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Concerning the Electronic Structure of the Ions $M(bpy)_3^{3+}$ (M = Fe, Ru, Os; bpy = 2,2′-Bipyridine)

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In the complexes $M(bpy)_3^{3+}$ (M = Fe, Ru, Os; bpy = 2,2′-bipyridine), the metal $d\pi(t_{2g})$ orbitals are resolved into A_1 and E components. Analyses of the electronic absorption and EPR spectra show that the A_1 orbital lies higher in energy than the E orbitals, so that the complexes have an $^2A_1$ ground state. An $^2A_1$ ground state is consistent with theoretical expectations. Further, the orbital splitting in the $d\pi$ levels is argued to increase in the order Fe < Ru < Os. The information obtained in the analysis should prove useful in analyzing the metal to ligand charge-transfer (MLCT) absorption spectra of the analogous species $M(bpy)_3^{2+}$.

There has been considerable interest in assigning the metal to ligand charge-transfer (MLCT) spectra of the ions $M(bpy)_3^{2+}$ (M = Fe, Ru, Os; bpy = 2,2′-bipyridine), particularly as an aid in understanding the detailed electronic structure of the MLCT excited states.[1-7] Given that the excited states have a $M^{III}(d^5)$ core, one approach to gaining information pertinent to the problem is by an analysis of the spectra of the analogous $M^{III}(bpy)_3^{3+}$ complexes. The EPR spectra of these ions have been reported,[8] but the interpretation of the results that was given is contrary to predictions based on MO theory.[2,3,5] Here, additional spectral data concerning $Os(bpy)_3^{3+}$ are reported. An analysis of the spectral data combined with a reanalysis of the earlier EPR data is found to give results consistent with theoretical expectations. In addition, the molecular parameters derived from the analyses are of value in the interpretation of the MLCT spectra of the related M(II) complexes, as described elsewhere.[7]

Results and Discussion

A schematic MO diagram for the complexes is shown in Figure 1, which is based on the molecular point group D_3. In the diagram, only the HOMO (π) and LUMO (π^*) orbitals of bpy are included. The symmetries of the orbitals have been predicted to be A_2 for the π orbital and B_2 for the π^* orbital by a variety of MO calculations.[3,5,9,10] A_2 and B_2 correspond respectively to the χ and ψ notation of Orgel.[10] Under the perturbation of the trigonal field, the $d\pi(t_{2g})$ orbitals of the metal and the $\pi(A_2)$ orbitals of bpy are split into A_1 and E components.

The concern of this paper is with the splitting between the $d\pi_{A_1}$ and $d\pi_E$ orbitals, which is given by the quantity Δ. Δ will be defined as positive if the $d\pi_{A_1}$ orbital occurs higher in energy than the $d\pi_E$ orbitals. Since the $d\pi_E$ orbitals can be stabilized by mixing with the π^*_E orbitals but such interactions do not exist for $d\pi_{A_1}$, Δ is expected to be positive. This orbital ordering has been predicted by several authors.[2,3,5,10] If it is correct, the ground state for the M(III) ions should be $^2A_1$ since there are five $d\pi$ electrons. However, on the basis of an analysis of EPR spectra, it was concluded that the ions have ^2E ground states.[8] The apparent discrepancy between the observed and predicted results spurred our interest in the electronic structure of the M(III) ions.

A theoretical basis for understanding electronic structure in $(d\pi)^5$ complexes has been discussed several times,[11] most recently by Hill[12] and DeSimone.[13] There is considerable confusion in the literature concerning the sign conventions for the spin–orbit coupling constant and orbital splitting parameters. Here, the conventions of Hill will be followed, but tetragonal splitting will be ignored. The definition of Δ as positive for an A above E scheme is consistent with Hill's convention although DeSimone defines Δ with the opposite sign convention.[13]

From the work of Sugano et al.[14] the explicit forms of the $d\pi$ orbitals are as shown in eq 1. The $(d\pi)^5$ wave functions

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

are abbreviated by listing only the orbital of residence for the odd electron. The five-electron states are denoted by dropping the π notation in order to distinguish the states from the orbitals; e.g., $d_{A_1} = (d\pi_{E+})^2(d\pi_{E-})^2(d\pi_{A_1})^1$. The spin–orbit coupling matrices for the six possible $(d\pi)^5$ states are readily calculated and are given in eq 2. In eq 2, the amount 2Δ has

$$\begin{array}{ccc} |d_{A_1}\alpha\rangle & |d_{E-}\beta\rangle & |d_{E+}\beta\rangle \\ (|d_{A_1}\beta\rangle) & (|d_{E+}\alpha\rangle) & (|d_{E-}\alpha\rangle) \\ -\Delta & -\lambda/2^{1/2} & 0 \\ -\lambda/2^{1/2} & -\lambda/2 & 0 \\ 0 & 0 & \lambda/2 \end{array} \tag{2}$$

been subtracted from the diagonal elements to simplify the matrix. Since the matrix elements were derived using five-electron states rather than one-hole states, λ is intrinsically positive. It should be recalled from the definition of Δ given here that, in the absence of spin–orbit coupling ($\lambda = 0$), the $(d\pi)^5$ ground state would be the $^2A_1$ state if Δ is positive.

One effect of spin–orbit coupling is to split the ^2E state into two states, so that a total of three Kramers doublets exist for the $(d\pi)^5$ configuration. The relative energies of the three

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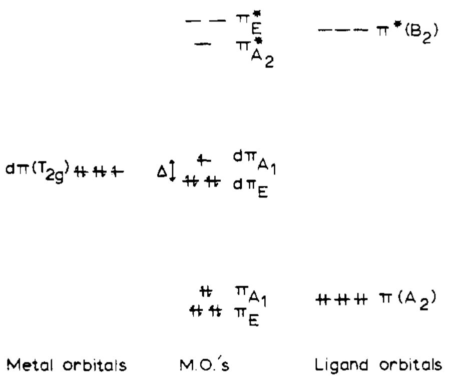

Figure 1. Schematic MO diagram for the $M(bpy)_3^{3+}$ complexes. Only the HOMO and LUMO orbitals for bpy are included.

Table I. Calculated Electronic Structure Parameters from EPR Data[a]

complex	$\lvert g_\perp \rvert$	$\lvert g_\parallel \rvert$	soln	k	Δ/λ
$Fe(bpy)_3^{3+}$	2.61 ± 0.02	1.61 ± 0.01	1	1.068	3.03
			2	1.230	0.331
$Ru(bpy)_3^{3+}$	2.64 ± 0.02	1.14 ± 0.03	1	0.932	1.91
			2	1.156	0.507
$Os(bpy)_3^{3+}$	2.49 ± 0.02	(1.74)[b]	(2)[b]	(1.191)[b]	(0.254)[b]

[a] As PF_6^- salts in a diamagnetic host lattice. Reference 8. For definitions of terms see text. [b] Calculated from near-infrared spectral data. See text.

states can be obtained by solving the matrix in eq 2. The results are given in eq 3. Since λ is positive, E_- is the ground

$$E(E_0) = \frac{\lambda}{2}$$
$$E(E_\pm) = \frac{1}{2}\left[-\Delta - \frac{\lambda}{2} \pm \left(\Delta^2 - \Delta\lambda + \frac{9}{4}\lambda^2\right)^{1/2}\right] \tag{3}$$

state for all values of Δ. In the D_3' double point group, the $^2A_1$ state transforms as $E_{1/2}$ and the ^2E state as $E_{1/2} + E_{3/2}$. It follows that E_+ and E_- should transform as $E_{1/2}$; E_+ and E_- result from the mixing of the $^2A_1$ and ^2E states, and only states of the same symmetries can mix. E_0 must then correspond to the $E_{3/2}$ representation. The two transitions $E_- \rightarrow E_+$ ($E_{1/2} \rightarrow E_{1/2}$) and $E_- \rightarrow E_0$ ($E_{1/2} \rightarrow E_{3/2}$) are both allowed and *x,y* polarized. The energies of the two transitions are readily derived and are given in eq 4. Since E_- is the ground

$$E_- \rightarrow E_+{:}\quad \left(\Delta^2 - \Delta\lambda + \frac{9}{4}\lambda^2\right)^{1/2}$$
$$E_- \rightarrow E_0{:}\quad \frac{\Delta}{2} + \frac{3\lambda}{4} + \frac{1}{2}\left(\Delta^2 - \Delta\lambda + \frac{9}{4}\lambda^2\right)^{1/2} \tag{4}$$

state, an EPR signal is expected. Two *g* values should be observable, and their values are given in eq 5. The range

$$g_\parallel = 2[\sin^2\alpha - (1 + k)\cos^2\alpha]$$
$$g_\perp = -2[2^{1/2}k\cos\alpha\sin\alpha + \sin^2\alpha] \tag{5}$$
$$\tan(2\alpha) = 2^{1/2}\Big/\frac{1}{2} - \frac{\Delta}{\lambda}$$

of α is $0 < 2\alpha < \pi$. The term *k* is the so-called orbital reduction factor, which typically has a value of ~1.

The EPR spectral data obtained by Drago and DeSimone[8] are summarized in Table I. Because the signs of the *g* values cannot be determined from a simple experiment, it is possible to obtain two distinct solutions to eq 5. If the two *g* values are assumed to have opposite signs, solution 1 shown in Table I results; if the signs are taken to be the same, then solution 2 results. For $Os(bpy)_3^{2+}$, only $g_\perp$ was observed, so a unique solution to eq 5 cannot be found.

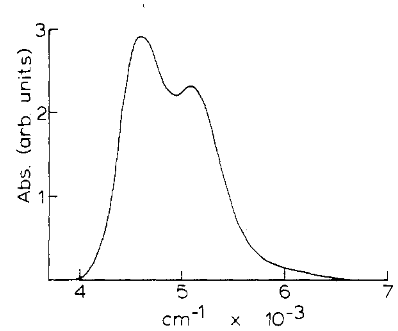

Figure 2. Near-infrared absorption spectrum of $[Os(bpy)_3](PF_6)_3$ in CD_3CN.

The most prominent feature of the analysis is that, for both possible solutions, the ratio Δ/λ is found to be positive. Since λ is intrinsically positive, this requires that Δ be positive. As previously discussed, this implies a $^2A_1$ ground state as anticipated on theoretical grounds. Magnetic susceptibility measurements on $Fe(bpy)_3^{3+}$ support this assignment.[15] However, it is opposite to the conclusion reached by Drago and DeSimone.[8] Their analysis was based on the hole formalism, which requires that the effective spin–orbit coupling constant be negative. The change in sign for λ leads to a change in sign of the term Δ/λ in eq 5 or to a change in the sign convention for Δ. Confusion over this point apparently led to the incorrect conclusion that Δ was negative.

The question then arises as to which of the solutions shown in Table I are the proper ones. Drago and DeSimone favored their analogues of solution 1 on the basis that they gave values for *k* that were close to or less than 1.[8] At first glance, the assumption that *k* should be less than 1 is reasonable given the original definition of *k* as the "orbital reduction factor". However, Thornley[16] and Griffith[17] have shown that configuration interaction (both by electrostatic interactions and spin–orbit coupling) between the $(d\pi)^4(d\sigma)^1$ excited states and the $(d\pi)^5$ states can have an important influence on the observed value for *k*. Hill[12] and Cotton[18] have shown that the experimentally observed *k* values are approximately related to the actual orbital reduction factors, *k'*, by the formula in eq 6. Here, *B* is the Racah interelectronic repulsion factor

$$k = k'(1 + 12BE) \tag{6}$$

and *E* is the average energy of the $(d\pi)^4(d\sigma)^1$ states relative to the $(d\pi)^5$ states. Because of the possibility of configuration interaction, it is *k'* rather than *k* that is expected to be less than 1. Since *B* and *E* are both positive quantities, values for *k* could be greater than 1.

In order to judge whether or not the derived values for *k* are reasonable, it is necessary to estimate values for *B* and *E*. For somewhat related complexes of Fe, Ru, and Os, values of B = 500–600 cm^{-1} have been suggested.[18,19] Estimates for the average energies of the $(d\pi)^4(d\sigma)^1$ states of E = 20000 cm^{-1} for $Fe(bpy)_3^{3+}$ [18] and of E = 30000 cm^{-1} and 40000 cm^{-1} for $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, respectively,[19] are probably reasonable. Using these values and eq 6 gives (1) for $Fe(bpy)_3^{3+}$ k' = 0.80 for solution 1 and k' = 0.92 for solution 2 and (2) for $Ru(bpy)_3^{3+}$ k' = 0.76 for solution 1 and k' = 0.95 for solution 2. Since the values for *k'* are all less than 1, neither solution 1 nor solution 2 can rightfully be disregarded.

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Additional data are required in order to ascertain which of the two solutions is correct. One approach is to locate the $d\pi \rightarrow d\pi$ transitions in the near-infrared spectrum (near-IR) whose energies are given in eq 4 in terms of Δ and λ. These transitions have been observed for other complexes of Os(III), and electronic structural information has been derived from the transition energies.[13,20]

The spectrum of $[Os(bpy)_3](PF_6)_3$ in CD_3CN solution is shown in Figure 2. Two bands are observed in the near-infrared region, one at 4580 cm^{-1} (ϵ = 450 M^{-1} cm^{-1}) and one at 5090 cm^{-1} (ϵ = 360 M^{-1} cm^{-1}). The absence of near-IR bands for $[Os(bpy)_3](PF_6)_2$ shows that the bands for $Os(bpy)_3{}^{3+}$ are not C–H or O–H overtones. Near-IR bands have been observed for a series of complexes of the type $Os^{III}(bpy)_2LL'^{n+}$,[21] and from comparisons among them it is clear that the bands can be assigned to the two anticipated $d\pi \rightarrow d\pi$ transitions.

From the transition energies and eq 4, values for Δ and λ can be calculated. As with the EPR data, there are two possible solutions: (1) $\Delta = -730$ cm^{-1}, $\lambda = 3200$ cm^{-1}; (2) $\Delta = 810$ cm^{-1}, $\lambda = 3190$ cm^{-1}. The value calculated for λ is the same for both solutions within experimental error and is consistent both with the estimated free-ion value for Os^{3+} of λ = 3000–3500 cm^{-1} [22] and with other experimentally determined values (λ = 2600–3600 cm^{-1}).[12,20b] However, of the two solutions, solution 2 is clearly preferable because, for it, the sign of Δ is positive.

Based on the values for Δ and λ from the near-IR spectrum and the value of $|g_\perp| = 2.49$ by EPR, it is possible to calculate values for k and $g_\parallel$ for $Os(bpy)_3{}^{3+}$, and these values are given in Table I. It should be noted that the calculated value for $g_\parallel$ shown in Table I has the same sign as $g_\perp$ and consequently the values listed are equivalent to those noted as "solution 2" for the EPR data. Although no signal corresponding to $|g_\parallel| \geq 0.45$ was detected in the EPR spectrum of $Os(bpy)_3{}^{3+}$, $g_\parallel$ is often quite difficult to detect, particularly for the heavier metals; note, for example, ref 8 and 23.

Given the results of the analysis described above, the goal now is to examine the various values for Δ in order to determine which ones provide the most reasonable fit of the EPR data for the Fe and Ru complexes. For this purpose, we will assume the values λ_{Fe} = 400 cm^{-1} and λ_{Ru} = 1100 cm^{-1},[22] which gives (1) for $Fe(bpy)_3{}^{3+}$ the values of Δ = 1200 cm^{-1} for solution 1 and Δ = 130 cm^{-1} for solution 2 and (2) for $Ru(bpy)_3{}^{2+}$ Δ = 2090 cm^{-1} for solution 1 and Δ = 610 cm^{-1} for solution 2. The fact that Δ is small for $Os(bpy)_3{}^{3+}$ (810 cm^{-1}) suggests that, of the two solutions for $M(bpy)_3{}^{3+}$ (M = Fe, Ru), the ones having smaller values of Δ (Δ_{Fe} = 130 cm^{-1}; Δ_{Ru} = 610 cm^{-1}) are preferred. With this assignment, the value of Δ is found to increase in the order Fe < Ru < Os. This order is expected since the magnitude of Δ should depend upon the extent of metal–ligand orbital overlap, which increases in the order Fe < Ru < Os as shown by the increasing values of $10Dq$. The fact that Δ is small is consistent with the view that bpy is a relatively weak π-acid ligand when compared, for example, to CO. As a final comment, we note that, if solution 2 for the EPR data is assumed to be correct, the values of k for all three complexes are similar; note Table I. Although this is not a criterion for distinguishing between the two possibilities in and of itself, it seems like a reasonable result since the complexes are so closely related.

From the analysis given above, it is concluded that (1) all three of the ions $M(bpy)_3{}^{3+}$ (M = Fe, Ru, Os) have a $^2A_1$ ground state and (2) of the two possible fits for the EPR data for $Fe(bpy)_3{}^{3+}$ and $Ru(bpy)_3{}^{3+}$, solution 2 appears to be the more reasonable. The values of Δ that result from the analysis given here have been used as part of an electronic structural model for the MLCT absorption spectra of the complexes $M(bpy)_3{}^{2+}$.[7] In that work it was found that the energy separation between two of the transitions was accounted for quantitatively by using the values of Δ derived here, which constitutes further evidence in support of the present assignment.

Experimental Section

$[Os(bpy)_3](PF_6)_3$ was prepared by a method similar to one previously described[24] except that the complex was precipitated from aqueous solution by the addition of NH_4PF_6. Its identity and purity were established by visible absorption spectra[25] and cyclic voltammetry.[26]

The near-IR absorption spectrum was measured vs. a solvent blank with a Cary 17 recording spectrophotometer and 1-cm matched quartz cells with CD_3CN (Aldrich) as the solvent.

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Registry No. $[Fe(bpy)_3](PF_6)_3$, 28190-88-7; $[Ru(bpy)_3](PF_6)_3$, 28277-54-5; $[Os(bpy)_3](PF_6)_3$, 28277-56-7.

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