6E, 7E, $4A_1$, $4A_2$	$-K + \Gamma + \Delta$
	$^3A_1$: 8E, $5A_2$	
	$^3A_2$: 9E, $5A_1$	
$d\pi_{A_1} \rightarrow \pi^*_{1E}$	^1E: 10E	$K + \Gamma$
	^3E: 11E, 12E, $6A_1$, $6A_2$	$-K + \Gamma$

$$\pi_{A_1,A_2} = \frac{1}{3^{1/2}}(\pi_p + \pi_q + \pi_r)$$
$$\pi_{E+} = -\frac{1}{3^{1/2}}(\pi_p + e^{-2\pi i/3}\pi_q + e^{2\pi i/3}\pi_r) \qquad (3)$$
$$\pi_{E-} = \frac{1}{3^{1/2}}(\pi_p + e^{2\pi i/3}\pi_q + e^{-2\pi i/3}\pi_r)$$

The four different $d\pi \rightarrow \pi^*_1$ transitions each result in excited states that are characterized as a promoted electron in a ligand-localized orbital and five electrons in metal-localized orbitals. Since the two types of orbitals occupy the same regions of space, the spin of the promoted electron and that of the odd electron in the d^5 core will couple to resolve the excited states into singlets and triplets. Specifically, the singlet states will be destabilized by an amount K_{nm} relative to the energy of the uncoupled state, and the triplet states will be stabilized by the same amount K_{nm}, where K_{nm} is the exchange integral between orbitals n and m.[24] The explicit form of K_{nm} is given in eq 4, where the number following the orbital labels

$$K_{nm} = \int d\pi_n(1)^\dagger \pi^*_{1m}(1)\left(\int \pi^*_{1m}(2)^\dagger d\pi_n(2)\frac{1}{r_{12}}\, d\tau_2\right) d\tau_1 \qquad (4)$$
$$n = A_1, E \qquad m = A_2, E$$

the electron in that orbital and $d\tau_1$ and $d\tau_2$ signify integration over the coordinates of the electron.

Since all four electronic configurations consist of an electron in a π^* orbital coupling to five electrons in $d\pi$ orbitals, the four values of K_{nm} probably will not be drastically different from one another. It shall be assumed that all four values are equal to a common value of *K*. However, it should be noted that mixing can occur between the $d\pi$ and π^* orbitals. In the present case, $d\pi_E$ can mix with π^*_{1E} and vice versa, but $d\pi_{A_1}$ cannot mix with $\pi^*_{1A_2}$ because of symmetry constraints. If eq 4 were expanded in terms of the "pure" orbitals (i.e., $d\pi_E = \alpha\cdot$"$d\pi_E$" $+ \beta\cdot$"π^*_{1E}"), integrals centered on the metal or the ligands would result, which would be different for each of the four configurations. Such terms would probably be responsible for the largest deviation from the ideal behavior of a common value of *K*. Since the extent of mixing between the metal and ligand orbitals is probably less than 20% (vide infra), it is assumed that such contributions do not overwhelm the model.

The result of including the singlet–triplet splitting is shown in Table I, where the relative energies of the excited states can

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Table II. Explicit Antisymmetrized Wave Functions of the $d\pi \rightarrow \pi^*_1$ Excited States Prior to Spin–Orbit Coupling

state	wave function[a]
1E	$(1/2)(d_{E+}\pi_A + \pi_A d_{E+})(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
2E	$(1/2)(d_{E+}\pi_A - \pi_A d_{E+})(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
3E	$(1/2^{1/2})(d_{E+}\pi_A - \pi_A d_{E+})\lvert\alpha\alpha\rangle$
4E	$(1/2^{1/2})(d_A\pi_A - \pi_A d_A)\lvert\beta\beta\rangle$
5E	$(1/2)(d_{E+}\pi_{E-} + \pi_{E-}d_{E+})(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
6E	$(1/2)(d_{E+}\pi_{E-} - \pi_{E-}d_{E+})(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
7E	$(1/2^{1/2})(d_{E+}\pi_{E-} - \pi_{E-}d_{E+})\lvert\alpha\alpha\rangle$
8E	$(1/2)(d_{E+}\pi_{E+} - \pi_{E+}d_{E+} + d_{E-}\pi_{E-} - \pi_{E-}d_{E-})\lvert\beta\beta\rangle$
9E	$(1/2)(d_{E+}\pi_{E+} - \pi_{E+}d_{E+} - d_{E-}\pi_{E-} + \pi_{E-}d_{E-})\lvert\beta\beta\rangle$
10E	$(1/2)(d_A\pi_{E-} + \pi_{E-}d_A)(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
11E	$(1/2)(d_A\pi_{E-} - \pi_{E-}d_A)(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
12E	$(1/2^{1/2})(d_A\pi_{E-} - \pi_{E-}d_A)\lvert\beta\beta\rangle$
$1A_2$	$(1/2)(d_{E+}\pi_A - \pi_A d_{E+})\lvert\alpha\alpha\rangle - (1/2)(d_{E-}\pi_A - \pi_A d_{E-})\lvert\beta\beta\rangle$
$2A_2$	$(1/2)(d_A\pi_A + \pi_A d_A)(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
$3A_2$	$(1/2(2^{1/2}))(d_{E+}\pi_{E+} + \pi_{E+}d_{E+} - d_{E-}\pi_{E-} - \pi_{E-}d_{E-})(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
$4A_2$	$(1/2)(d_{E+}\pi_{E-} - \pi_{E-}d_{E+})\lvert\beta\beta\rangle - (1/2)(d_{E-}\pi_{E+} - \pi_{E+}d_{E-})\lvert\alpha\alpha\rangle$
$5A_2$	$(1/2(2^{1/2}))(d_{E+}\pi_{E+} - \pi_{E+}d_{E+} + d_{E-}\pi_{E-} - \pi_{E-}d_{E-})(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
$6A_2$	$(1/2)(d_A\pi_{E+} - \pi_{E+}d_A)\lvert\beta\beta\rangle + (1/2)(d_A\pi_{E-} - \pi_{E-}d_A)\lvert\alpha\alpha\rangle$
$1A_1$	$(1/2)(d_{E+}\pi_A - \pi_A d_{E+})\lvert\alpha\alpha\rangle + (1/2)(d_{E-}\pi_A - \pi_A d_{E-})\lvert\beta\beta\rangle$
$2A_1$	$(1/2)(d_A\pi_A - \pi_A d_A)(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
$3A_1$	$(1/2(2^{1/2}))(d_{E+}\pi_{E+} + \pi_{E+}d_{E+} + d_{E-}\pi_{E-} + \pi_{E-}d_{E-})(\lvert\alpha\beta\rangle - \lvert\beta\alpha\rangle)$
$4A_1$	$(1/2)(d_{E+}\pi_{E-} - \pi_{E-}d_{E+})\lvert\beta\beta\rangle + (1/2)(d_{E-}\pi_{E+} - \pi_{E+}d_{E-})\lvert\alpha\alpha\rangle$
$5A_1$	$(1/2(2^{1/2}))(d_{E+}\pi_{E+} - \pi_{E+}d_{E+} - d_{E-}\pi_{E-} + \pi_{E-}d_{E-})(\lvert\alpha\beta\rangle + \lvert\beta\alpha\rangle)$
$6A_1$	$(1/2)(d_A\pi_{E+} - \pi_{E+}d_A)\lvert\beta\beta\rangle - (1/2)(d_A\pi_{E-} - \pi_{E-}d_A)\lvert\alpha\alpha\rangle$

[a] For simplicity, the following abbreviations are used: $d_A = d_{A_1}$, $d_E = d_E$, $\pi^*_{1A_2}$, $\pi_{E\pm} = \pi^*_{1E\pm}$.

be defined in terms of the three parameters Δ, Γ and K. The zero of energy is the $d\pi_{A_1} \rightarrow \pi^*_{1A_2}$ transition before including singlet–triplet splitting. Each state is listed first by its spin and spatial symmetry labels and then by its total symmetry label, which is the product of the spin and spatial symmetries. As examples, a singlet state, e.g., ^1E, has $S = 0$, which transforms as A_1 so that the total symmetry is $A_1 \times E = E$; a triplet state, e.g., ^3E, has $S = 1$, which transforms as A_2 for $m_s = 0$ and E for $m_s = \pm 1$, so the total symmetry is $(A_2 + E) \times E = E + E + A_2 + A_1$. It is thus seen that the spin degeneracy of the triplet states is partially resolved and that the six "triplet" states corresponding to the six singlet states are actually eighteen distinct states. (If the point group of the molecule contains no degenerate states, the spin degeneracy would be totally resolved.) The resulting states from the analysis are numbered sequentially for clarity.

The explicit antisymmetrized wave functions are listed in Table II. The metal d^5 configurations are abbreviated by indicating which orbital is occupied by the odd electron and dropping the π label to distinguish the states from the orbitals, e.g., $d_{A_1} = (d\pi_{E+})^2(d\pi_{E-})^2(d\pi_{A_1})$. Only one of the two possible forms of the E-symmetry orbitals is given in Table II. The degenerate partners can be obtained by replacing all of the $d\pi_E$ and π^*_{1E} orbitals with their degenerate partners and inverting the spins.

The effects of spin–orbit coupling upon these states can now be calculated. First, it should be noted that the spin–orbit coupling operator, H_{so}, transforms as A_1 and can thus only mix states of the same total symmetry. Also, H_{so} is a one-electron operator so that the matrix elements can be expanded as shown in eq 5. Since the orbitals that are being used are

$$\langle d_n(1)\pi^*_{1m}(2)|H_{so}|d_{n'}(1)\pi^*_{1m'}(2)\rangle = \langle d_n(1)|H_{so}(1)|d_{n'}(1)\rangle\langle\pi^*_{1m}(2)|\pi^*_{1m'}(2)\rangle + \langle d_n(1)|d_{n'}(1)\rangle\langle\pi^*_{1m}(2)|H_{so}(2)|\pi^*_{1m'}(2)\rangle \quad (5)$$

an orthonormal set, the first term on the right-hand side of eq 5 vanishes unless $\pi^*_{1m} = \pi^*_{1m'}$ and the second term in eq 5 vanishes unless $d\pi_n = d\pi_{n'}$ (this includes the electron's spin). Given orthonormality, all terms of the form $\langle d\pi_n(1)|H_{so}(1)|\pi^*_{1m'}(1)\rangle\langle\pi^*_{1m}(2)|d\pi_{n'}(2)\rangle$ vanish because of the second integral.

For simplification of the calculations, two standard approximations were made: (1) The actual $d\pi_{A_1}$ and $d\pi_E$ orbitals are taken to have the same amount of pure metal d-orbital character; i.e., the orbital reduction factor, k, is taken to be isotropic. (2) The actual $\pi^*_{1A_2}$ and π^*_{1E} wave functions are taken to have a negligible amount of pure metal d character mixed in. Since the extent of metal–ligand orbital mixing appears to be small (vide infra), the approximations are justified. The two approximations allow the spin–orbit coupling matrix elements between the excited states to be expressed in terms of the spin–orbit coupling matrix elements between the metal d^5 states.

The matrix elements between the six posisble d^5 configurations are readily calculated by using eq 1. The two resulting 3×3 matrices are given in eq 6. The results are calculated

$$\begin{array}{ccc} \lvert d_{A_1}\alpha\rangle & \lvert d_{E-}\beta\rangle & \lvert d_{E+}\beta\rangle \\ (\lvert d_{A_1}\beta\rangle) & (\lvert d_{E+}\alpha\rangle) & (\lvert d_{E-}\alpha\rangle) \end{array} \\ \begin{bmatrix} 0 & -\lambda/2^{1/2} & 0 \\ -\lambda/2^{1/2} & -\lambda/2 & 0 \\ 0 & 0 & \lambda/2 \end{bmatrix} \quad (6)$$

by using the five-electron wave functions, and not by using the hole formalism, so that λ is positive. The effects of spin–orbit coupling on the excited states can now be determined by using the explicit wave functions of Table II and eq 6. The resulting matrices, after block diagonalization, are given in Table III with the zero-order energies included on the diagonals.

Table III. Spin-Orbit Coupling Matrices for $d\pi \rightarrow \pi^*_1$ Excited States after Block Diagonalization[a]

$$\mathrm{I}\ \begin{array}{c} \begin{array}{ccc} 1E & 2E & 4E \end{array} \\ \begin{bmatrix} K + \Delta & -\lambda/2 & -\lambda/2 \\ -\lambda/2 & -K + \Delta & -\lambda/2 \\ -\lambda/2 & -\lambda/2 & -K \end{bmatrix} \end{array} \qquad \mathrm{II}\ \begin{array}{c} 3E \\ [-K + \Delta + \lambda/2] \end{array}$$

$$\mathrm{III}\ \begin{array}{c} \begin{array}{ccc} 5E & 6E & 12E \end{array} \\ \begin{bmatrix} K + \Gamma + \Delta & -\lambda/2 & -\lambda/2 \\ -\lambda/2 & -K + \Gamma + \Delta & -\lambda/2 \\ -\lambda/2 & -\lambda/2 & -K + \Gamma \end{bmatrix} \end{array} \qquad \mathrm{IV}\ \begin{array}{c} \begin{array}{cc} 7E' & 11E \end{array} \\ \begin{bmatrix} -K + \Gamma + \Delta - \lambda/2 & -\lambda/2^{1/2} \\ -\lambda/2^{1/2} & -K + \Gamma \end{bmatrix} \end{array}$$

$$\mathrm{V}\ \begin{array}{c} \begin{array}{cc} 8E' & 10E \end{array} \\ \begin{bmatrix} -K + \Gamma + \lambda/2 & -\lambda/2^{1/2} \\ -\lambda/2^{1/2} & K + \Gamma \end{bmatrix} \end{array} \qquad \mathrm{VI}\ \begin{array}{c} 9E' \\ [-K + \Gamma + \Delta + \lambda/2] \end{array} \qquad \mathrm{VII}\ \begin{array}{c} \begin{array}{cc} 1A_2 & 2A_2 \end{array} \\ \begin{bmatrix} -K + \Delta - \lambda/2 & \lambda/2^{1/2} \\ -\lambda/2^{1/2} & K \end{bmatrix} \end{array}$$

$$\mathrm{VIII}\ \begin{array}{c} \begin{array}{ccc} 3A_2 & 5A_2 & 6A_2 \end{array} \\ \begin{bmatrix} K + \Gamma + \Delta & -\lambda/2 & -\lambda/2 \\ -\lambda/2 & -K + \Gamma + \Delta & -\lambda/2 \\ -\lambda/2 & -\lambda/2 & -K + \Gamma \end{bmatrix} \end{array} \qquad \mathrm{IX}\ \begin{array}{c} 4A_2 \\ [-K + \Gamma + \Delta + \lambda/2] \end{array}$$

$$\mathrm{X}\ \begin{array}{c} \begin{array}{cc} 1A_1 & 2A_1 \end{array} \\ \begin{bmatrix} -K + \Delta - \lambda/2 & -\lambda/2^{1/2} \\ -\lambda/2^{1/2} & -K \end{bmatrix} \end{array} \qquad \mathrm{XI}\ \begin{array}{c} \begin{array}{ccc} 3A_1 & 5A_1 & 6A_1 \end{array} \\ \begin{bmatrix} K + \Gamma + \Delta & -\lambda/2 & -\lambda/2 \\ -\lambda/2 & -K + \Gamma + \Delta & -\lambda/2 \\ -\lambda/2 & -\lambda/2 & -K + \Gamma \end{bmatrix} \end{array} \qquad \mathrm{XII}\ \begin{array}{c} 4A_1 \\ [-K + \Gamma + \Delta + \lambda/2] \end{array}$$

[a] Block diagonalization results in the following redefinition of basis functions: $7E' = (1/2^{1/2})(7E + (1/2^{1/2})(8E + 9E))$, $8E' = (1/2^{1/2})(7E - (1/2^{1/2})(8E + 9E))$, $9E' = (1/2^{1/2})(8E - 9E)$.

In their treatment of the spectra of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ by their electron–ion coupling model, Crosby et al.[5,12] attempted to take spin–orbit coupling into account. However, their calculations only included spin–orbit coupling between the d^5 core states, which only involves solving eq 6. Their procedure is not equivalent to calculating the coupling between the $(d\pi)^5(\pi^*_1)^1$ excited states as evidenced by the lack of similarity between Table III and eq 6. The complete excited-state wave functions, which include the proper symmetry spin coordinates and are antisymmetrized, must be used to solve the problem correctly. Otherwise, matrix elements between states of different symmetry will be found to be nonzero when by symmetry considerations they must be equal to zero.

The matrices in Table III can be solved to give the relative energies of the actual 24 $d\pi \rightarrow \pi^*_1$ excited states and their compositions in terms of the pure singlet and triplet states of Table I as a function of the four parameters Δ, Γ, K, and λ. The resulting excited states, which should approximate those in the molecule, will be designated by double primes (e.g., 1E″) to distinguish them from the unperturbed pure singlet and triplet states, which are designated by unprimed or single-primed labels (e.g., 1E or 7E′). The resulting states are numbered according to which unperturbed states contribute to their character; i.e., 1E″, 2E″, and 4E″ each have contributions from the 1E, 2E, and 4E states. The highest order polynomial that results form the matrices is cubic, so the results can be calculated exactly in a straightforward fashion. The four parameters Δ, Γ, K, and λ can then be varied to obtain a best fit for a given spectrum.

Analysis

Several factors must be considered before an in-depth examination of the spectra is made. The ground state has A_1 symmetry so that transitions to E states are XY polarized, transitions to A_2 states are Z polarized, and transitions to A_1 states are dipole forbidden and probably not observed. It is well established that the visible absorption spectra of all three molecules are predominantly XY polarized.[6,25] The rationalization of this fact is that the ligand orbitals are located in the X and Y directions with respect to the metal and there is virtually no ligand orbital density in the Z direction from the metal.[6,16,25] For the transitions to E states, the direction of the electron transfer can coincide with the sense of the transition dipole so the transitions can carry CT intensity and they are expected to be relatively strong. For the transitions to A_2 states, the direction of electron transfer and the sense of the transition dipole cannot coincide so that the transitions cannot carry any CT intensity and are expected to be relatively weak. The transitions could acquire intensity by mixing with the strongly allowed, Z-polarized $\pi_1 \rightarrow \pi^*_1$ transitions, but this is presumably a small effect so that transitions to the A_2 CT states remain weaker than those of E CT states.

The ground state does not couple to any of the excited states by spin–orbit coupling and so remains a pure singlet. The spin-selection rule of $\Delta S = 0$ for electronic transitions still holds, but this requires only that the excited state have some singlet character mixed into it for the transition to be "allowed". Further, the intensity of a transition to a state will be proportional to the amount of singlet character mixed into that state.

For the E states, five triplet states (2E, 4E, 6E, 8E, 12E) mix with the three singlet states (1E, 5E, 10E) to give eight states with some singlet character (note Table III). For transitions to states with a common source of singlet character, the relative intensities can be calculated by the amount of singlet character each possesses. For example, 1E″, 2E″, and 4E″ all acquire their singlet character from 1E. The relative intensities of these three transitions would then be expected to be proportional to the amount of 1E character present in resultant states. This model does not allow one to calculate the relative intensities of transitions to the three parent singlet states (1E, 5E, 10E). It is assumed that they are all allowed and their relative intensities will be varied to give a best fit of the spectra. (Note that these three states do not mix with one another via spin–orbit coupling.) The remaining four E states that do not mix with singlet $d\pi \rightarrow \pi^*_1$ states (3E″, 7E″, 9E″, 11E″) could acquire "allowedness" by mixing with higher energy singlet states. This effect is expected to be small compared to the mixing within the $d\pi \rightarrow \pi^*_1$ manifold because of the energy differences involved. These states will be treated as essentially pure triplet states to which transitions are forbidden to first order.

Since the transitions to A_2 states apparently acquire the majority of their intensity by mixing with states other than those of the type $d\pi \rightarrow \pi^*_1$, their relative intensities cannot be predicted simply from their amount of singlet $d\pi \rightarrow \pi^*_1$ character. One of the A_2 states remains a pure triplet ($4A''_2$), and it is not clear at this point whether it can acquire singlet character from higher energy states as efficiently as the other A_2 states. The present model is limited to estimating only the relative energies of these states and not their intensities.

Examination of Table III reveals several other features. First, it can be seen that matrices III, VIII, and XI are identical. This means that each of the three E states from matrix III will occur at the same energy as an A_2 state and an A_1 state from matrices VIII and XI, respectively. Similarly, matrices VI, IX, and XII are identical. The degeneracies arise from the fact that the $d_E \rightarrow \pi^*_{1E}$ transition gives rise to E_1, A_2, and A_1 states whose accidental degeneracy is not lifted by spin–orbit coupling. The degeneracy could be lifted by configuration interaction terms. However, it follows that one would expect to see pairs of transitions, one XY polarized and the other Z polarized, occurring at similar energies that arise from these states.

Second, it can be seen that matrix I differs from matrix III only in having the amount Γ subtracted from each diagonal element. (Matrix VII shows the same relationship to matrix V, as matrix X does to matrix IV.) Thus, the three states resulting from matrix I should "shadow" those from matrix III, being displaced by the amount Γ.

Finally, it should be noted that, whenever the quantity Γ appears in a matrix, it appears only on the diagonal and it is present in all of the diagonal elements of that matrix. Thus Γ does not determine the extent of mixing between the pure singlet and triplet states. It only determines the energies of certain sets of states relative to one another. The calculated relative intensities of the E states (i.e., 5E″ vs. 6E″ vs. 12E″) will depend *only* upon the values of Δ, K, and λ.

$Fe(bpy)_3^{2+}$. The low-temperature (8 K) polarized spectrum of this complex as a dopant in single crystals of $Zn(bpy)_3^{2+}$ salts has been reported by Ferguson et al.[6a,c] Their spectra are reproduced here, although with a slightly different numbering scheme, and are shown in Figure 3. The reader is referred to the original papers for experimental details. The strongest band observed in the XY polarization has ϵ ca. 15 000 M^{-1} cm^{-1}, and the strongest band in the Z polarization has ϵ ca. 1500 M^{-1} cm^{-1}.

The bands occurring below 23 000 cm^{-1} can be assigned as $d\pi \rightarrow \pi^*_1$, with those occurring at higher energy being either $d\pi \rightarrow \pi^*_2, \pi^*_3$ or $(\pi_1 \rightarrow \pi^*_1)^3$ transitions. It has been reasonably well established that the transition $3XY$ is *not* part of a vibrational progression originating from $2XY$,[6] as has been proposed by earlier workers.[17] Since spin–orbit coupling is a rather small effect for first-row transition metals, it is straightforward to assign $2XY$ and $3XY$ as spin-allowed

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(25) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864–78.

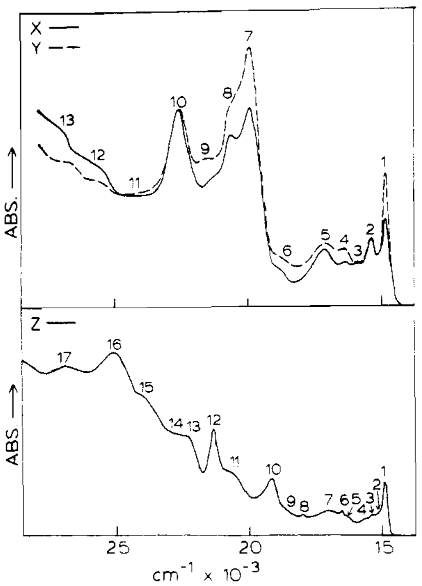

Figure 3. Absorption spectra of $Fe(bpy)_3^{2+}$, adapted from ref 6a,c. Absorbance is in arbitrary units.

charge-transfer transitions to states whose predominant components would be 1E, 5E, or 10E. The weak band 1*XY* is then probably a transition to a state predominantly triplet in character. It could also possibly be a d–d transition. Little can be said about the *Z*-polarized spectra at this point.

So that a more detailed assessment of the spectrum can be made, estimates of some of the parameters are required. The spin–orbit coupling constant of the free ion Fe^{3+} has been found to be 460 cm^{-1},[26] and values of λ = 400–460 cm^{-1} have been found for Fe(III) complexes by temperature-dependent magnetic susceptibility measurements.[27] A value of λ = 440 cm^{-1} is certainly reasonable, and this is taken as an initial estimate. From a fit of the EPR spectrum of $Fe(bpy)_3^{3+}$, the value of Δ/λ = 0.331 can be determined, which gives Δ = 120 cm^{-1}.[28]

The value of *K* can be estimated from the energy separation between the observed "singlet" and "triplet" states. Scrutinization of the matrices in Table III reveals that the energy separation between the highest and lowest energy states resulting from any one matrix is $\sim 2K + \lambda$.[29] With 1*XY* assumed to be the "triplet" partner of the "singlet" 2*XY*, the separation between the two of ~2000 cm^{-1} implies that $K \approx$ 800 cm^{-1}. (If it is assumed that 1*XY* is the "triplet" analogue of 3*XY*, then *K* is larger, but in that case it must be assumed that the "triplet" analogue of 2*XY* is not observed.)

Given these values, a comparison with the experimental spectrum allows Γ to be determined. Regardless of the value of Γ, it is found that the two "singlet" states that are predominantly 10E and 5E in character are split apart by only ca. 100 cm^{-1}. (The splitting only depends upon Δ and is approximately equal to Δ.) These two states together can account for only one of the two "singlet" transitions, 2*XY* or 3*XY*. The other transition must be the other "singlet" transition to the state predominantly 1E in character. As was mentioned previously, the separation between the two states that are predominantly 1E and 5E in character is $|\Gamma|$. The separation between 2*XY* and 3*XY* therefore gives $|\Gamma|$ = 1500 cm^{-1}.

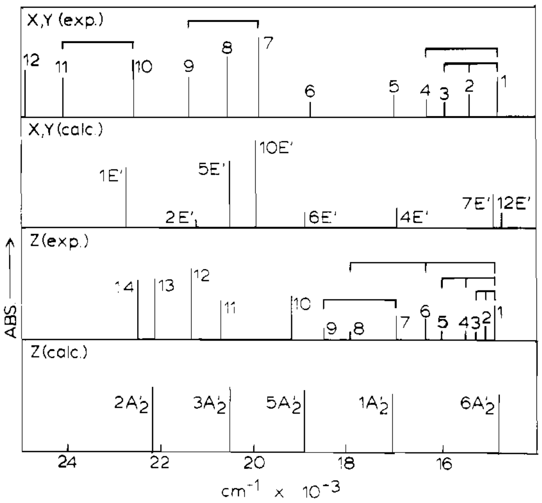

Figure 4. Schematic representation of the absorption spectrum of $Fe(bpy)_3^{2+}$ and comparison to a calculated spectrum with Δ = 100 cm^{-1}, Γ = −1500 cm^{-1}, *K* = 800 cm^{-1}, and λ = 440 cm^{-1}. Brackets indicate assigned vibrational structure. For the *X,Y* spectra, the band heights and positions are averaged. The stick heights represent solely peak height and do not reflect widths. For overlapping bands, the true peak height was estimated. The *Z*(calcd) spectrum shows only peak positions, since peak heights could not be calculated (see text).

Table IV. Composition and Relative Energy of $d\pi \rightarrow \pi^*_1$ Excited States for $Fe(bpy)_3^{2+}$: $\Delta = 100$ cm^{-1}, $\Gamma = -1500$ cm^{-1}, $K = 800$ cm^{-1}, $\lambda = 440$ cm^{-1}

state	energy[a]	compn[b]
1E″	950	0.987(1E) − 0.117(2E) − 0.110(4E)
2E″	−525	0.021(1E) + 0.773(2E) − 0.633(4E)
3E″	−480	3E
4E″	−1025	0.159(1E) + 0.624(2E) + 0.766(4E)
5E″	−550	0.987(5E) − 0.117(6E) − 0.110(12E)
6E″	−2025	0.021(5E) + 0.773(6E) − 0.633(12E)
7E″	−2675	0.787(7E′) + 0.617(11E)
8E″	−2475	0.171(10E) + 0.985(8E′)
9E″	−1980	9E′
10E″	−645	0.985(10E) − 0.171(8E′)
11E″	−2045	0.617(7E′) − 0.787(11E)
12E″	−2525	0.159(5E) + 0.624(6E) + 0.766(12E)
$1A''_2$	−975	$0.171(2A_2) + 0.985(1A_2)$
$2A''_2$	855	$0.985(2A_2) - 0.171(1A_2)$
$3A''_2$	−550	$0.987(3A_2) - 0.117(5A_2) - 0.110(6A_2)$
$4A''_2$	−1980	$4A_2$
$5A''_2$	−2025	$0.021(3A_2) + 0.773(5A_2) - 0.633(6A_2)$
$6A''_2$	−2525	$0.159(3A_2) + 0.624(5A_2) + 0.766(6A_2)$
$1A''_1$	−1175	$0.787(1A_1) + 0.617(2A_1)$
$2A''_1$	−545	$0.617(1A_1) - 0.787(2A_1)$
$3A''_1$	−550	$0.987(3A_1) - 0.117(5A_1) - 0.110(6A_1)$
$4A''_1$	−1980	$4A_1$
$5A''_1$	−2025	$0.021(3A_1) + 0.773(5A_1) - 0.633(6A_1)$
$6A''_1$	−2525	$0.159(3A_1) + 0.624(5A_1) + 0.766(6A_1)$

[a] In cm^{-1} relative to the uncoupled $(d_{A_1})(\pi^*_{A_2})$ state. [b] For definitions of the states, see Tables I–III.

The sign of Γ cannot be uniquely determined from the data for the iron complex. For the spectra of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, Γ is found to be negative, so it shall be assumed here that Γ = −1500 cm^{-1}. The calculated spectrum is shown vs. a schematic representation of the observed spectrum in Figure 4. The relative peak heights of the *XY* calculated spectra represent the amount of singlet character each state possesses. The height of the 1E″ transition is set equal to the

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(26) (a) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 192. (b) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 99. (c) Dunn, T. M. *Trans. Faraday Soc.* **1961**, *57*, 1441–4.

(27) (a) Figgis, B. N.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1966**, 422–6. (b) Figgis, B. N. *Trans. Faraday Soc.* **1961**, *57*, 204–10.

(28) Kober, E. M.; Meyer, T. J., submitted for publication.

(29) For the simplest case the value of $\Delta = 0$ is assumed. (The value of Γ is immaterial and is taken as 0.) The roots of the 3 × 3 matrices are then $E = \lambda/2, D, -D$, where $D = {}^1/_2[(2K + \lambda)^2 - 1/4\lambda^2]^{1/2}$. Similarly, the roots of the 2 × 2 matrices involving a singlet state are $E = D, -D$. Since $(2K + \lambda)^2 > ({}^1/_2\lambda)^2$, one can approximate $D \approx K + {}^1/_2\lambda$. Since $2K + \lambda > {}^1/_2\lambda$ (*K* being intrinsically positive), the difference in energy of the highest and lowest energy roots is $2D \approx 2K + \lambda$. For $\Delta \neq 0$, this difference is $\sim 2K + \lambda + |\Delta|$.

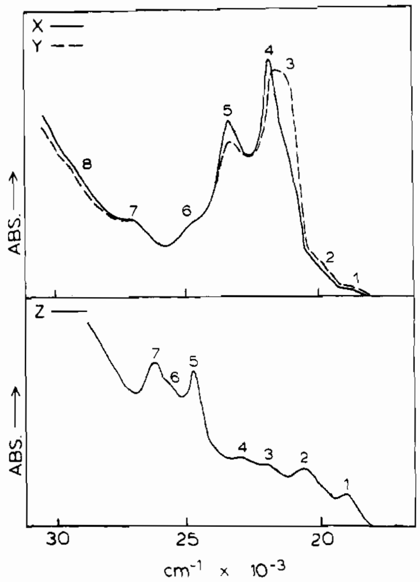

Figure 5. Absorption spectra of $Ru(bpy)_3^{2+}$, adapted from ref 6a,b. Absorbance is in arbitrary units.

height of peak 3*XY*. It is assumed that 5E″ and 10E″ contribute equally to 2*XY*. For the *Z* calculated spectrum, only peak positions are calculated; no prediction concerning peak height is implied. The calculated compositions of the excited states and their relative energies are listed in Table IV.

Vibrational structure is indicated by the brackets in Figure 4. The constant spacing among 3*XY*, 4*XY*, and 5*XY* of ca. 1500 cm^{-1} suggests that this is a vibrational progression originating at 3*XY*. Similarly, 6*Z* occurs ca. 1500 cm^{-1}higher in energy than 5*Z*, and so it might also be a vibrational satellite. Ferguson et al.[6] reported shoulders on the high-energy sides of 2*XY* and 3*XY* occurring about 700 cm^{-1} above the peak maxima. These are not readily discernible in their spectra and are not included, but if they are present, they probably represent a vibrational progression with $\hbar\omega$ ca. 700 cm^{-1}. The spectrum of $Os(bpy)_3^{2+}$ clearly exhibits vibrational structure with a spacing of ca. 600 cm^{-1}.

Since 6*XY* occurs ca. 6000 cm^{-1} higher in energy than 2*XY*, it can probably be assigned as a "singlet" $d\pi \rightarrow \pi^*_2$ transition. Since 6*Z* occurs ca. 6000 cm^{-1} higher in energy than 1*Z*, it can possibly be assigned as a "triplet" $d\pi \rightarrow \pi^*_2$ transition (as opposed to being a vibrational satellite of 5*Z*). 7*Z* and 8*Z* could have similar origins. Another possible assignment for these three transitions is that there are "triplet" $\pi_1 \rightarrow \pi^*_1$ transitions that occur at ca. 22 000 cm^{-1} and above.[21,30] However, these transitions are typically much weaker than the bands observed here, and the assignment seems unlikely.

If one refers back to the $d\pi \rightarrow \pi^*_1$ transitions, fair agreement between the observed and calculated spectra is found. Because of the lack of observable detail, the model is not severely tested. The major point of interest is that the position and intensity of the "triplet" 1*XY* band relative to the "singlet" 2*XY* band are well accounted for. The values of $\lambda = 440$ cm^{-1} and $K = 800$ cm^{-1} can be varied by up to 20% without significantly worsening this aspect of the fit. The assignment does not depend significantly upon Δ or Γ and so is independent of the detailed band assignments in the spectrum.

$Ru(bpy)_3^{2+}$. The spectrum of this complex was obtained under conditions similar as to those for $Fe(bpy)_3^{2+}$ by Ferguson et al.[6] It is shown in Figure 5 with a numbering scheme slightly different from that originally given. The reader is referred to the original papers for experimental details. The strongest *XY*-polarized band has ϵ ca. 15 000 M^{-1} cm^{-1}, and the strongest *Z*-polarized band has ϵ ca. 3000 M^{-1} cm^{-1}. By analogy to the $Fe(bpy)_3^{2+}$ spectrum, the three strong bands (3*XY*, 4*XY*, 5*XY*) can be assigned as transitions to states whose major components are the three singlet states 1E, 5E, and 10E. The two weaker bands (1*XY*, 2*XY*) are then assigned as transitions to states that are predominantly triplet in character.

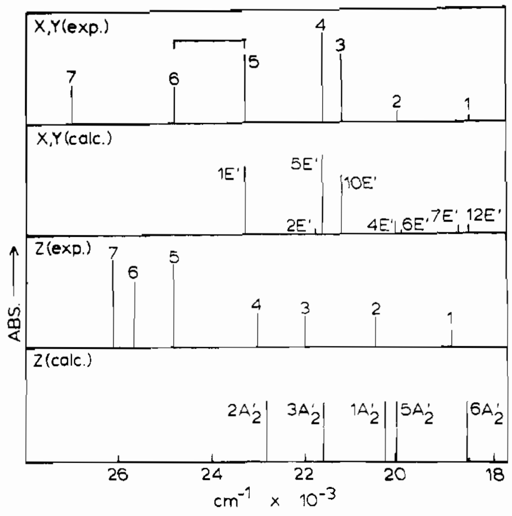

Figure 6. Schematic representation of absorption spectrum of $Ru(bpy)_3^{2+}$ and comparison to a calculated spectrum with $\Delta = 500$ cm^{-1}, $\Gamma = -1600$ cm^{-1}, $K = 850$ cm^{-1}, and $\lambda = 1200$ cm^{-1}. See the caption to Figure 4 for details.

For a more specific assignment, estimates of the various parameters are again required. The spin–orbit coupling constant for the Ru^{3+} ion has been given as $\lambda = 1180-1250$ cm^{-1}.[26] For complexes of Ru(III), values of $\lambda = 880-1100$ cm^{-1} have been derived from temperature-dependent magnetic susceptibility measurements[27a,31] or EPR and electronic spectral measurements.[32] A value of $\lambda = 1100$ cm^{-1} is assumed as an initial estimate. From the EPR of $Ru(bpy)_3^{3+}$, the value of $\Delta/\lambda = 0.507$ was obtained,[28] giving $\Delta \approx 500$ cm^{-1}. Again, the separation in energy between the lowest "triplet" state (1*XY*) and the lowest "singlet" state (3*XY*) should be ca. $2K + \lambda$. This difference is found to be ca. 2900 cm^{-1}, implying that $K \approx 900$ cm^{-1}.

From these values, it is found that the "singlet" transitions to the state that is predominantly 5E in character should occur ca. 500 cm^{-1} higher than the "singlet" transition to the state that is predominantly 10E in character. The broad peak labeled 3*XY*,4*XY* appears to consist of two such closely spaced transitions, and it is proposed that they are transitions to 5E and 10E. This leaves the band 5*XY* to be assigned as the "singlet" transition to the state that is predominantly 1E in character. Since the band occurs 1600 cm^{-1} higher in energy than 4*XY*, which is a transition to the state predominantly 5E in character, the band assignments as made give $\Gamma = -1600$ cm^{-1}. Given the assignments made here, 1*XY* and 4*XY* should have *Z*-polarized partners which are taken to be 1*Z* and 3*Z*.

A spectrum calculated by using values for the parameters λ, Δ, *K*, and Γ determined above agreed reasonably well with the observed spectrum. A slightly better fit is obtained if the magnitudes of the parameters are modified slightly to the values $\Delta = 500$ cm^{-1}, $\Gamma = -1600$ cm^{-1}, $K = 850$ cm^{-1}, and $\lambda = 1200$ cm^{-1}. The calculated spectrum based on these quantities are shown in Figure 6, where a comparison is also made to a schematic representation of the observed spectrum. The heights of the peaks labeled 10E″, 5E″, and 1E″ are scaled

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Table V. Composition and Relative Energy of $d\pi \rightarrow \pi^*_1$ Excited States for $Ru(bpy)_3^{2+}$: $\Delta = 500$ cm^{-1}, $\Gamma = -1600$ cm^{-1}, $K = 850$ cm^{-1}, $\lambda = 1200$ cm^{-1}

state	energy[a]	compn[b]
1E″	1610	0.955(1E) − 0.236(2E) − 0.175(4E)
2E″	35	0.089(1E) + 0.795(2E) − 0.600(4E)
3E″	250	3E
4E″	−1495	0.282(1E) + 0.557(2E) + 0.780(4E)
5E″	10	0.955(5E) − 0.236(6E) − 0.175(12E)
6E″	−1565	0.089(5E) + 0.795(6E) − 0.600(12E)
7E″	−3350	0.728(7E′) + 0.686(11E)
8E″	−2885	0.369(10E) + 0.929(8E′)
9E″	−1350	9E′
10E″	−415	0.929(10E) − 0.369(8E′)
11E″	−1650	0.686(7E′) − 0.727(11E)
12E″	−3095	0.282(5E) + 0.557(6E) + 0.780(12E)
$1A''_2$	−1285	$0.369(2A_2) + 0.929(1A_2)$
$2A''_2$	1185	$0.929(2A_2) - 0.369(1A_2)$
$3A''_2$	10	$0.955(3A_2) - 0.236(5A_2) - 0.175(6A_2)$
$4A''_2$	−1350	$4A_2$
$5A''_2$	−1565	$0.089(3A_2) + 0.795(5A_2) - 0.600(6A_2)$
$6A''_2$	−3095	$0.282(3A_2) + 0.557(5A_2) + 0.780(6A_2)$
$1A''_1$	−1750	$0.728(1A_1) + 0.686(2A_1)$
$2A''_1$	−50	$0.686(1A_1) - 0.728(2A_1)$
$3A''_1$	10	$0.955(3A_1) - 0.236(5A_1) - 0.175(6A_1)$
$4A''_1$	−1350	$4A_1$
$5A''_1$	−1565	$0.089(3A_1) + 0.795(5A_1) - 0.600(6A_1)$
$6A''_1$	−3095	$0.282(3A_1) + 0.557(5A_1) + 0.780(6A_1)$

[a] In cm^{-1}, relative to the uncoupled $(d_{A_1})(\pi^*_{A_2})$ state. [b] For definitions of the states, see Tables I–III.

to match those labeled 3*XY*, 4*XY*, and 5*XY*, respectively, and the heights of the remaining peaks are calculated relative to these three on the basis of the fraction of singlet character in the excited state. The data for the A_2'' states only give the relative energies of the states and are not meant to imply anything concerning band intensities. The calculated compositions and relative energies of the excited states are given in Table V.

Since 6*XY* occurs 1500 cm^{-1} higher in energy than 5*XY*, it is assigned as a vibrational satellite of 5*XY*. Since 7*XY* occurs ca. 6000 cm^{-1} higher in energy than the lowest energy "singlet" $d\pi \rightarrow \pi^*_1$ transition (3*XY*), it is most likely assignable as a "singlet" transition to the next highest set of π^* orbitals, $d\pi \rightarrow \pi^*_2$. Since 5*Z* occurs ca. 6000 cm^{-1} higher in energy than the lowest energy "triplet" $d\pi \rightarrow \pi^*_1$ transition (1*Z*), it is most likely assignable to a "triplet" transition to the next highest π^* set, $d\pi \rightarrow \pi^*_2$. 6*Z* and 7*Z* can probably also be assigned to such transitions. It is possible that these bands could be "triplet" $\pi_1 \rightarrow \pi^*_1$ transitions. As noted earlier, however, "triplet" $\pi_1 \rightarrow \pi^*_1$ transitions are typically much weaker than the bands observed here.[21,30]

Overall, the match between the calculated and observed spectrum is reasonably good. Again, the positions and intensities of the "triplet" bands relative to those of the "singlet" bands are fairly independent of Δ and Γ but strongly dependent on K and λ. The values of K and λ cannot be varied by more than 10% without seriously affecting the quality of the fit. Different specific assignments for the "singlet" and "triplet" bands (which would give different values of Δ and Γ) would not change this conclusion. Different assignments for the "singlet" and "triplet" bands were attempted, but none of the alternate assignments gave as good a match between the calculated and observed peak positions as the assignment proposed above.

$Os(bpy)_3^{2+}$. The spectrum of this complex was also obtained by Ferguson et al.[6] Their spectrum is reproduced here in Figure 7 with use of a numbering scheme slightly different from that in ref 6. The strongest band in *XY* polarization has ϵ ca. 15 000 M^{-1} cm^{-1}, and the strongest band in *Z* polarization has ϵ ca. 5000 M^{-1} cm^{-1}. Three bands in the *XY* polarization (7*XY*, 8*XY*, 10*XY*) are noticeably stronger than the remainder of the bands. By analogy to the Fe and Ru spectra, these strong bands are assigned as transitions to the three E″ states that are predominantly singlet in character. The lower energy weaker bands are then assigned as transitions to E″ states that are predominantly triplet in character.

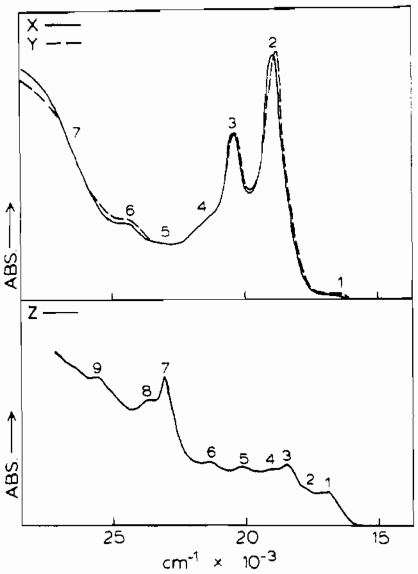

Figure 7. Absorption spectra of $Os(bpy)_3^{2+}$, adapted from ref 6a,c. Absorbance is in arbitrary units.

For a more detailed assignment, estimates of the various parameters are again required. For the free ion Os^{3+}, it has been estimated that $\lambda = 3000$–3500 cm^{-1}.[26] For complexes containing Os(III), values of $\lambda = 2600$–2950 cm^{-1} have been determined through a combination of EPR and either electronic spectra or temperature-dependent magnetic susceptibility measurements.[32,33] From the electronic absorption spectra of $Os(bpy)_3^{3+}$, values of $\lambda =$ ca. 3200 cm^{-1} and $\Delta =$ ca. 800 cm^{-1} have been determined.[28] The latter two values will be used as initial estimates.

The energy separation between the lowest energy "triplet" state (1*XY*) and the lowest energy "singlet" state (7*XY*) is 5100 cm^{-1}. Since this difference should be ca. $2K + \lambda$, this implies that $K \approx 950$ cm^{-1}. The value of Δ of ca. 800 cm^{-1} suggests that the transition to the "singlet" state that is predominantly 5E in character should occur ca. 700 cm^{-1} higher in energy than the transition to the "singlet" state that is predominantly 10E in character. Examination of the spectrum suggests that 8*XY* is the transition to 5E and 7*XY* the transition to 10E. 10*XY* is then assigned as the "singlet" transition to the state that is predominantly 1E in character. That 10*XY* occurs 2100 cm^{-1} above 8*XY* determines that $\Gamma = -2100$ cm^{-1}. This assignment requires that 1*XY*, 6*XY*, and 8*XY* should have *Z*-polarized partners. They are taken to be 1*Z*, 10*Z*, and 11*Z*, respectively.

The values derived or assumed for the parameters K, Δ, Γ, and λ can be used to calculate a model spectrum. Comparison of the calculated and observed spectra suggests a slightly better fit can be obtained with the following set of parameters: $\Delta = 800$ cm^{-1}, $\Gamma = -2100$ cm^{-1}, $K = 850$ cm^{-1}, $\lambda = 3000$ cm^{-1}. This fit is shown in Figure 8, where a comparison is also made with a schematic representation of the observed spectrum. The heights of the peaks labeled 10E″, 5E″, and 1E″ are scaled to match those of 7*XY*, 8*XY*, and 10*XY*, respectively. The heights of the remaining E″ peaks are calculated on the basis of the amount of singlet character present. For the A''_2 states, only the relative energies are represented, and the height of

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(33) Hill, N. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 427–34.

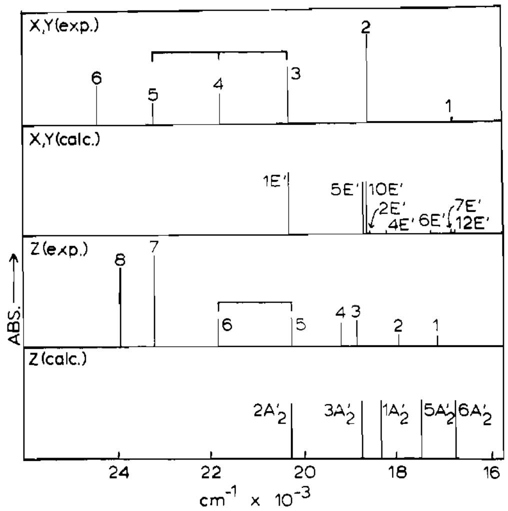

Figure 8. Schematic representation of absorption spectra of $Os(bpy)_3^{2+}$ and comparison to calculated spectra with $\Delta = 800$ cm^{-1}, $\Gamma = -2100$ cm^{-1}, $K = 850$ cm^{-1}, and $\lambda = 3000$ cm^{-1}. See the caption to Figure 4 for details.

Table VI. Compositions and Relative Energy of $d\pi \rightarrow \pi^*_1$ Excited States for $Os(bpy)_3^{2+}$: $\Delta = 800$ cm^{-1}, $\Gamma = -2100$ cm^{-1}, $K = 850$ cm^{-1}, $\lambda = 3000$ cm^{-1}

state	energy[a]	compn[b]
1E''	2650	0.899(1E) – 0.375(2E) – 0.255(4E)
2E''	1065	0.134(1E) + 0.727(2E) – 0.673(4E)
3E''	1450	3E
4E''	–2965	0.416(1E) + 0.576(2E) + 0.704(4E)
5E''	450	0.899(5E) – 0.375(6E) – 0.255(12E)
6E''	–1135	0.134(5E) + 0.727(6E) – 0.673(12E)
7E''	–5550	0.762(7E') + 0.647(11E)
8E''	–4985	0.504(10E) + 0.864(8E')
9E''	–750	9E'
10E''	–115	0.864(10E) – 0.504(8E')
11E''	–1250	0.647(7E') – 0.763(11E)
12E''	–5165	0.416(5E) + 0.576(6E) + 0.704(12E)
$1A''_2$	–2785	$0.504(2A_2) + 0.864(1A_2)$
$2A''_2$	2085	$0.864(2A_2) - 0.504(1A_2)$
$3A''_2$	450	$0.899(3A_2) - 0.375(5A_2) - 0.255(6A_2)$
$4A''_2$	–750	$4A_2$
$5A''_2$	–1135	$0.134(3A_2) + 0.727(5A_2) - 0.673(6A_2)$
$6A''_2$	–5165	$0.416(3A_2) + 0.576(5A_2) + 0.704(6A_2)$
$1A''_1$	–3350	$0.763(1A_1) + 0.647(2A_1)$
$2A''_1$	950	$0.647(1A_1) - 0.763(2A_1)$
$3A''_1$	450	$0.899(3A_1) - 0.375(5A_1) - 0.255(6A_1)$
$4A''_1$	–750	$4A_1$
$5A''_1$	–1135	$0.134(3A_1) + 0.727(5A_1) - 0.673(6A_1)$
$6A''_1$	–5165	$0.416(3A_1) + 0.576(5A_1) + 0.704(6A_1)$

[a] In cm^{-1}, relative to the uncoupled $(d_{A_1})(\pi^*_{A_2})$ state. [b] For definitions of the states, see Tables I–III.

the lines are not meant to represent calculated peak heights. The compositions and relative energies of the various excited states are listed in Table VI.

Probable vibrational structure is indicated by the brackets in Figure 8. Several peaks are observed to occur ca. 1500 cm^{-1} higher in energy than assigned peaks and these are presumed to represent vibrational progressions. Vibrational progressions with $\hbar\omega$ ca. 600 cm^{-1} and $\hbar\omega$ ca. 200 cm^{-1} also appear to be present. Since 12*XY* occurs ca. 5000 cm^{-1} higher in energy than the lowest energy "singlet" $d\pi \rightarrow \pi^*_1$ transition (7*XY*), a possible assignment of the band is as a "singlet" $d\pi \rightarrow \pi^*_2$ transition. Since 12*Z* occurs ca. 6000 cm^{-1} higher in energy than the lowest energy "triplet" $d\pi \rightarrow \pi^*_1$ transition (1*Z*), a likely assignment would be as a "triplet" $d\pi \rightarrow \pi^*_2$ transition. Again, these transitions appear to be too intense to be assigned as "triplet" $\pi_1 \rightarrow \pi^*_1$ transitions.[21,30]

As was noted for the previous complexes, the positions and intensities of the "triplet" bands relative to the "singlet" bands depend greatly upon K and λ. Changing their values by more than 10% greatly diminishes the quality of the spectral fit. The specific assignments of the bands within the "singlet" and "triplet" manifolds do not greatly affect the relative positions and intensities of the "triplet" and "singlet" bands, but no other assignment produced nearly the quality of the fit observed here.

Discussion

The emphasis of the present work is the determination of the effects of spin–orbit coupling on the charge-transfer spectra of the title complexes. The approach that was taken was as follows: (1) It was assumed that the intensity of transitions to "triplet" states was proportional to the amount of singlet character mixed into that state by spin–orbit coupling (provided the transition to the parent singlet state carried CT intensity). (2) The energy and intensity of the "triplet" transitions relative to those of the "singlet" transitions were used to determine the value K, where $2K$ is the amount of splitting between the singlet and triplet states. The validity of this approach is attested to by the success of similar models in accounting for charge-transfer spectra of other second- and third-row transition-metal complexes.[13–15]

By use of values for the spin–orbit coupling constant that are well justified, it is found that the singlet–triplet splitting ($2K$) must be in the range 1600–1800 cm^{-1} to account for the observed spectra. The reasonableness of this quantity can be judged by comparisons with values determined from other MLCT spectra. Those that have been analyzed in a similar manner involve square-planar complexes of Pd(II), Pt(II), Ir(I), and Rh(I).[13–15] Here, the charge-transfer transition is to a π^* orbital of CN^- or CNR or to a d orbital of PR_3. Values of the singlet–triplet splitting were found to be in the range of 2000–5000 cm^{-1}. Considering that these π^* and d orbitals are much smaller and localized much closer to the metal orbitals than are the bipyridine π^* orbitals and that there is probably much greater metal–ligand orbital mixing for CN^-, CNR, or PR_3 as ligands, it is reasonable to expect singlet–triplet splitting to be smaller for the metal–bipyridine complexes. Thus, the value determined in the present study appears to be entirely reasonable. In the assignments proposed by Crosby et al.,[5,12] values of $2K$ are found to be <200 cm^{-1}, which when compared with the results obtained for other complexes seems to be far too small.

Ferguson et al.[6] had previously assigned the weaker low-energy absorption bands as being "triplet" transitions because their intensity relative to the strongest bands increased as λ.[2] In the present work the nature of the transitions has been treated quantitatively and this assessment has been substantiated. Further, the energy separation between the "triplet" and "singlet" transitions is found to increase as λ, in accordance with the predictions of the model. There are no obvious reasons for doubting the assignments as involving transitions to largely singlet and triplet states.

The present model and assignments are at odds with those proposed by Crosby et al.[5,12] The defect in the development of Crosby's model appears to be that the complete antisymmetrized, excited-state wave functions were not used for calculating the effects of spin–orbit coupling. The Crosby model cannot account for the variation in intensities of the bands that are assigned here as transitions to "triplet" states. We disagree with the assertion by Crosby et al. that it is useless to assign the lowest lying MLCT excited states as being predominantly triplet in character since the present work shows that such a delineation is relatively straightforward and meaningful.

Secondarily, a complete assignment of all of the bands for the three complexes has been attempted. Since this was done on the basis of a model with four parameters, it might be argued that any spectrum could be reasonably well fit.

Table VII. Parameters Derived from M(bpy)$_3{}^{2+}$ Spectral Fits[a]

M	Δ	Γ	K	λ
Fe^{2+}	100	-1500	800	440
Ru^{2+}	500	-1600	850	1200
Os^{2+}	800	-2100	850	3000

[a] All quantities are in cm^{-1}.

However, two of the parameters (Δ and λ) are determined from spectral measurements of the analogous M(bpy)$_3{}^{3+}$ complexes. The third parameter (K) is estimated directly from the M(bpy)$_3{}^{2+}$ spectra and does not rely on complex fitting procedures. Further, its value appears to be justified by comparisons with other analyses. Thus, the only freely floating parameter is Γ, and its value was also arrived at in a fairly direct manner.

Admittedly, the model that was used is quite crude and involves many approximations, but the spectral fits arrived at are quite pleasing in their quality considering that two of the quantities used in the fits are available independently. Our model is relatively simple and therefore somewhat suspect. It is not clear how correct the band assignments proposed here are. Clearly, more experimental data (specifically, circular dichroism studies) and more extensive calculations (including configuration interaction and electrostatic repulsion terms) are needed for a definitive assignment.

However, our results do provide a basis for exploring the significance of the parameters presented in Table VII in the context of our model. As was previously mentioned, the values for λ are consistent with previous measurements.[26,27,31-33] Also, the value for K appears to be in good agreement with other experimentally determined values from MLCT spectra.[13-15] The values for Δ, the splitting between the dπ_E and dπ_{A_1} orbitals, are essentially equal to values determined from spectral analyses of the analogous M(bpy)$_3{}^{3+}$ complexes.[28] As is discussed in that paper, the sign and magnitude of Δ and its increase in magnitude in the series Fe < Ru < Os are intuitively reasonable.

This leaves the value of Γ, which measures the splitting between the π^*_{1E} and $\pi^*_{1A_2}$ orbitals, to be discussed. It is found to be negative for all three complexes. This point is in disagreement with the results of MO calculations, which predict that Γ should be positive.[10,17,18] The negative value implies that the π^*_{1E} orbitals are lower in energy than the $\pi^*_{1A_2}$ orbital. If just the interactions between the dπ and π^*_1 orbitals are considered, the opposite behavior would be expected: the π^*_{1E} orbitals would be destabilized by mixing with the dπ_E orbitals while the $\pi^*_{1A_2}$ orbital cannot mix with dπ_{A_1}. This approach, however, ignores interactions with the π^*_2 orbitals. The π^*_{1E} orbital can be stabilized by mixing with π^*_{2E}, while $\pi^*_{1A_2}$ cannot mix with $\pi^*_{2A_1}$. The negative value of Γ suggests that the $\pi^*_1 \rightarrow \pi^*_2$ interaction is stronger than the π^*_1–dπ interaction. Since the π^*_1–π^*_2 energy separation (ca. 7000 cm^{-1}) is appreciably smaller than the π^*_1–dπ energy separation (ca. 20 000 cm^{-1}), this result is not totally surprising. As both π^*_{1E} and π^*_{2E} can mix with the dπ_E orbital, increasing the metal–ligand mixing results in greater π^*_{1E}–π^*_{2E} interactions. This rationalizes the increase in magnitude of Γ in the series Fe < Ru < Os. Overall, this result suggests that, for explicit molecular orbital calculations, configuration interaction between the d$\pi \rightarrow \pi^*_2$ and d$\pi \rightarrow \pi^*_1$ states should not be ignored.

In the modeling of the absorption spectra, it was assumed that each of the transitions to the three singlet E states was strongly allowed. This supposition is somewhat at variance with other theoretical analyses, which are in turn at variance with one another. One recent study assumed that only one of the transitions to the singlet E states ($A_1 \rightarrow 5E$ in the present analysis) carried appreciable intensity.[10] The basis for this conclsuion was the assumption that the complexes (which have D_3 symmetry) could be approximated by O symmetry. The bpy π^* orbitals were stated to transform as T_1 in this point group, and since the dπ orbitals transform as T_2, the (dπ)^5(π^*)^1 configuration results in states of T_1, T_2, E, and A_2 symmetries. Only the transition to the T_1 state would be dipole allowed in O symmetry. Since lowering the symmetry from O to D_3 would split the T_1 state into E and A_2 states, it was concluded that only the transition of this one E state would be strongly allowed.

It was not stated how it was determined that the bpy π^* orbitals transform as T_1. Since the symmetry operations C_3 and C_2 (oriented along the bipyridine C_2 axes) are common to both point groups, it seems that they should be used to determine the basis for the bpy π^* orbitals. The A_2 and E representations of the O group behave exactly the same as the A_2 and E representations of the D_3 group with respect to these operations. Since the bpy π^*_1 orbitals transform as A_2 and E in D_3, it appears that they should also be the basis set in O symmetry, and not T_1 as was stated. The excited states that result from the (dπ)^5(π^*_1)^1 configuration are then $T_2 \times (A_2 + E) = T_1 + T_1 + T_2$. Since two T_1 states result, two dipole-allowed transitions are predicted. One of these, T_2(dπ) $\rightarrow$ A_2(π^*), corresponds to the $A_1 \rightarrow 1E$ transition. The other, T_2(dπ) $\rightarrow$ E(π^*), appears to correspond to the $A_1 \rightarrow 5E$ transition.

A different analysis, based on a Mulliken-type treatment,[34] has recently been presented.[9] Here, it was argued that, since the dπ_{A_1} orbital cannot mix with the π^*_1 orbitals, the d$\pi_{A_1} \rightarrow \pi^*_{1E,A_2}$ transitions will lack intensity because of the absence of transfer terms (integrals of the type $\langle \pi^*_1 | \vec{d} | \pi^*_1 \rangle$ where $\vec{d}$ is the dipole moment operator). In this work it is assumed that the predominant intensity for charge transfer arises from the transfer terms, a view which has been reasonably well supported for other systems by explicit calculations using the dipole length method.[35,36] (It should be noted that in these analyses all transitions had transfer terms, so that the importance of a lack of a transfer term was not clearly established. It is also worth noting that, in the dipole velocity method, integrals of the type $\langle \mathrm{d}\pi | \nabla | \pi^* \rangle$ are important.[36]) The result of the analysis gave the prediction that only the transitions $A_1 \rightarrow 1E$ and $A_1 \rightarrow 5E$ should carry appreciable intensity.

Finally, in two other theoretical analyses,[17,18] the oscillator strengths of the various transitions were calculated directly apparently by the dipole length method. A result of both studies was that only one transition, $A_1 \rightarrow 5E$, carries appreciable intensity. In view of the disagreements obtained between the different methods, it appears that further calculations of the intensities by both the dipole length and the dipole velocity methods whould be in order to clarify the point.

The following two points concerning the observed spectra should be noted: (1) The spectrum of Os(bpy)$_3{}^{2+}$ (Figure 7) clearly shows three strong peaks (7*XY*, 8*XY*, 10*XY*). When comparison is made to the spectra of the Fe and Ru analogues, it seems unlikely that 8*XY* could be assigned as a vibrational satellite of 7*XY*, so one must account for the three peaks as independent transitions. (2) When comparison is made to the spectra of the Fe and Os analogues, it appears that the spectrum of Ru(bpy)$_3{}^{2+}$ (Figure 5) also shows the presence of three strong peaks (i.e., that 3*XY* and 4*XY* are two independent peaks). This result would be consistent with a recent analysis of the circular dichroism spectra of Ru(bpy)$_3{}^{2+}$.[11] It would appear that a successful model must somehow account for the appearance of three intense bands.

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If it is assumed that only the $A_1 \rightarrow 1E$ and $A_1 \rightarrow 5E$ transitions carry intensity, as suggested by Vanquickenborne,[9] the presence of three bands cannot be accounted for by spin–orbit coupling interactions. The only transitions that could acquire significant intensity in this instance would be those resulting from matrices I and III of Table III. Since both matrices are displaced by an amount Γ relative to each other, one would expect to see two sets of three transitions which have similar energy splittings and relative intensities. The observation of three intense bands would predict the presence of a fourth, which is not observed. No matter what values of Δ, Γ, and K are selected, the observed spectra (i.e., three strong peaks within 3000 cm^{-1} of one another) cannot be accounted for by the above hypothesis.

We are then led to conclude that each of the three transitions ($A_1 \rightarrow 1E$, 5E, and 10E) carries appreciable intensity. Three possible explanations can be suggested: (1) In disagreement with the previous theoretical analyses, each of the three transitions does in fact have intensity of its own. (2) There is appreciable mixing among the 1E, 5E, and 10E states so that the transitions to the three resultant states carry approximately equal intensities. (3) Transitions that do not have intensity of their own (i.e., $A_1 \rightarrow 10E$) acquire intensity by mixing with the $d\pi \rightarrow \pi^*_2$ transitions. The second option has been explored by several workers,[10,17,18] who have shown that configuration interaction induced mixing of the three E states can be appreciable. However, from this work it does not appear likely that the mixing could be sufficiently strong to cause the three transitions to have approximately equal intensities.

The third possibility has not been previously explored. It has been argued that the $d\pi_{A_1} \rightarrow \pi^*_{2E}$ transition is quite strongly allowed.[9] (The $d\pi_{A_1}$ orbital can readily mix with the $\pi^*_{2A_1}$ orbital, so a transfer term is present.) It seems likely that this transition could readily mix with the $d\pi_{A_1} \rightarrow \pi^*_{1E}$ transition ($A_1 \rightarrow 10E$), supplying the latter with significant intensity. Since the negative value of Γ determined from the proposed spectral assignments was interpreted as implying substantial $\pi^*_1 \rightarrow \pi^*_2$ mixing, this explanation appears reasonable and merits further investigation.

Another important point that pertains to the theoretical analyses concerns the singlet–triplet splitting energy ($2K$). Here, the energy and intensity of the "triplet" transitions relative to the "singlets" was used to establish that $2K \approx 1600$ cm^{-1}. This value is significantly smaller than values found in the molecular orbital calculations.[10,18] The MO calculations predict that the lowest lying triplet state of $Ru(bpy)_3^{2+}$ occurs at least 5000 cm^{-1} lower in energy than the singlet state assigned to the strong MLCT absorption band. Experimentally, the energy separation is only $\sim$2000 cm^{-1}, and it appears that the MO calculations seriously overestimate the singlet–triplet separation.

One possible explanation for the overestimate of $2K$ is an overestimate of the amount of metal–ligand orbital mixing. In the two calculations,[10,18] the HOMO was calculated to be only $\sim$60% metal $d\pi$ in character and $\sim$40% bpy π^* character. The relatively small shift in energy of the bpy framework stretching modes upon coordination to Ru^{2+} suggests that the amount of π^* character mixed into the HOMO cannot be more than $\sim$20%.[37,38] This small extent of mixing is consistent with various other analyses.[16,17,21,39] Since the exchange integral (K) depends upon $1/r_{12}$, one-center exchange integrals will have comparatively large values. Overestimating the extent of metal–ligand orbital mixing results in the overestimate of the contributions of one-center integrals to the total value of the exchange integral.

A similar criticism could then be made concerning the configuration interaction terms where one-center integrals are often also important factors. In the most recent work on $Ru(bpy)_3^{2+}$,[10] it was calculated that the three singlet E states were spread out over ca. 5000 cm^{-1}. For the present assignment, the three singlet E states are found to be within 2500 cm^{-1} of one another. It should be noted that evaluating configuration interaction terms involves several approximations and assumptions whose validity is difficult to ascertain. In the previous work, it was assumed that only one of the XY-polarized transitions carried intensity. Since two strong XY-plarized transitions are readily apparent, the assumption would require large configuration interaction terms (to provide sufficient mixing between the E states) to explain the data. It therefore seems quite likely that assumptions resulting in greater configuration interaction were favored. Greater exploration of these points is obviously required but goes far beyond the scope of the present work.

Concluding Remarks

Here, it has been established that it is reasonable to assign the electronic transitions of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ as being to "singlet" or "triplet" states, though there is appreciable mixing between the spin states. Consequently, the luminescences from the lower lying MLCT states of these complexes can be assigned as originating from "triplet" states. Further, it was found that the lower lying states of $Os(bpy)_3^{2+}$ contained 0–30% singlet character, while those of $Ru(bpy)_3^{2+}$ contained only 0–10%. On the basis of purely electronic effects, one would expect the excited-state lifetime of the Ru excited state(s) to be 3 times longer than for Os. In fact, the difference in lifetimes is more on the order of a factor of 10–20[5,7,8] because, as will be discussed in a later paper, vibrational overlaps play an important role in determining excited-state lifetimes.[40]

The question of whether the excited states are best described as having the promoted electron delocalized over all three bpy ligands, or localized on a single ligand, must also be addressed. Although a delocalized model was used to account for absorption spectra, it does *not* necessarily follow that the excited electron is delocalized. Because all of the bpy ligands are equivalent in the ground state, exciton theory *requires* that the absorption spectra must be dealt with by using delocalized molecular orbitals.[39,41] The appropriate argument is that there is no force to counteract the coupling of the transition moments involving the individual bpy ligands by Coulombic interactions. Subsequent to the excitation, the bpy ligands are no longer required to be equivalent, so that vibrational equilibration and localization of the excited electron could occur.

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