Inorg. Chem. **1996,** *35,* 1616−1620

Absorption, Circular Dichroism, and Luminescence Spectroscopy of Electrogenerated Δ-$[Ru(bipy)_3]^{+/0/-}$ and Δ-$[Os(bipy)_3]^{+/0/-}$ (bipy = 2,2′-Bipyridine)

Brian Noble and Robert D. Peacock*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

Received August 23, 1995[⊗]

The electronic absorption and circular dichroism (CD) spectra of the complexes produced by the one, two, and three electron reduction of Δ-$[Ru(bipy)_3]^{2+}$ and Δ-$[Os(bipy)_3]^{2+}$ are reported. The CD spectra give unequivocal proof that the added electrons are localized on individual bipiridine ligands and thus that the complexes are correctly formulated $[M(bipy)_2(bipy^-)]^+$, $[M(bipy)(bipy^-)_2]^0$, and $[M(bipy^-)_3]^-$. The absorption spectra of the triply reduced species $[M(bipy^-)_3]^-$ (M = Ru, Os) are compared to those of the Fe^{II} and Ir^{III} analogs. The luminescence spectra of the two triply reduced complexes $[Ru(bipy^-)_3]^-$ and $[Os(bipy^-)_3]^-$. are also presented. The MLCT luminescence found in the parent complexes is completely quenched and is replaced by a weak luminescence attributed to the $\pi_{10} \rightarrow \pi_7$ transition of the (coordinated) $[bipy]^-$ ion.

Introduction

It is over 10 years since the nature of the singly, doubly, and triply reduced forms of $[Ru(bipy)_3]^{2+}$ were established as $[Ru(bipy)_2(bipy^-)]^+$, $[Ru(bipy)(bipy^-)_2]^0$ and $[Ru(bipy^-)_3]^-$ respectively by the spectroelectrochemical studies of Braterman, Heath, and Yellowlees[1a] and the ESR and luminescence studies of Motten, Hanck, and DeArmond.[1b] Since then an enormous body of work[2] has been published on the redox behavior and spectroelectrochemistry of a wide variety of tris, bis, and mono complexes of Ru^{II} with diimine ligands, and the work has been extended to complexes of Ir^{III} [3] and $Fe.^{II}$ [4] Some time ago we reported in a preliminary form[5] the circular dichroism spectra of the reduced Ru^{II} species Δ-$[Ru(bipy)_2(bipy^-)]^+$, Δ-$[Ru(bipy)(bipy^-)_2]^0$, and Δ-$[Ru(bipy^-)_3]^-$ and showed that the CD spectra unambiguously supported the model in which the added electrons are localized on the bipy ligands. Notable by its absence is the spectroelectrochemistry of tris(diimine) complexes of Os^{II}, despite the many papers on the electrochemistry of such species. Apart from the ESR of reduced $[Os(bipy)_2(bipy^-)]^+$, $[Os(bipy)(bipy^-)_2]^0$, and $[Os(bipy^-)_3]^-$ [6] and the NMR of $[Os(bipy)_2(bipy^-)]^+$ and $[Os(bipy^-)_3]^-$ [7] there has been no work published[8] on the spectroscopy of the reduced forms of $[Os(bipy)_3]^{2+}$. It is also remarkable that despite the enormous body of work on the luminescence[9] of $[Ru(bipy)_3]^{2+}$ there is no report of the luminescence spectra of the reduced species.

We now report the electronic absorption and circular dichroism spectra spectra of electrogenerated Δ-$[M(bipy)_2(bipy^-)]^+$, Δ-$[M(bipy)(bipy^-)_2]^0$, and Δ-$[M(bipy^-)_3]^-$ (M = Ru^{II}, Os^{II}) and the luminescence spectra of the triply reduced species Δ-$[M(bipy^-)_3]^-$ (M = Ru^{II}, Os^{II}).

Experimental Section

$[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ were prepared and resolved by literature methods.[10] In each case the Δ isomers were converted to the $[BF_4]^-$ salt by ion exchange chromatography. The literature preparation affords pure $[Ru(bipy)_3]^{2+}$. Significant quantities of $[Os(bipy)_2Cl_2]$ are always produced during the synthesis of $[Os(bipy)_3]^{2+}$, and it is extremely difficult to separate $[Os(bipy)_3]^{2+}$ from traces of $[Os(bipy)_2Cl_2]$ by crystallization. An important part of the procedure involved purification of the resolved Δ-$[Os(bipy)_3][BF_4]_2$ by chromatography on Sephadex LH20 using methanol as eluent. The purity of the Δ-$[Os(bipy)_3][BF_4]_2$ was confirmed by ^1H and ^{13}C NMR spectroscopy.

The cyclic voltammograms (CV) of Δ-$[Ru(bipy)_3][BF_4]_2$ (**I**) and Δ-$[Os(bipy)_3][BF_4]_2$ (**II**) were obtained in dry, purified acetonitrile using 0.1 mol L^{-1} $[Bu_4{}^n][BF_4]$ as electrolyte. The CV of **I** showed the expected oxidation wave for Δ-$[Ru(bipy)_3]^{2+} \rightarrow \Delta$-$[Ru(bipy)_3]^{3+}$ (E = +0.95 V (vs Ag/Ag^+)) and three reduction waves Δ-$[Ru(bipy)_3]^{2+} \rightarrow \Delta$-$[Ru(bipy)_3]^+$ (E = −1.58 V), Δ-$[Ru(bipy)_3]^+ \rightarrow \Delta$-$[Ru(bipy)_3]$ (E = −1.83 V), and Δ-$[Ru(bipy)_3] \rightarrow \Delta$-$[Ru(bipy)_3]^-$ (E = −2.09 V), and the CV of **II** showed the corresponding waves at +0.38, −1.62, −1.81, and −2.10 V. The singly, doubly and triply reduced Ru (Os) complexes were produced by controlled-potential electrolysis, at −1.78 (−1.74), −2.00 (−2.00) and −2.30 (−2.29) V vs Ag/Ag^+, respectively, of 10^{-4} mol L^{-1} solutions of Δ-$[Ru(bipy)_3][BF_4]_2$ (Δ-$[Os(bipy)_3][BF_4]_2$) in purified acetonitrile in a 1 mm quartz cell equipped with a platinum gauze working electrode. The supporting electrolyte was 0.1 mol L^{-1} $[Bu_4{}^n][BF_4]$, the auxiliary electrode was Pt wire, and the reference and auxiliary electrodes were separated from the bulk solution by porous Vycor glass frits. The reduction potentials were chosen to maximise the proportion of the particular species being studied. Thus at a potential of −1.74 V (to produce $\mathbf{II}^-$) application of the Nernst equation shows that the concentration of **II** is less than 10^{-7} mol L^{-1}. Electrolyses were performed at room temperature or at −40 °C and the solutions were checked for decomposition and racemization at each stage by regenerating the 2+ species.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1996.

(1) (a) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287. Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, *92*, 646. (b) Moten, A. G.; Hanck, K; DeArmond, M. K. *Chem. Phys. Lett.* **1991**, *79*, 541. Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.

(2) Recent reviews: Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. Juris, A.; Balzani, V.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. De Armond, M. K.; Myrick, M. L. *Acc. Chem. Res.* **1989**, *22*, 364.

(3) Coombe, V. T.; Heath, G. A.; MacKenzie, A. J.; Yellowlees, L. J. *Inorg. Chem.* **1984**, *23*, 3423.

(4) Braterman, P. S.; Song, J.-I.; Peacock, R. D. R. D. *Inorg. Chem.* **1992**, *31*, 555.

(5) Braterman, P. S.; Noble, B. C.; Peacock, R. D. *J. Phys. Chem.* **1986**, *90*, 4913

(6) DeArmond, M. K.; Hanck, K. W.; Morris, D. E. *Inorg. Chem.* **1985**, *24*, 977.

(7) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383.

(8) We have recently published a preliminary communication on the reduced Os^{II} species: Noble, B. C.; Peacock, R. D. *Spectrochim Acta, A* **1994**, *50A*, 1777.

(9) Krauze, E. *Struct. Bonding* **1987**, *67*, 1.

(10) Burstall, F. H.; Dwyer, F. P.; Gyarfas, E. C. *J. Chem. Soc.* **1950**, 953.

0020-1669/96/1335-1616$12.00/0 © 1996 American Chemical Society

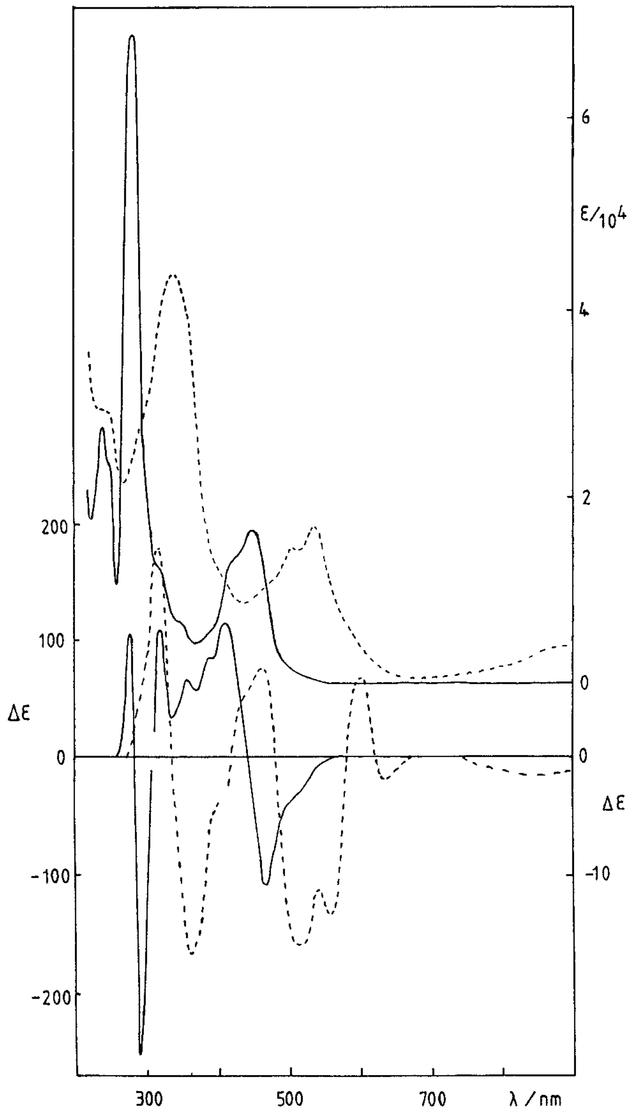

Figure 1. Absorption and CD spectra of Δ-$[Ru(bipy)_3]^{2+}$ (solid line) and Δ-$[Ru(bipy^-)_3]^-$ (dashed line) both in acetonitrile solution. Note the scale change in the CD spectra between the ligand and charge-transfer regions.

Absorption spectra were run on a Beckman 5270 or Perkin Elmer Lambda 9 UV−vis−near IR spectrometer. CD spectra were obtained on a home-built instrument constructed round a Jobin-Yvon 0.6 m monochrometer, a Morvue photoelastic modulator, and a Bentham lock-in amplifier. Luminescence spectra were collected in backscattering mode using Ar^+ laser (496.5 nm) excitation. In this case the platinum gauze working electrode had a 1 mm hole cut in it through which the laser beam passed.

Δ-$[Ru(bipy)_3]^-$ and Δ-$[Os(bipy)_3]^-$ (as the Li salts) were also synthesized by chemical reduction of Δ-$[Ru(bipy)_3]Cl_2$ or Δ-$[Os(bipy)_3]Cl_2$ by lithium metal in DMF using vacuum line techniques. The solid complexes (contaminated by a little LiCl) were obtained by decanting the solution of the reduced species from LiCl and removal of solvent. The solids were very air sensitive but could be manipulated in a dry inert atmosphere box.

Results and Discussion

It is now accepted that the electrons added to $[M(bipy)_3]^{2+}$ are localized on the bipy ligands so that, for example, the singly reduced species $[Ru(bipy)_3]^+$ is correctly formulated as $[Ru(bipy)_2(bipy^-)]^+$. It is therefore appropriate to summarize the spectroscopic properties of (*cis*) bipy and the (*cis*) $[bipy]^-$ ion. In both cases there are six bonding orbitals (π_1−π_6) and six antibonding orbitals (π_7−π_{12}). In bipy itself all the bonding orbitals are fully occupied and all the antibonding orbitals are empty; the lowest electronic transition is therefore $\pi_6 \rightarrow \pi_7$ (at around 30 000 cm^{-1}). The $[bipy]^-$ has the open shell configuration $(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_4)^2(\pi_5)^2(\pi_6)^2(\pi_7)^1$. The electronic spectrum[11,12] of Li[bipy] shows, in addition to the $\pi_6 \rightarrow \pi_7$ transition (at 26, 030 cm^{-1}) three further transitions: $\pi_7 \rightarrow \pi_{10}$ (18 370 cm^{-1}), $\pi_7 \rightarrow \pi_9$ (at 10 680 cm^{-1}), and $\pi_7 \rightarrow \pi_8$ (at 6600 cm^{-1}). The $[bipy]^-$ ion also show a weak luminescence ($\pi_{10} \rightarrow \pi_7$) at 16 315 cm^{-1}.

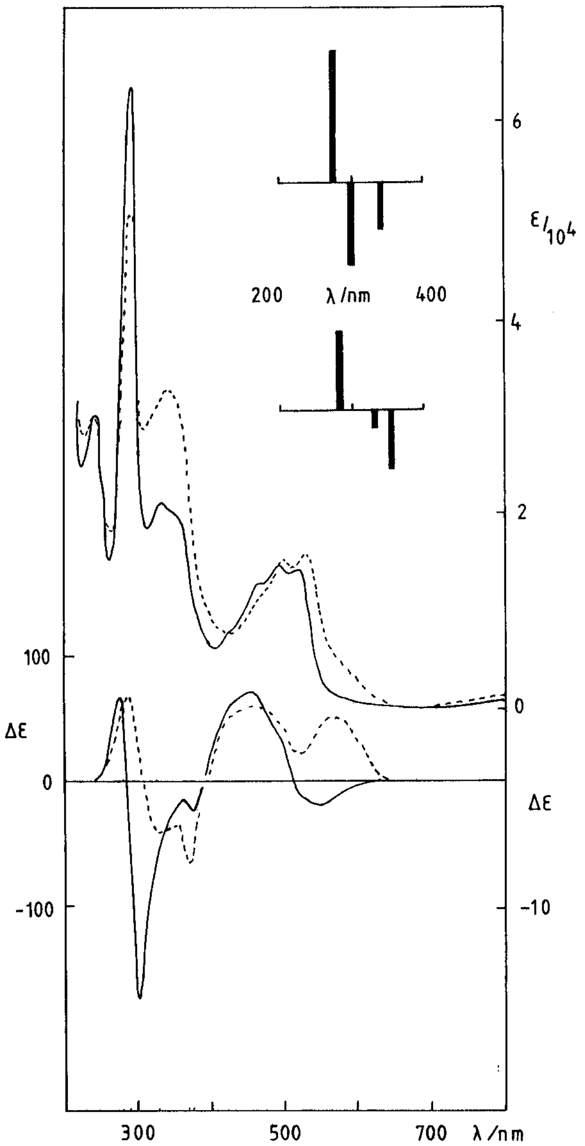

Figure 2. Absorption and CD spectra of Δ-$[Ru(bipy)_2(bipy^-)]^+$ (solid line) and Δ-$[Ru(bipy)(bipy^-)_2]^0$ (dashed line) both in acetonitrile solution. Note the scale change in the CD spectra between the ligand and charge-transfer regions. The inserts show the calculated CD spectra (see text) for the singly and doubly reduced species (upper and lower diagrams respectively).

The reduced species Δ-$[M(bipy)_3]^{+/0/-}$ (M = Ru^{II}, Os^{II}) were synthesized by electrochemical reduction of the divalent complexes in acetonitrile solution at an optically transparent electrode. The fully reduced anions Δ-$[M(bipy)_3]^-$ were also prepared by chemical reduction in DMF solution. All the reduced species are optically stable in solution except Δ-$[Ru(bipy^-)_3]^-$, which racemized[5] in MeCN solution with a half-life of approximately 1 h at room temperature. Δ-$[Ru(bipy^-)_3]^-$

---

[11] Konig, E.; Kremer, S. *Chem. Phys. Lett.* **1970**, *5*, 87.

[12] Noble, B. C.; Peacock, R. D. *Spectrochim. Acta, A* **1990**, *46A*, 407.

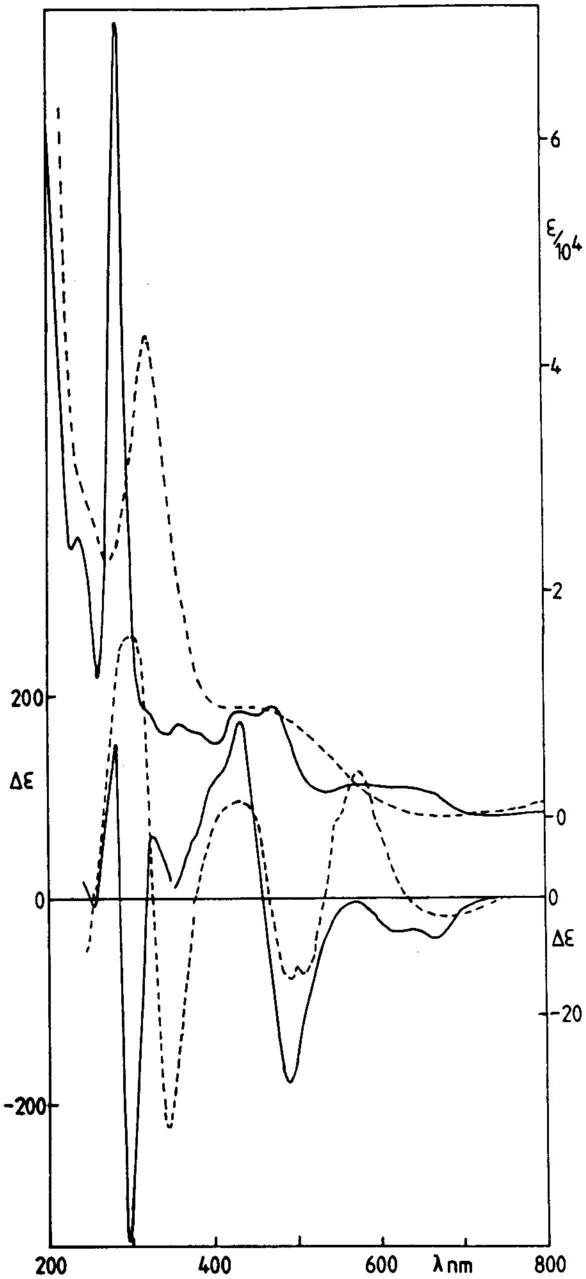

Figure 3. Absorption and CD spectra of Δ-[Os(bipy)$_3$]$^{2+}$ (solid line) and Δ-[Os(bipy$^-$)$_3$]$^-$ (dashed line) both in acetonitrile solution. Note the scale change in the CD spectra between the ligand and charge-transfer regions.

is, however, optically stable in DMF solution and in the solid state. There are three possible reasons why Δ-[Ru(bipy)$_3$]$^-$ is more easily racemized than the parent or singly or doubly reduced species: there is substantial electron delocalization from ligand to metal producing a partial d^7 species, the ligand field of [bipy]$^-$ is considerably less than that of bipy, or repulsion between the negatively charged bulky [bipy]$^-$ ligands leads to easier dissociation. The fact that the racemization is solvent dependent suggests the last possibility is most likely, with MeCN coordinating to ruthenium and stabilizing the intermediate although the fact that the triply reduced osmium species is optically stable implies that the ligand field (which will be larger for osmium) is also of importance.

Absorption Spectra of Δ-[Ru(bipy)$_3$]$^{2+/+/0/-}$ and Δ-[Os(bipy)$_3$]$^{2+/+/0/-}$. The absorption and CD spectra are presented in two sets for each metal: the tris(ligand) pairs [M(bipy)$_3$]$^{2+}$ and [M(bipy$^-$)$_3$]$^-$ (M = Ru^{II}, Figure 1; M = Os^{II}, Figure 3) and the mixed ligand pairs [M(bipy)$_2$(bipy$^-$)]$^+$ and [M(bipy)(bipy$^-$)$_2$] (M = Ru^{II}, Figure 2; M = Os^{II}, Figure 4). The absorption spectra of the ruthenium species are identical to those reported[1] by Braterman *et al.* The absorption spectrum of the triply reduced osmium complex is very similar to the ruthenium analog and to [bipy]$^-$ itself with one noticeable difference. Unlike the Fe^{II} and Ru^{II} analogs the spectrum of [Os(bipy$^-$)$_3$]$^-$ shows a complete absence of vibronic structure in $\pi_7 \rightarrow \pi_{10}$ and $\pi_7 \rightarrow \pi_9$ transitions. It is not clear why this should be so, but it may indicate that there is more mixing between the ligand $\pi \rightarrow \pi^*$ transitions and the MLCT transitions in the Os^{II} complexes possibly due to the larger spin−orbit coupling in the Os^{II} species.

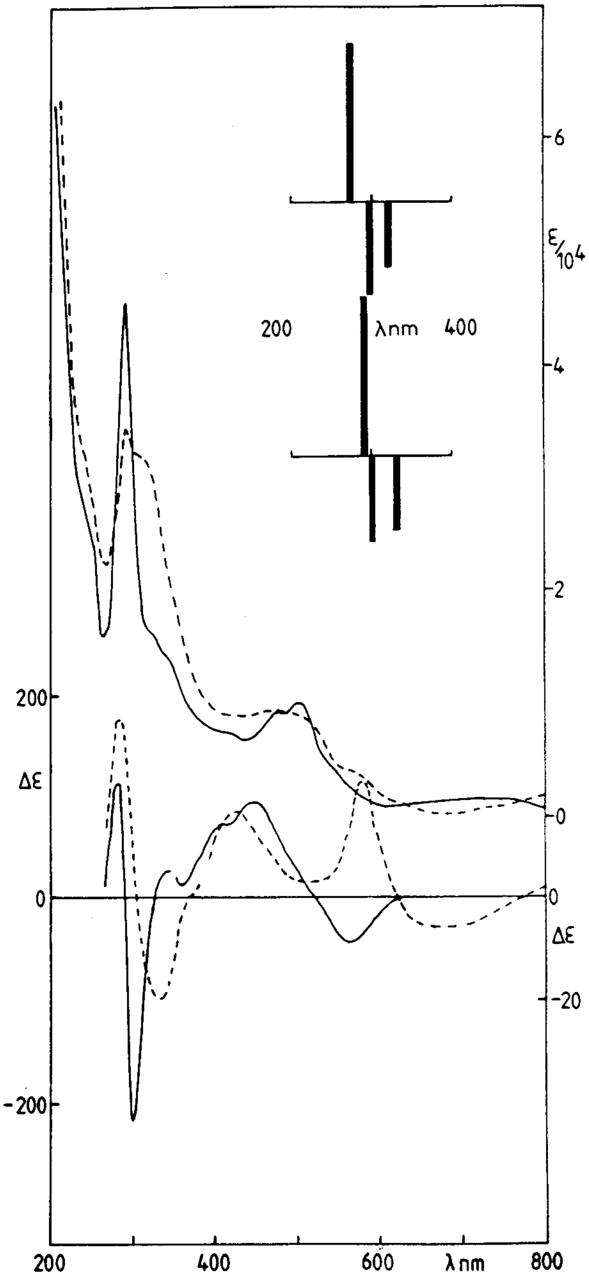

Figure 4. Absorption and CD spectra of Δ-[Os(bipy)$_2$(bipy$^-$)]$^+$ (solid line) and Δ-[Os(bipy)(bipy$^-$)$_2$]^0 (dashed line) both in acetonitrile solution. Note the scale change in the CD spectra between the ligand and charge-transfer regions. The inserts show the calculated CD spectra (see text) for the singly and doubly reduced species (upper and lower diagrams respectively).

As is the case for the ruthenium and iron complexes the absorption spectra of the singly and doubly reduced osmium complexes are the appropriate sums of the parent and triply reduced complexes. The absorption (and luminescence *vide*

Table 1. Comparison of the Absorption Band Positions (in cm^{-1}) for $[bipy]^-$ and for $[Fe(bipy^-)_3]^-$, $Ru(bipy^-)_3]^-$, $Os(bipy^-)_3]^-$, and $Ir(bipy^-)_3]^0$

	$\pi_6 \rightarrow \pi_7$	$\pi_7 \rightarrow \pi_{10}$	$\pi_7 \rightarrow \pi_9$	$\pi_7 \rightarrow \pi_8$	luminescence $\pi_{10} \rightarrow \pi_7$	ref
$[bipy]^-$	26 030	18 370	10 680	6600	16 315	12
$[Fe(bipy^-)_3]^-$	26 400	17 800	10 200	*a*		4
$[Ru(bipy^-)_3]^-$	29 400[b]	18 300	9 900	*a*	17 650[c]	1,6, this work
$[Os(bipy^-)_3]^-$	31 050	19 400[c]	11 100[c]	*a*	17 314[c]	this work
$[Ir(bipy^-)_3]^0$	25 400	19 600	10 700	*a*		3,13

[a] Although $\pi_7 \rightarrow \pi_8$ can be detected in the spectrum of $[bipy]^-$ it has not been possible to measure its position accurately in any of the complexes. [b] Underlying MLCT may distort the energy a little. [c] These bands show no vibronic structure; the band origin position has been estimated.

Table 2. Energies ($\nu/10^3$ cm^{-1}) and (in Parentheses) Rotational Strengths ($R/10^{38}$ cgs) for the CD Spectra of Δ-$[M(bipy)_3]^{2+/+/0/-}$ (M = Ru, Os)

	experiment		calculated		
Δ-$[Ru(bipy)_3]^{2+}$	36.4 (+1.5)	34.0 (−3.3)	36.4 (5.6)	33.5 (−5.6)	
Δ-$[Os(bipy)_3]^{2+}$	36.1 (+2.1)	33.9 (−4.1)			
Δ-$[Ru(bipy)_2(bipy^-)]^+$	35.7 (+1.2)	33.3, 26.6 (−4.14)	35.9 (4.5)	33.3 (−2.9)	29.4 (−1.6)
Δ-$[Os(bipy)_2(bipy^-)]^+$	35.6 (+1.2)	33.6 (−2.5), 27.9 (sh)			
Δ-$[Ru(bipy)(bipy^-)_2]$	33.8 (+1.8)	30.2, 27.0 (−2.4)	35.0 (+2.7)	30.1 (−0.6)	28.0 (−2.1)
Δ-$[Os(bipy)(bipy^-)_2]$	35.4 (+3.0)	31.9 (−2.5), 26.6 (sh)			
Δ-$[Ru(bipy^-)_3]^-$	31.3 (+3.5)	28.0 (−4.2)	32.2 (4.2)	28.0 (−4.2)	
Δ-$[Os(bipy^-)_3]^-$	33.5(+7.2)	29.1 (−4.2)			

[a] The calculated values are for the Ru spectra

infra) spectra of $[M(bipy^-)_3]^-$ (M = Fe^{II}, Ru^{II}, Os^{II} and Ir^{III}) and of $[bipy]^-$ are collected in Table 1.

Having completed the series $[M(bipy)_3]^{+/0/-}$ (M = Fe^{II}, Ru^{II}, Os^{II}), we can make some comments about trends in the spectra. First it is clear (Table 1) that the $\pi_6 \rightarrow \pi_7$ transition of $[bipy]^-$ moves to higher energy as we go from Fe^{II} to Os^{II}. The other two $[bipy]^-$ transitions are less dependent on the nature of the metal ion and appear to vary somewhat randomly in energy. These trends are is also seen in the spectrum of $[Ir(bipy^-)_3]^0$.[3,14] This suggests that the energy of the π-bonding π_6 orbital of $[bipy]^-$ is more affected by interaction with the metal ion states than are the π-antibonding orbitals.

CD Spectra of Δ-$[Ru(bipy)_3]^{2+/+/0/-}$ and Δ-$[Os(bipy)_3]^{2+/+/0/-}$. The CD spectrum of the parent Ru^{II} complex is well known and has been discussed in detail[14]. The strongest feature is a couplet (centerd at 284 nm) derived from the bipyridine $\pi \rightarrow \pi^*$ ($\pi_6 \rightarrow \pi_7$) transition which is split by exciton coupling into A_2 and E components which have CD of opposite sign and essentially equal magnitude. The principal feature in the visible region is a pair of oppositely signed transitions under the ^{1}MLCT band . The CD spectum of the Os^{II} parent complex is similar[14] to the Ru^{II} analog, the main difference being the presence of a ^{3}MLCT band at ~650 nm. The assignmemt of the charge-transfer transitions has been fully discussed by Ferguson and Herren.[15]

The CD spectra of the triply reduced species in the region of the $\pi_6 \rightarrow \pi_7$ ligand transition is straightforward. As in the parent species, the transitions located on the three ligands interact to give A_2 (320 nm, Ru; 300 nm, Os) and E (364 nm, Ru; 343 nm, Os) components which show extremely clear exciton couplets. The band width of the $\pi_6 \rightarrow \pi_7$ transition is slightly narrower and the exciton couplet slightly more symmetric in Δ-$[Os(bipy^-)_3]^-$ than in the Ru^{II} analog giving support to the suggestion [1] that in the Ru^{II} complex there is a ^{1}MLCT transition underlying $\pi_6 \rightarrow \pi_7$. The CD in the visible region of both Ru^{II} and Os^{II} species is more problematic. The transition at ~520 nm in both complexes is undoubtedly the $\pi_7 \rightarrow \pi_{10}$ transition of $[bipy]^-$. This transition, like $\pi_6 \rightarrow \pi_7$, is long-axis polarized, and so we would expect to see a single conservative CD couplet with the same sign as $\pi_6 \rightarrow \pi_7$. The best explanation we can offer is that the major + (high energy)/−(low energy) couplet seen in the spectra of both the triply reduced Ru^{II} and Os^{II} complexes is due to the $\pi_7 \rightarrow \pi_{10}$ transition of $[bipy]^-$ and that the additional CD bands are assigned to either underlying ligand field or charge transfer transitions.

The CD Spectra of the Partially Reduced Species. The CD spectra of Δ-$[M(bipy)_2(bipy^-)]^+$ and Δ-$[M(bipy)(bipy^-)_2]^0$ (M = Ru^{II}, Os^{II}) are shown in Figures 2 and 4. While the absorption spectra of the partially reduced complexes are essentially the sums of the unreduced and fully reduced species, the CD spectrum of the four Ru^{II} and four Os^{II} complexes are quite distinct. This is extremely important as it gives direct evidence that the partially reduced species behave as *mixed-ligand complexes* where the ligands are distinct bipy and $[bipy]^-$. The spectra bear a strong resemblance to those desrcibed by Bosnich[16] for the $[Ru(bipy)_n(phen)_{3\text{-}n}]^{2+}$ series (with the difference that the high energy $\pi \rightarrow \pi^*$ transition of phen comes to shorter wavelength to that of bipy, while that of $[bipy]^-$ comes to longer wavelength). This confirms that the partially reduced complexes are correctly formulated as Δ-$[M(bipy)_2(bipy^-)]^+$ and Δ-$[M(bipy)(bipy^-)_2]^0$ with distinct bipy and $[bipy]^-$ ligands. This qualitative result can be quantified by the results of exciton calculations for the UV ($\pi_6 \rightarrow \pi_7$) bands of the eight complexes. The theory required to reproduce the rotational strengths and energy splittings of the long-axis polarized $\pi_6 \rightarrow \pi_7$ transitions of homotrischelated and heterotrischelated $[ML_nL'_{3-n}]^{2+}$ complexes has been given by Mason[14] and Bosnich[16] respectively. The eight spectra are reasonably well reproduced using experimental values of the energies and dipole strengths of the $\pi_6 \rightarrow \pi_7$ transition in bipy and $[bipy]^-$, the experimental distance between the metal and the center of the ligand (2.63 Å) and three parameters representing the Coulombic interactions between bipy and bipy (V_{11}, 970 cm^{-1}), $[bipy]^-$ and $[bipy]^-$ (V_{22}, 1400 cm^{-1}), and bipy and $[bipy]^-$ (V_{12}, 1200 cm^{-1}) The results of the calculations are compared with experiment in Table 2 and represented as stick diagrams in Figures 2 and 4. Such calculations are not expected to be quantitativly accurate (in particular due to the cancellation of the oppositly signed CD

---

(13) Noble, B. C. Ph.D. Thesis, University of Glasgow, 1987.

(14) McCaffery, A. J.; Mason, S. F.; Norman, B. J. J. *Chem. Soc. A* **1969**, 1428.

(15) Ferguson, J.; Herren, F. *Chem. Phys. Lett.* **1982**, *89*, 371.

(16) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 2379.

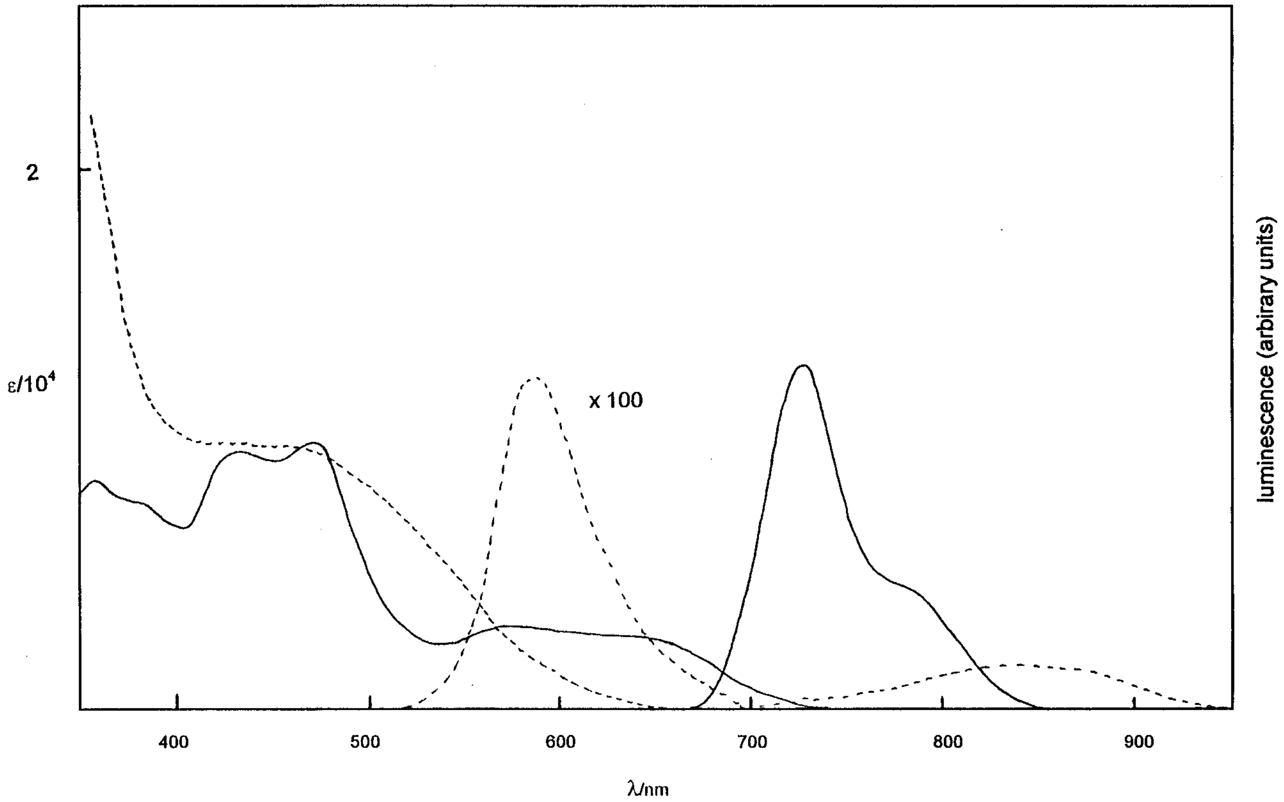

Figure 5. Absorption and luminescence spectra of Δ-$[Os(bipy)_3]^{2+}$ (solid line), and Δ-$[Os(bipy^-)_3]^-$ (dashed line), all in acetonitrile solution. Excitation was by the 488.0 nm Ar^+ laser line.

bands they are always larger than experiment); however, they reproduce some of the most noticeable qualitative features of the spectra such as the relative magnitudes of the two negative bands in the spectra of Δ-$[M(bipy)_2(bipy^-)]^+$ and Δ-$[M(bipy)(bipy^-)_2]^0$ and the fact that the CD of both the partially reduced species is weaker than that of either the parent complex or the fully reduced compound.

Luminescence spectra of Δ-$[Ru(bipy)_3]^{2+/+/0/-}$ and Δ-$[Os(bipy)_3]^{2+/+/0/-}$. The absorption and luminescence spectra of Δ-$[Os(bipy)_3]^{2+}$ and Δ-$[Os(bipy^-)_3]^-$ are shown in Figure 5. The ruthenium system shows similar behavior (Table 1) but the osmium spectra are somewhat clearer because the two different emission bands are widely separated. The luminescence spectra of the parent species $[M(bipy)_3]^{2+}$ have been the subject of a multitude of publications. It is generally accepted that the emitting state is $^3[M^{III}(bipy)_2(bipy^-)]^{2+}$, the luminescence maxima are at 16 300 (Ru) and 13 800 cm^{-1} (Os), and both transitions occur with large quantum yields. The luminescence spectrum of the $[bipy]^-$ ion consists[12] of a single weak band at 16 315 cm^{-1} assigned to the $\pi_{10} \rightarrow \pi_7$ transition. The quantum yield has not been measured, but the intensity of the emission is very weak, being comparable to that of the associated resonance Raman scattering.

It can clearly be seen that in the triply reduced species Δ-$[Os(bipy^-)_3]^-$ that the MLCT emission is completely quenched and is replaced by a weak luminescence attributed to the $\pi_{10} \rightarrow \pi_7$ transition of the (coordinated) $[bipy]^-$ ion. The emission spectra of Δ-$[Os(bipy^-)_3]^-$ and Δ-$[Ru(bipy^-)_3]^-$ are identical irrespective of whether the species are produced electrochemically or by chemical reduction. The emission is stronger when excitation is close to the origin of the $[bipy]^-$ $\pi_7 \rightarrow \pi_{10}$ absorption but the spectrum is essentially the same when obtained with UV excitation.

The interpretation of the luminescence spectra of the partially reduced species is problematic and they are not presented in detail. Addition of the first electron ($[M(bipy)_2(bipy^-)]^+$) results in a dramatic reduction in the MLCT emission (by a factor of about 15 in the ruthenium species and 20 in the osmium complex) and the emergence of a weak emission in the energy range of the $[bipy]^-$ $\pi_{10} \rightarrow \pi_7$ region. Addition of the second electron ($[M(bipy)(bipy^-)_2]$) further quenches the MLCT emission and increases the $[bipy]^-$ emission. The potentials are such that the ratio of the concentrations of $[Os(bipy)_3]^{2+}/[Os(bipy^-)_3]^-$ should be $\sim 10^{-3}$ in the vicinity of the OTTLE. However taking into account the fact that the emission of $[Os(bipy)_3]^{-2/+}$ is about 100 times stronger than that of $[Os(bipy^-)_3]^-$ reduces the ratio of the emission intensity to ~0.1. Thus it is posible that the residual MLCT emission seen after the addition of the first electron is due to residual unreduced $[Os(bipy^-)_3]^{-2/+}$. If this is so then the addition of a single electron completely quenches the MLCT luminescence.

Acknowledgment. We thank the SERC for a studentship (to B.N.).

IC951096E